High-Performance Plastic Transistors Fabricated by Printing Techniques

Zhenan Bao,* Yi Feng,* Ananth Dodabalapur, V. R. Raju, and Andrew J. Lovinger

Bell Laboratories, Lucent Technologies 600 Mountain Avenue Murray Hill, New Jersey 07974

Received February 26, 1997

Considerable advances have been made recently in organic/polymeric electronic materials and devices.[1−5] These materials are useful as active layers in applications such as nonlinear optical devices,[6−8] light-emitting diodes (LED),[9,10] and thin-film field-effect transistors (FETs).[11−20] We have been studying different materials for thin-film FETs in which the active semiconductor layer consists of organic molecular or polymeric materials.[15,19−21] Organic FETs have potential applications in low-cost large area flexible displays and low-end data storage devices such as smart cards. Organic materials offer numerous advantages for easy processing (e.g., spin-coating, printing, evaporation), good compatibility with a variety of substrates including flexible plastics, and great opportunities in structural modifications.[18,22]

Screen printing is a simple and environment-friendly way to produce electronic circuitry and make interconnections.[23] It is a purely additive method in which ink is added where needed. Therefore, patterns can be formed in a single step. With a pitch of printed lines as fine as 250 μm, the printing process can significantly reduce the time and cost associated with photolithography. If liquid-phase processable organic semiconductors can be used, low-cost large-area electronics with flexible plastic substrates for display or data storage can be realized by using only a printing technique.[18,22,24] Recently, Garnier et al. have demonstrated the usefulness of printing in organic field-effect transistor fabrication.[22] In their transistors, however, only the gate electrode and a pair of drain and source electrodes, respectively, were printed separately on each side of a sheet of polyester film (1.5 μm thick) which acts as the dielectric layer. This film with electrodes was then taped to a plastic substrate followed by vacuum deposition of an organic semiconductor layer of insoluble dihexyl-α-hexathienylene (DH-α-6T). For practical applications, it is desirable that all the necessary components may be printed in a continuous process. However, all the soluble, film-castable, and processable organic semiconductors studied thus far have very poor transistor performance, and the field-effect mobilities in those devices are only of the order of 10^{-5}−10^{-3} cm^2/V s.[13,14,17,18] Alternatively, a soluble precursor can be deposited and then converted to the active layer. With such materials, higher mobilities have been obtained. This approach, however, does not appear to be promising for applications where continuous or semicontinuous processing is required.[25] Therefore, to realize high-performance FETs by the printing technique, it is crucial that a solution-processable organic semiconductor with high mobility be employed.

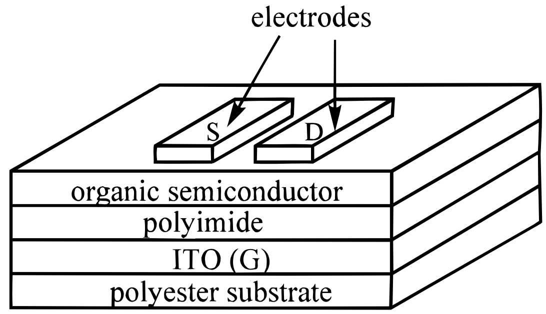

Figure 1. Structure of a printed plastic transistor. S, source; D, drain; G, gate.

We have recently developed organic transistors with high field-effect mobilities (ca. 0.015−0.045 cm^2/V s) using regioregular poly(3-hexylthiophene) (PHT).[20] Since PHT is soluble in various common organic solvents, it can be processed by spin-coating, casting, or printing. Here, we demonstrate the first high-performance plastic transistor (shown schematically in Figure 1) in which all the essential components are printed directly onto plastic substrates.

An ITO-coated poly(ethylene terephthalate) film (from Southwall Technologies) is chosen as the plastic substrate since it is readily available commercially and is commonly used as the substrate for large-area displays. In our devices, the ITO layer acts as the gate electrode. It is also possible to print a conducting polymer such as polyaniline to form the gate electrode.[10] A polyimide (OPTIMER AL 3046 from Japan Synthetic Rubber Co.)

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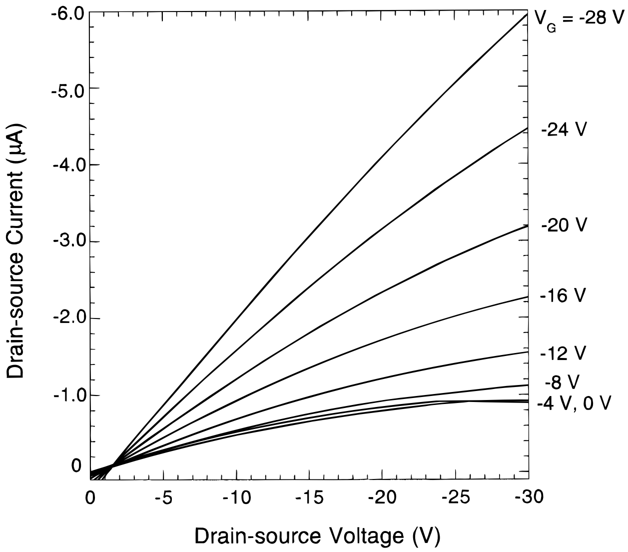

Figure 2. Current−voltage characteristics of a printed plastic transistor operated in the accumulation mode at different gate voltages.

layer is then printed through a screen mask onto the ITO surface. The screen mask is made of a stainless steel fabric with 400 mesh count/in.; an emulsion thickness of about 7.5 μm is used. After being printed, the polyimide dielectric layer is baked at 120 °C for an hour. The capacitance of such a film is about 2.0×10^{-8} F/cm^2, measured with a Hewlett-Packard (HP) 4284A Precision LCR meter. An organic semiconductor layer consisting of regioregular poly(3-alkylthiophene)s with different alkyl chain lengths is then put down by spin-coating, casting, or printing using chloroform as the solvent. The regioregular poly(3-alkylthiophene)s employed in this study are commercially available from Aldrich Chemical Co. These polymers were prepared using the method developed by Rieke et al. and have better than 98.5% head-to-tail (HT) linkages.[26] We have further purified the polymer by dissolving it in toluene and precipitating from acetone. This procedure is repeated twice and the polymer is then extracted with boiling acetone for 3 days. Finally, the device is completed by printing the drain and source electrodes using a conductive ink (479SS from Acheson Co.) through a screen mask made of the same fabric and using the same thickness of emulsion. The drain and source electrodes are two strips 0.5 mm × 4 mm each, separated by a gap of 100 μm, and are about 10 μm thick. Therefore, the channel width (W) and channel length (L) of this device are 4 mm and 100 μm, respectively. Four pairs of such electrodes are printed on each 0.8 × 1.0 cm printed polyimide pad consisting of a layer of polyimide covered with a layer of regioregular poly(3-alkylthiophene). By using the above procedure, many devices with different shapes or geometries can be easily obtained in large quantities simply by printing through suitable screen masks. To our knowledge, these are the first plastic transistors in which all the components are printed.

The electrical characteristics of these devices have been measured in air and under vacuum (10^{-2} and 10^{-5} Torr) using an HP 4145B analyzer. Figure 2 shows the transistor characteristics of a typical printed device fabricated with regioregular poly(3-hexylthiophene) (PHT). All the transistors are *p*-channel devices and can operate in both accumulation-mode and depletion-mode. The slope of the linear region of the drain-source current (I_{DS}) vs the drain-source voltage (V_{DS}) at different gate voltages (V_G) in Figure 2 is plotted vs V_G, and the slope of this plot is equal to $(WC_i/L)\mu$, where μ is the field-effect mobility, W is the channel width (4 mm), L is the channel length (100 μm), and C_i is the capacitance per unit area of the polyimide layer (C_i = 20 nF/cm^2).[27,28] The field-effect mobility calculated using this method for many devices with the same parameters and geometries as shown in Figure 1 was found to be between 0.01 and 0.03 cm^2/V s. This is one of the highest values achieved for polymer FETs. It is comparable to the results obtained for regioregular poly(3-hexylthiophene) by using a Si substrate and SiO_2 as the dielectric layer with lithographically defined electrodes.[20] In addition, changing of the electrodes from Au to Ag does not seem to affect the performance of these transistors. As suggested by our earlier results, the relatively high mobilities in these polythiophenes might be related to better ordering and preferred orientation which would place the transport direction (i.e., between thienyl ring backbones) close to parallel to the substrate. Using electron diffraction on PHT thin films, we have found that regioregular poly(3-alkylthiophene)s are deposited with a preferred orientation, such that the side chains may be close to normal to the substrate and the backbones close to parallel to the substrate.[20]

Transistors made from regioregular poly(3-alkylthiophene)s with octyl (POT) and dodecyl (PDT) substituents have also been fabricated, and their electrical characteristics have been studied. POT is found to have a similar field-effect mobility as PHT, while PDT has a much lower mobility of the order of 10^{-6} cm^2/V s. We have performed X-ray diffraction analysis on cast films of these polymers. Both PHT and PDT have very strong, sharp diffraction peaks at 5.4° 2θ (16.36 Å) and 4.4° 2θ (20.10 Å), respectively. These spacings correspond to the chain distances of a well-organized molecular layer structure, which is consistent with literature reports.[26] PDT showed a much weaker diffraction peak at 3.2° 2θ (27.10 Å), indicating lower crystallinity or orientation. In addition, its higher volume fraction of insulating side chains may also contribute to its low field-effect mobility.

We have electrically tested our printed transistors both in air and under vacuum (10^{-2} or 10^{-5} Torr). Their field-effect mobilities are slightly higher (about 2 times) when measured in air. Spin-coated films tend to have lower mobility than cast or printed films possibly because the latter films have better ordering resulting from slower solvent evaporation and consequent slower crystal growth.

In summary, we have demonstrated that high-mobility plastic transistors can be fabricated by screen printing techniques. This has been made possible due to the high performance and easy processability of soluble regioregular poly(3-alkylthiophene)s. The field-

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effect mobilities of such transistors are very similar to those formed on Si substrates with SiO_2 gate dielectric layer. Further studies will be carried out to optimize the device structure and the printing process. A range of dielectric materials, conductive inks, and semiconducting polymers are currently under investigation.

Acknowledgment. The authors thank our colleagues M. Berggren, E. A. Chandross, H. E. Katz, J. G. Laquindanum, E. Reichmanis, and R. E. Slusher for useful discussions.

CM9701163