Ambipolar rubrene thin film transistors

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(Received 5 October 2005; accepted 28 April 2006; published online 8 June 2006)

We report ambipolar field-effect transistors fabricated from rubrene thin films on SiO_2/Si substrates. The mobilities of both holes and electrons were extremely low, ranging from 2.2×10^{-6} to 8.0×10^{-6} cm^2/V s, due to disorder in the films. Rubrene forms three-dimensional circular islands even at extremely low coverages and x-ray diffraction observations suggest that the film is amorphous. The formation of the conducting channel of the transistor follows the geometric percolation of rubrene islands. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2210294]

Among organic semiconductor field-effect transistors (FETs), the highest mobilities range from 1 to 20 cm^2/V s and are found in devices fabricated on single crystals. These crystals have a high degree of molecular ordering and low densities of charge traps. Rubrene ($C_{42}H_{28}$) transistors have particularly high values of the surface carrier mobility compared with devices formed on other single crystals up to 20 cm^2/V s.[1] Thin films of a wide range of organic semiconductor materials are desirable, however, because they have the potential to facilitate flexible and large-area electronics using low cost manufacturing. The properties of films depend on the transport of charge induced at the gate dielectric-semiconductor interface and are affected by the structure and composition of the first few layers of molecules.[2–4] The highest mobilities observed in thin film transistors are lower than single crystal devices, ranging from 0.3 to 1.5 cm^2/V s.[5–7] Haemori *et al.*[8] and Stingelin-Stutzmann *et al.*[9] have made rubrene-pentacene bilayers on sapphire substrates and solution-processed rubrene devices have recently been demonstrated.

Most organic thin film FETs are *p*-channel enhancement mode devices. Until ambipolar behavior was discovered very recently, single-crystal rubrene FETs exhibited only *p*-type conductivity.[7,10,11] Although some ambipolar organic FETs have been fabricated using blends,[12,13] bilayers,[14] or assistant materials together with an organic semiconductor,[15] only a few observations of ambipolar behavior in high-purity single component materials have been reported.[9,10,16] In this letter, we present an ambipolar rubrene thin film transistor in which the interfaces and island structure of the rubrene thin film have an important role in the formation of the FET.

We used a bottom-contact thin film transistor geometry to form rubrene FETs. Rubrene thin films were deposited onto lithographically defined electrodes on heavily doped *p*-type silicon wafers that were thermally oxidized to form a 200 nm SiO_2 gate insulator. The silicon substrate acted as the gate electrode. A channel of 800 μm wide and 10 μm long separated by 50 nm thick Au source and drain contacts on 10 nm thick Cr adhesion layers. The rubrene source material was purified before deposition by preheating for 12 h in the effusion cell.

The drain current I_D for an approximately 200 nm thick rubrene film is plotted as a function of the drain voltage with negative gate voltages in Fig. 1(a) and with positive gate voltages in Fig. 1(b). The output characteristics were measured for both negative and positive drain-source voltages at gate voltages from $V_G=-80$ to 90 V. With negative gate voltages exceeding the threshold voltage for holes, −36 V, *p*-type conduction was observed [Fig. 1(a)] and I_D saturated at large negative drain voltages. For gate voltages in the range of $-30\leqslant V_G\leqslant 0$ V the drain current increased abruptly with drain voltages of larger magnitude, due to *n*-type conductivity. These electron currents did not saturate at large negative drain voltages. Likewise, electron enhancement

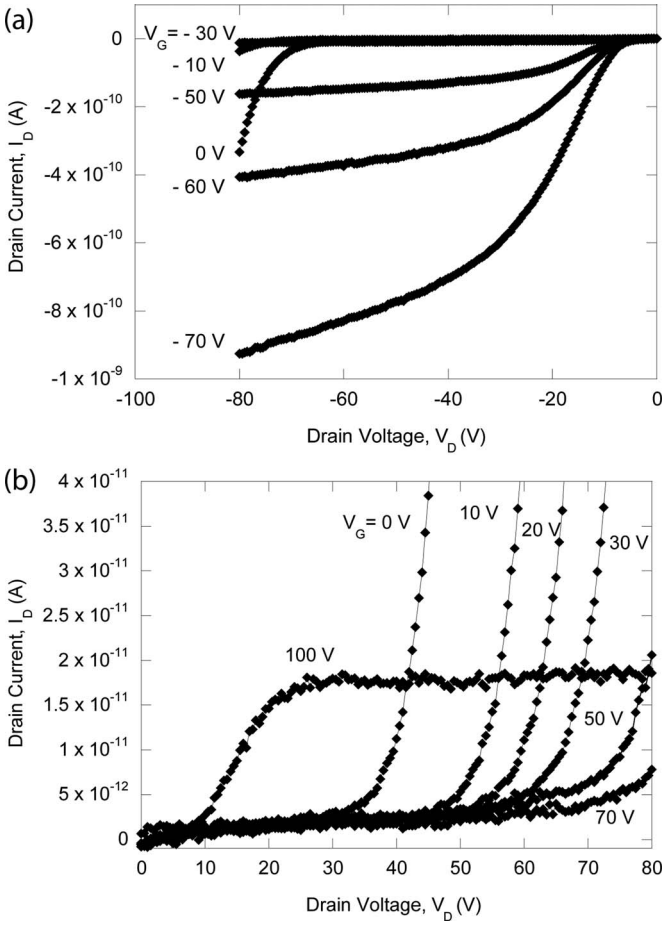

FIG. 1. Ambipolar output characteristics of a rubrene thin film transistor for (a) negative gate voltages ranging from 0 to −70 V and (b) positive gate voltages between 0 and 100 V.

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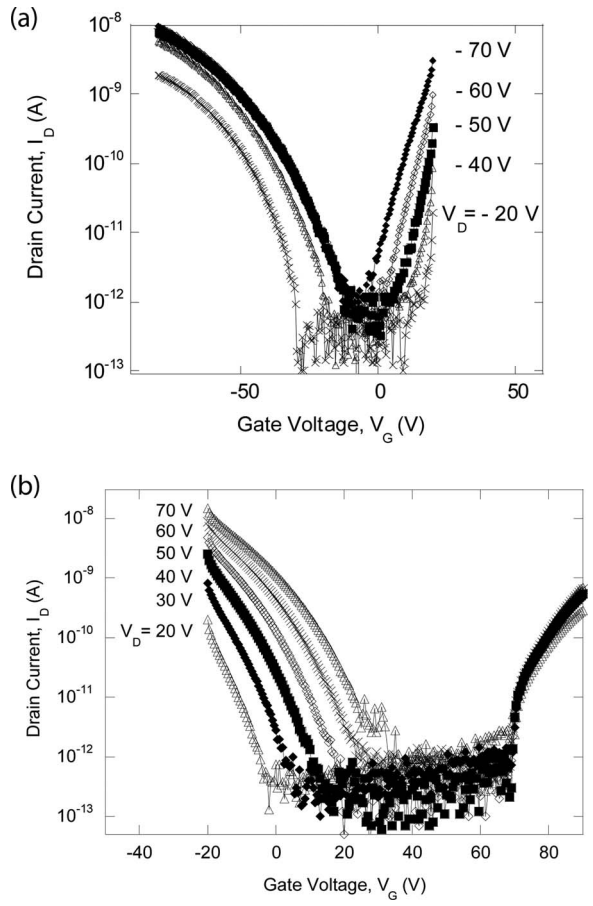

FIG. 2. Drain current vs gate voltage transfer characteristics for a (a) positive and (b) negative drain voltages applied to a rubrene thin film transistor.

mode behavior was observed for the positive gate voltage, V_G=100 V in Fig. 1(b) at which the electron current dominated. At V_G less than 70 V, the current due to hole injection at the drain contact increased for drain voltages higher than 30 V. The current-voltage curves in Fig. 1 are similar to the transistor characteristics of other ambipolar devices.[14,17,18]

The transfer characteristics shown in Figs. 2(a) and 2(b) for negative and positive drain voltages also exhibit device operation in both hole enhancement and electron enhancement modes. In Fig. 2(a), as the gate voltage is decreased from positive values the drain current first decreases until small negative values of V_G and increases again for more negative V_G. The electron current dominates for the gate voltages higher than the threshold voltage for *n*-type transport. In devices with only *p*-type or *n*-type behavior, an appreciable drain current would be observed with only one sign of the gate voltage.

The electrical measurements demonstrating ambipolar transistor behavior were performed *in situ* following the deposition of rubrene thin films. Upon exposure to air the rubrene transistors continued to have *p*-type characteristics, but exhibited an irreversible loss of *n*-type behavior. Single-crystal rubrene FETs investigated in ambient conditions have shown no *n*-type transport.[1,3,10] A number of mechanisms can combine to suppress electron conduction in air, including the formation of electrically active defects and the oxidation of electrodes.[15,19] Transistors fabricated with 1 nm rather than 10 nm Cr adhesion layers had electron currents smaller than the background of 2–4 pA.

Ambipolar transport is widely thought to be a generic property of organic semiconductors. In device structures, the observation of ambipolar characteristics depends on the alignment of the work functions of the source and drain contacts and the energy levels of the organic semiconductor.[9] The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of rubrene are estimated to be 5.36 and 3.15 eV below the vacuum, respectively.[20] The alignment of the HOMO level of rubrene with the Au work function of 5.1 eV results in a small barrier for hole injection from Au to rubrene. The lower work function of Cr, 4.5 eV, provides better electron injection into the LUMO level of rubrene than Au. Using a value for the Schottky barrier based on the Schottky-Mott rule and the band alignment proposed by Hamada *et al.*,[20] we estimate that the thermionic electron current between a Cr contact and rubrene would be a factor of 10^8 larger than with an Au contact. The difference in work functions between Cr and Au has a significant role in promoting electron conduction through the contacts.

The saturation mobilities extracted from the rubrene FET characteristics in Fig. 1 are 8.0×10^{-6} $cm^2/V\,s$ for holes and 2.2×10^{-6} $cm^2/V\,s$ for electrons. These mobilities of holes and electrons are much smaller than the mobility of holes in rubrene single crystal transistors.[1] Although Fourier transform infrared spectroscopy (FTIR) data show that the material deposited on the substrate is rubrene, the thin films lack the strong x-ray reflections commonly observed in other materials, suggesting that they may have an amorphous rather than crystalline structure. Fong *et al.* demonstrated that randomness in intermolecular separations in rubrene films leads to geometric disorder.[21]

The formation of the conducting channel depends on the shape and arrangement of the rubrene islands. This dependence can be probed by measuring the drain current as a function of time during the initial stages of the transistor formation as rubrene is deposited onto the bottom-contact FET structure. During deposition, the substrate was held at room temperature and the gate voltage V_G was repeatedly scanned from 0 to −70 V in approximately 90 s sweeps with the drain held at −50 V. The deposition time was converted to average rubrene thickness using atomic force microscopy (AFM) to measure the volume of rubrene islands after 12 min of deposition. The average thickness at this time gave a deposition rate of 1.0 nm/min, with an uncertainty of approximately 0.2 nm/min due to island counting statistics. Figure 3 shows the drain current with V_G=−70 V as a function of average thickness. A small leakage current up to 25 pA flowed through the gate insulator at low average thicknesses. The sudden increase in the drain current between 5 and 6 nm corresponds to the formation of a conducting channel connecting the source and drain. Current began to flow between the source and the drain electrodes at this sharp threshold.

The rapid onset of current in Fig. 3 is due to the geometric percolation of rubrene islands. The geometric percolation threshold is reached when the fraction of the surface covered by islands reaches 0.67 and does not vary significantly with changes in the shape or size of compact islands.[22] Under the assumption that all islands are the same shape and size and the nucleation density is constant, the total volume required for percolation can be estimated in terms of the average radius required to reach this area fraction, and converted to the

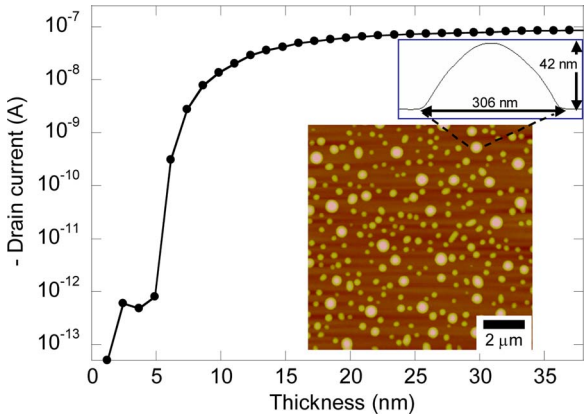

FIG. 3. (Color online) The drain current for $V_G=-70$ V and $V_D=-50$ V as a function of average rubrene thickness. An AFM image (inset) shows rubrene islands on the SiO_2/Si substrate with average thickness less than the percolation threshold. The sectional image shows the three-dimensional (3D) growth of a rubrene island.

average thickness. Based on the island shapes described below, the geometrical prediction of the percolation threshold is 4.5 nm, in reasonable agreement with our observation, given the uncertainty in deposition rate.

Rubrene islands continuously nucleate and grow in three dimensions up to heights of tens of nanometers even at the initial stages of growth (Fig. 3, inset). The rubrene-SiO_2 contact angle was 23°, independent of rubrene thickness. The energetics of the rubrene-SiO_2 interface thus apparently favor forming three dimensional rather than monolayer-high islands. In comparison with pentacene, which easily forms single-molecule-thick films, this property is highly undesirable.

Although the mobility in these rubrene thin film FETs is much lower than in single-crystal rubrene FETs, the ambipolar transport characteristics of the thin film devices allow greater flexibility in organic circuit design. Our observations that apparently amorphous three-dimensional rubrene islands appear even at the initial stages of growth, and that a volume of rubrene far higher than the equivalent of a single molecular layer must be deposited before the islands come into contact with each other show that rubrene does not yet form the optimum layer structures for thin film devices. The potential to realize ambipolar circuits based on rubrene FETs depends on the optimization of thin film deposition techniques to develop crystalline layers.

This work was supported by the National Science Foundation through the University of Wisconsin Materials Research Science and Engineering Center, Grant No. DMR-0520527, and by the Petroleum Research Fund of the American Chemical Society.

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