

Integration of reduced graphene oxide into organic field-effect transistors as conducting electrodes and as a metal modification layer

Chen-Guan Lee,^{1,a)} Sungjin Park,² Rodney S. Ruoff,² and Ananth Dodabalapur¹

¹Microelectronics Research Center, University of Texas at Austin, Texas 78758, USA

²Department of Mechanical Engineering and the Texas Materials Institute, University of Texas at Austin, Texas 78712, USA

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The characteristics of thin-film transistors (TFTs) with pentacene active layers and source/drain contact layers consisting of either Au, Au coated with highly reduced graphene oxide (HRG), or plain HRG, are compared. It is shown that the incorporation of HRG as an interfacial material between gold source/drain contacts and pentacene in TFT devices results in improved electrical characteristics. The effect of the HRG layer is to improve the gold/pentacene interface leading to better charge injection, lower losses at the interface, and, consequently, higher effective carrier mobility. © 2009 American Institute of Physics. [DOI: 10.1063/1.3176216]

Organic field-effect transistors (OFETs) have been intensively investigated in the past two decades for low-cost, large-area, and flexible electronic applications. The performance and stability of OFETs critically depends on the dielectric/organic and contact/organic interfaces. The dielectric/organic interface affects the grain formation of the active layer and determines channel resistance. Different approaches have been studied to modify the dielectric surface, such as forming a hydrophobic self-assembled monolayer^{1,2} with hexamethyldisilazane or octadecyltrichlorosilane,³⁻⁵ possibly through lowering the surface energy of the dielectric and removal of residual water and polar groups.⁶ On the other hand, as the channel length decreases, contact resistance, which is related to the contact/organic interface, starts to dominate the charge injection from the contact.⁷ The nature of this contact/organic interface is complicated, and the interface quality can be affected by the disorder of the organic semiconductor near the contact or by the presence of an unfavorable interface dipole. Different methods have been studied to modify this contact/organic interface, such as assembling a monolayer of 4-nitrobenzenethiol^{1,8} and coating a thin layer of poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) (PEDOT:PSS) to the metal contact.⁹ We report here using a highly reduced graphene oxide film (HRG, prepared by reduction in mixed solvent of graphene oxide sheets using hydrazine monohydrate) to improve the quality of the contact/organic semiconductor interface.

In this study, we integrated HRG sheets into pentacene field-effect transistors (FETs) with the two following approaches: by using overlapped and stacked HRG sheets as the source/drain electrodes (“HRG electrodes”) and by coating the gold electrodes with HRG sheets (“HRG-coated gold electrodes”). A bottom-contact device geometry¹⁰ was employed in both approaches, as shown in Fig. 1. The HRG sheets were deposited by dipping a patterned sample into a HRG colloidal suspension. The solvent for this HRG suspension is a mixture of DMF (*N,N* dimethylformamide) and water in a volume ratio of 9:1 (DMF:H₂O).¹¹ In order to confine the HRG sheets in the source/drain regions, patterned

samples possessing regions with a large surface energy difference were employed.¹²

To fabricate a pattern containing regions with a large difference in surface energy, a heavily doped *n*-type silicon wafer with 160-nm-thick thermally grown oxide was used as the substrate. A thin layer of hydrophobic CYTOP® (5-nm-thick) was applied by spin coating a diluted CYTOP® solution (CYTOP®: solvent=1:7) on the substrate at a spin speed of 6500 rpm for 50 s, followed by thermal annealing on a 180 °C hot plate for 20 min in air. The source/drain regions were then patterned with photolithography. For the sample that uses HRG electrodes [Fig. 1(a)], the CYTOP® in the electrode region was removed by applying 50 W oxygen plasma for 20 s. For the sample that uses HRG-coated gold electrodes [Fig. 1(b)], the undesirable CYTOP® was removed with oxygen plasma, and a depth of 36 nm for the recessed electrodes was etched with a reactive ion etcher, and a layer of titanium (2.5 nm) and gold (34 nm) was deposited with a thermal evaporator to form the gold electrodes. The gold in the channel region was removed by lift off. Then, these samples were dipped into the HRG suspension for deposition of the HRG sheets. We note that patterned hydrophobic regions can also be formed by procedures such as stamping and microcontact printing.^{13,14}

After dipping, the HRG suspension preferentially adhered to the most hydrophilic regions. For the sample that has HRG electrodes [Fig. 1(a)], the most hydrophilic source/drain region is the silicon dioxide (S/D electrode region) and the HRG electrodes were formed by repeated (20 times) dip coating and air drying. For the sample that has HRG-coated

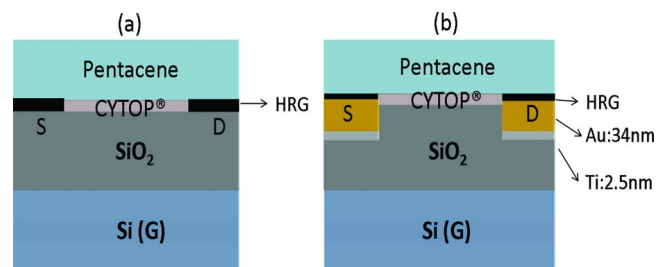


FIG. 1. (Color online) Structure of (a) a device with HRG electrodes and (b) a device with HRG-coated gold electrodes.

^{a)}Electronic mail: chenguanlee@gmail.com.

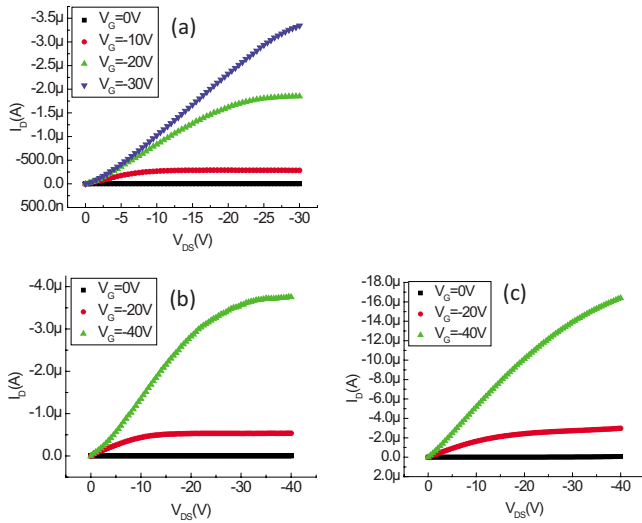


FIG. 2. (Color online) Output characteristics of (a) a device with HRG electrodes, (b) a device with regular gold electrodes, and (c) a device with HRG-coated gold electrodes.

gold electrodes [Fig. 1(b)], the most hydrophilic region is the gold (S/D electrode region), and the HRG sheets were applied by dip coating and air drying for three times. For comparison, a sample with regular gold electrodes was fabricated in a parallel process. There is no detectable HRG deposition in the channel region between source and drain at zero gate bias. This is evident from the very low currents (picoampere level) between source and drain at zero gate bias. After annealing on a hot plate at 120 °C for 10 min in air, pentacene was deposited to a thickness of 25 nm at a deposition rate of 0.1 Å/s and a substrate temperature of 50 °C.

Figure 2 shows the output characteristics of devices with different electrodes. The W/L is 200/12 ($\mu\text{m}/\mu\text{m}$) for all configurations. Figure 3 shows the saturation mobility versus gate voltage for these devices. As can be seen, transistors with the HRG electrodes have similar performance (mobility of 0.03 $\text{cm}^2/\text{V s}$) to those with regular gold electrodes (mobility of 0.045 $\text{cm}^2/\text{V s}$), even though the conductivity of the HRG electrodes is more than five orders of magnitude

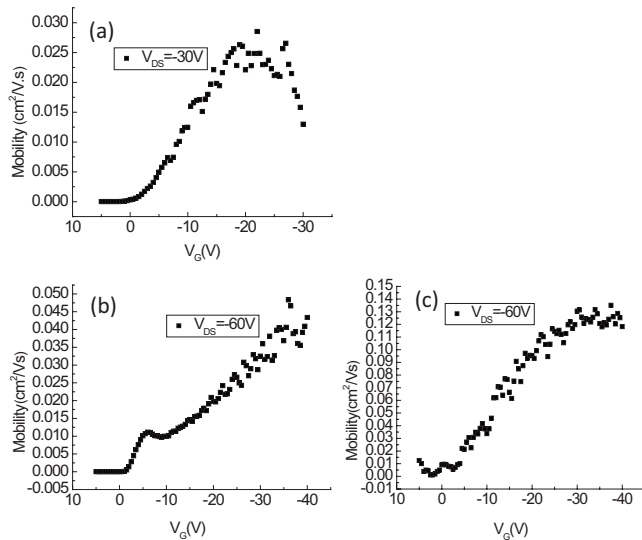


FIG. 3. Mobility vs gate voltage of (a) a device with HRG electrodes, (b) a device with regular gold electrodes, and (c) a device with HRG-coated gold electrodes.

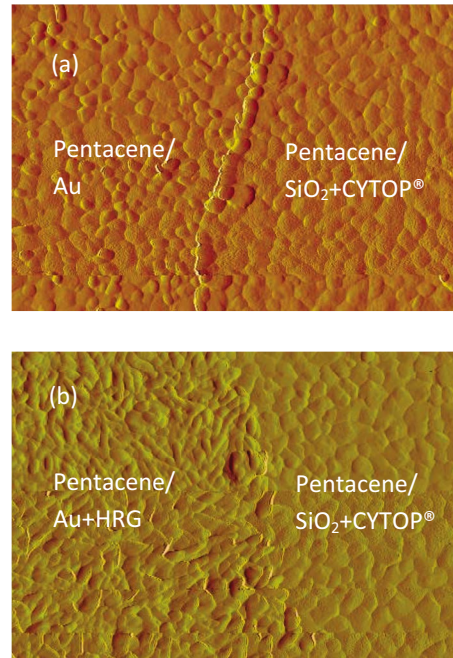


FIG. 4. (Color online) The AFM images of a pentacene film deposited on the interface (a) between CYTOP®-coated SiO_2 and Au and (b) between CYTOP®-coated SiO_2 and HRG-coated Au.

less than that of the gold electrodes. The highest mobility (mobility of 0.13 $\text{cm}^2/\text{V s}$) is obtained from the device with HRG-coated gold electrodes. This implies the carrier injection between HRG and pentacene is superior to that between gold and pentacene. The field-effect mobility of the device with the HRG-coated gold electrodes has increased by a factor of 3 compared to the device with regular gold electrodes (from 0.045 to 0.13 $\text{cm}^2/\text{V s}$). This result shows that using HRG as an interfacial layer to improve charge injection from metal contacts will help the performance of organic transistors. The improvement in mobility with HRG-coated S/D Au electrodes relative to plain Au or plain HRG was reproduced several times. We attribute this performance improvement to better organization of the pentacene molecules. Additionally, the gold/pentacene interface exhibits a significant interface dipole, which results in a large vacuum level shift and high carrier injection barrier.¹⁵ In contrast, the interface dipole in an organic/organic interface is small, leading to a small carrier injection barrier. This lowered barrier caused by the HRG/pentacene interface makes the carrier injection less contact limited and leads to higher effective field-effect mobility. The same behavior has also been observed in gold electrodes coated with a thin layer of organic metal PEDOT:PSS, even though PEDOT:PSS has a lower work function than gold.¹⁶

The atomic force micrograph images of the pentacene grown on Au and on SiO_2 coated with thin CYTOP® do not show a significant difference in grain size [Fig. 4(a)]. However, there is a clearly discernible interface between pentacene grown in the two areas. This interface is much less marked for the case of pentacene grown on HRG-coated gold and SiO_2 coated with CYTOP®. This can be seen in Fig. 4(b). The work of Lee *et al.*¹⁷ showed that pentacene growth on gold is such that the molecule lies flat along its long axis whereas pentacene grown on SiO_2 and hydrophobic surfaces is oriented with the main molecular axis almost perpendicu-

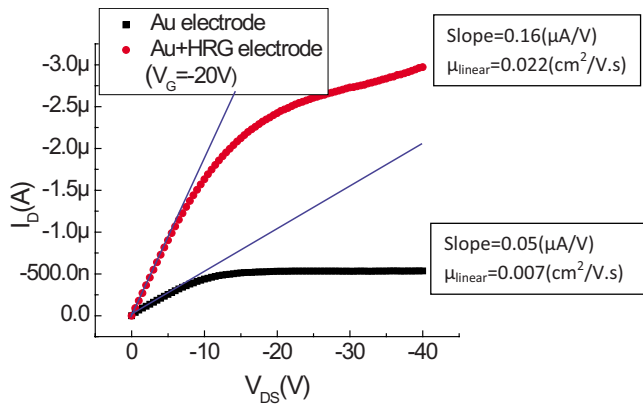


FIG. 5. (Color online) Comparison of the linear mobility of devices with Au and HRG-coated Au electrodes.

lar to the surface. The latter orientation is beneficial for charge transport. The orientation of pentacene molecules on HRG will be very similar to that on most organic hydrophobic surfaces. Thus, there is a change in orientation of the pentacene molecules for pentacene grown on Au versus pentacene grown on SiO₂/CYTOP®, resulting in enhanced contact resistance and therefore a lower measured mobility. In the case of HRG-coated Au electrodes, this difference in orientation is not expected to be present, resulting in better contacts. The improved electrical behavior of the HRG-coated Au contacts is evident in Fig. 5 in which the output characteristics are shown in the linear region for the two cases. Thus, the morphological evidence of Fig. 4 is in agreement with the electrical characteristics shown in Figs. 3 and 5.

Interfaces are critical in organic semiconductor electronics. We have shown that the use of highly reduced graphene oxide (HRG) as an interfacial material between gold source/drain electrodes and an exemplary *p*-channel FET forming material (pentacene) yields improved performance and higher effective mobility (by a factor of 3). We anticipate that the use of an HRG interface will also improve the long-term stability of organic electronic circuits. Given the wide

chemical tunability of graphene (in principle, because the chemistry of carbon is extremely broad), it is possible that other chemically modified graphenes that have good electrical conductivity, including pristine graphene, might perform even better than HRG.

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