C_{70} Thin Film Transistors

R. C. Haddon

Bell Laboratories
Lucent Technologies
Murray Hill, New Jersey 07974-0636

Received November 20, 1995

Organic semiconductors are being tested as the active electronic elements of thin film field effect transistors (TFTs) and light-emitting diodes.[1−4] Rigorously purified α-sexithiophene (α-6T)[4] shows field effect mobilities of $\mu = 0.01-0.05$ cm^2/V·s and on−off current ratios of greater than 10^6. The switching speeds of α-6T TFTs are typically 10 μs; hence, such devices are fast enough to be considered for use in display applications.[4] Most organic materials function as p-type semiconductors, with holes as the current carriers, but C_{60} is known to be an n-type material that transports electrons.[5] Recently we have shown that C_{60} thin films that are prepared and studied in ultrahigh vacuum (UHV) exhibit excellent device characteristics. C_{60}-based TFTs show on−off ratios of 10^6 and field effect mobilities of $\mu = 0.08$ cm^2/V·s.[6] Heterostructure field effect transistors based on thin films of α-6T and C_{60} have demonstrated both p- and n-channel operation in a single device.[7] The basis for understanding the criteria for materials selection in organic TFTs is currently quite primitive,[8] and in order to provide information on this question, the present work reports a study of TFTs fabricated from C_{70}. The fullerenes C_{60} and C_{70} are found to exhibit markedly different performances as the active semiconductor in TFT devices.

We followed the general scheme developed to study metal-doped C_{60} films and TFTs in UHV.[6,9] The C_{70} source material was obtained from Hoechst Chemical (Gold grade, purity greater than 99.4% by HPLC). The UHV chamber used in this work is equipped with a C_{70} source so that the C_{70} films were grown *in situ* and were not exposed to oxygen prior to their evaluation in field effect devices. Sublimation of C_{70} in this manner produces small grain, mixed-phase films containing orientationally disordered C_{70} molecules.[10] The field effect measurements were carried out using devices that were identical to those used previously to study the C_{60} TFTs.[6] The substrates (Figure 1) were fabricated from heavily n-type-doped silicon wafers which were oxidized to leave a 3000 Å thick layer of silicon dioxide on one surface. On top of this surface, chromium (250 Å) and gold (250 Å) pads were defined using lithographic techniques to give the source (S) and drain (D) electrodes. The substrates were wired to a UHV feed-through similar to those previously used for conductivity studies.[9] The C_{70} films were deposited on the substrates through a mask to give the profile shown in Figure 1.

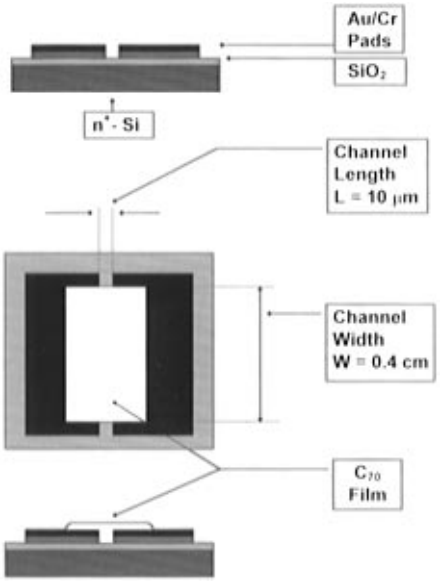

Figure 1. Device structure of the C_{70} thin film transistors used in the present study. The Au/Cr pads comprise the drain and source electrodes, whereas the n-type doped Si acts as the gate electrode. The C_{70} films were deposited through a mask after the substrate had been introduced into the UHV chamber.

A transistor is a three-terminal device that acts as switch or an amplifier. With connections to the D and S electrodes (Au/Cr pads, Figure 1), the current in an electrical circuit (I_D) may be modulated by the voltage applied to the gate electrode (n-Si wafer), because it is the C_{60} or C_{70} film that completes the circuit between drain and source. C_{60} is a semiconductor and, because it has few carriers (electrons or holes), shows a low conductivity, and therefore when the device is turned off ($V_G = 0$) very little current is passed by the device. However, doping solid C_{60} with alkali metals transfers electrons to the conduction band and leads to moderately high conductivities. The same principle is used in the transistors fabricated from C_{60}, but now the gate electrode plays the role of the counterions; when a positive potential is applied to the gate ($V_G > 0$), the C_{60} functions as the other plate of a capacitor and electrons are drawn into the film, and the increased carrier concentration strongly enhances the conductivity (accumulation mode). The on−off ratio refers to the current passed by the device with the gate voltage on and off, and in α-6T and C_{60} TFTs, values of 10^6 have recently been achieved.[4,6]

The n-channel transistor characteristics of an 800 Å thick film of C_{70} are shown in Figure 2. For a given gate voltage (V_G), an ideal field effect transistor is expected to show a drain current (I_D) that increases linearly with drain−source voltage (V_{DS}) before gradually leveling off to approach the saturation current (I_D^{sat}). The value of the gate voltage required to turn on the device is known as the threshold voltage (V_T) in conventional MOSFETs, as expressed here

$$I_D^{sat} = \mu((CW)/2L)(V_G - V_T)^2 \qquad (1)$$

where μ is the channel mobility, C is the capacitance of the gate oxide layer, W is the channel width, and L is the channel length. For the devices reported in this work these parameters had values of $C = 1.2 \times 10^{-8}$ F/cm^2, $W = 0.4$ cm, and $L = 10$ μm. Use of eq 1 to analyze the data shown in Figure 2 gives a field effect mobility of the electrons $\mu_e = 2 \times 10^{-3}$ cm^2/V·s and a threshold voltage $V_T = 27$ V for the C_{70} TFT. This analysis shows that the threshold voltage for channel formation in the these devices is even higher than that found for C_{60} ($V_T = 15$ V).[6] Thus at low gate voltages, carriers injected into the

(1) Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc.* **1993**, *115*, 8716−8721. Garnier, F.; Hajlaoui, R.; Yassar, A.; Srivasta, P. *Science* **1994**, *265*, 1684−1686.
(2) Fuchigami, H.; Tsumara, A.; Koezuka, H. *Appl. Phys. Lett.* **1993**, *63*, 1372−1374.
(3) Tang, C. W.; Van Slyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913−916.
(4) Dodabalapur, A.; Torsi, L.; Katz, H. E. *Science* **1995**, *268*, 270−2.
(5) Kastner, J.; Paloheimo, J.; Kuzmany, H. In *Springer Series in Solid State Sciences*; Kuzmany, H., Mehring, M., Fink, J., Eds.; Springer-Verlag: Berlin, 1993; Vol. 113, pp 512−515.
(6) Haddon, R. C.; Perel, A. S.; Morris, R. C.; Plastra, T. T. M.; Hebard, A. F.; Fleming, R. M. *Appl. Phys. Lett.* **1995**, *67*, 121−123.
(7) Dodabalapur, A.; Katz, H. E.; Torsi, L.; Haddon, R. C. *Science* **1995**, *269*, 1560−1562.
(8) Haddon, R. C.; Siegrist, T.; Fleming, R. M.; Bridenbaugh, P. M.; Laudise, R. A. *J. Mater. Chem.* **1995**, *5*, 1719−1724.
(9) Haddon, R. C.; Kochanski, G. P.; Hebard, A. F.; Fiory, A. T.; Morris, A. S. *Science* **1992**, *258*, 1636−1638.
(10) Vaughan, G. B. M.; Heiney, P. A.; Fischer, J. E.; Luzzi, D. E.; Ricketts-Foot, D. A.; McGhie, A. R.; Hui, Y.-W.; Smith, A. L.; Cox, D. E.; Romanow, W. J.; Allen, B. H.; Coustel, N.; McCauley, J. P.; Smith, A. B., III. *Science* **1991**, *254*, 1350−1353.

0002-7863/96/1518-3041$12.00/0

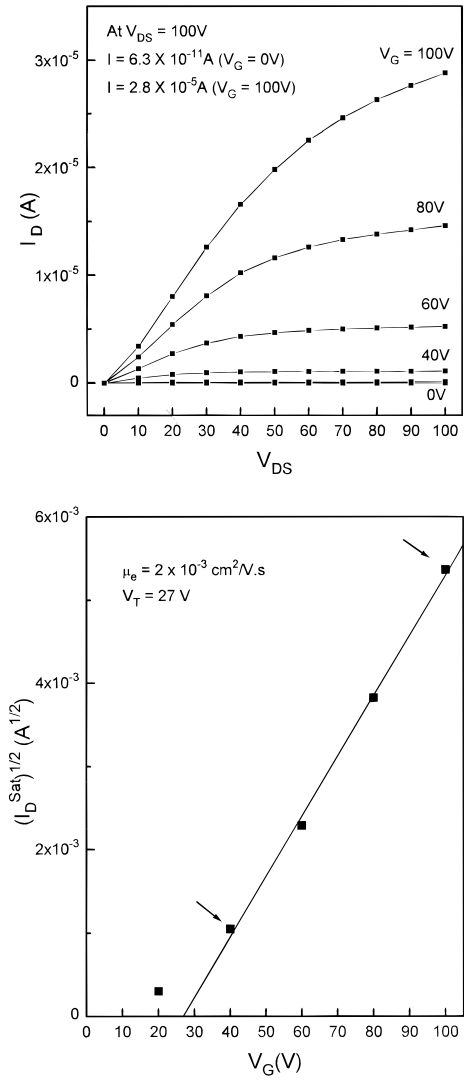

Figure 2. Drain current (I_D) versus drain−source voltage (V_{DS}) for various gate voltages (V_G), for a C_{70} thin film transistor (top). Analysis of saturation currents with eq 1 (bottom).

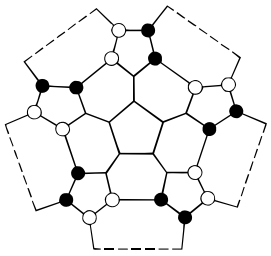

Figure 3. Schlegel diagram of the A″ LUMO of C_{70} from an HMO calculation, viewed down the C_5 axis. Only the atoms in and above the symmetry plane that bisects the molecule at the equator are shown. The orbital is antisymmetric with respect to this plane.

C_{70} layer are trapped at the interface to the dielectric in low-mobility states. The difficulty in injecting electrons into these materials may be related to the mismatch in the energies of the conduction band of the fullerenes and the work function of gold.[6,7] As in the case of C_{60}, pretreatment of the devices with tetrakis(dimethylamino)ethylene (TDAE) effectively eliminates the threshold voltage in the C_{70} devices, but at the expense of the on−off ratio. The TDAE is expected to form a charge transfer salt[11] with the fullerene at the interface, and this presumably screens the interface and removes most of the deep traps that ordinarily pin the carriers in the TFTs at low gate voltages.

The performance of the C_{70} TFTs degraded on exposure to the atmosphere, but not as rapidly at those fabricated from C_{60}. The high threshold voltages and sensitivity to oxygen exhibited by the fullerenes probably both originate from the transport of charge by electrons rather than holes as is common in most organics. The conductivities of the C_{70} films in the TFT devices were about 2×10^{-9} S/cm, an order of magnitude lower than those of the C_{60} films.[6] The threshold voltage is increased, $V_T = 27$ V (C_{70}) compared to $V_T = 15$ V (C_{60}), and the field effect mobility is lowered, $\mu = 2 \times 10^{-3}$ $cm^2/V{\cdot}s$ (C_{70}) compared to $\mu = 8 \times 10^{-2}$ $cm^2/V{\cdot}s$ (C_{60}). In addition, the on−off ratio is lower by an order of magnitude in the C_{70} devices. The present results serve to emphasize the sensitivity of TFT performance to the properties of the active electronic material. Apart from exhibiting a higher electron affinity[12] and a greater ease of reduction,[13] C_{70} is slightly larger than C_{60} and thus should be effective in delocalizing the carriers and thereby preventing the formation of deep traps by lattice relaxation.[8] However, C_{70} is anisotropic, and the disorder[10] that is introduced into the films by this additional variable apparently perturbs the solid state electronic structure to the point that the mobility is seriously impaired. Furthermore, the increased threshold voltage suggests that the lower symmetry of C_{70} pins more carriers at the dielectric/semiconductor interface. It is also possible that some of the differences seen in the semiconductor properties of these two fullerenes stem from band structure effects. The lowest unoccupied molecular orbital (LUMO) of C_{60} is triply degenerate and effectively delocalized over the whole molecule,[14] and this leads to a well-developed dispersion in the conduction band in the solid state.[8] The band structure of C_{70} has not been reported, but reference to Figure 3 shows that the LUMO of C_{70} is of an entirely different character. The C_{70} LUMO has nodes at 30 of the 70 carbon atoms, and this includes the 10 carbon atoms at each cap of the molecule (the carbon atoms closest to the 5-fold (C_5) axis), as well as the 10 carbon atoms at the equator (furthest from the C_5 axis). Thus to first order, there will be no dispersion from the interaction of the molecules along the C_5 axis, and we infer that the conduction band arising from the C_{70} LUMO will be rather different from the isotropic electronic structure characteristic of n-type-doped C_{60}.[8] Photoemission experiments[15] on potassium-doped films of these fullerenes show that electrons in the C_{70} LUMO give emission well below the Fermi level, in contrast to the behavior of C_{60} at low doping levels.

Acknowledgment. I am grateful to A. Dodabalapur, A. F. Hebard, H. E. Katz, T. T. M. Palstra, and L. Torsi for valuable discussions.

JA953881W

(11) Wudl, F.; Thompson, J. D .*J. Phys. Chem. Solids* **1992**, *53*, 1449−1455.
(12) Yang, S.; Pettiete, C. L.; Conceicao, J. J.; Cheshnovsky, O.; Smalley, R. E. *Chem. Phys. Lett.* **1987**, *139*, 233−238. Wang, L. S.; Conceicao, J. J.; Jin, C. M.; Smalley, R. E. *Chem. Phys. Lett.* **1991**, *182*, 5−11. Boltalina, O. V.; Sideov, L. N.; Vorschevsky, A. Y.; Sukhanova, E. V.; Skokan, E. V. *Rapid Commun. Mass. Spectrom.* **1993**, *7*, 1009.
(13) Xie, Q.; Perez-Coredero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978−3980.
(14) Haddon, R. C. *Acc. Chem. Res.* **1992**, *25*, 127−133.
(15) Benning, P. J.; Poirer, D. M.; Ohno, T. R.; Chen, Y.; Jost, M. B.; Stepniak, F.; Kroll, G. H.; Weaver, J. H.; Fure, J.; Smalley, R. E. *Phys. Rev. B* **1992**, *42*, 6899−6913.