Unipolarization of ambipolar organic field effect transistors toward high-impedance complementary metal-oxide-semiconductor circuits

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Ambipolar organic field effect transistors (OFETs), consisting of a composite of polyhexylthiophene (PHT) and [6,6]-phenyl C61-butylic acid methyl ester (PCBM), was converted into a *p*- or *n*-type OFET by insertion of a thin tetracyanoquinodimethane (TCNQ) or tetrathiafluvalene (TTF) buffer layer. The interface in the Au/TCNQ/PHT:PCBM composite transports hole but blocks electron, while the transported carrier was switched to electron with insertion of a TTF layer. The selective transport is probably due to vacuum level matching or temporal doping. High impedance in a complementary metal-oxide-semiconductor inverter was demonstrated with unipolarized ambipolar FETs, resulting in a decrease in the through current. © *2007 American Institute of Physics*.
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In working toward ubiquitous flexible electronic devices, fabrication of complementary metal-oxide-semiconductor (CMOS) inverter based on soluble semiconductors has become an attractive goal for realizing printable logic circuits. Ambipolar organic field effect transistors (OFETs) composed of fusible materials are desirable as they can be fabricated with a one-step deposition process.[1] Both *p*-type and *n*-type FETs are required to realize complementary switching. For CMOS inverters using ambipolar FETs, there is a fundamental issue of the large through currents (I_t) under holding potentials. Tunablility of ambipolar characteristics promises to overcome such problems. Tuning of ambipolar FET characteristics is possible during the preparation of composites, electrodes, or double-layer structures,[2,3] enabling various tailor-made devices with large variations in characteristics. Fabrication of ambipolar FETs with composite film consisting of *p*- and *n*-type semiconductors was, therefore, gained much attention due to the large validation of carrier transport characteristics.[4] Unipolarization is probably an important tuning procedure for fabricating high-impedance CMOS inverter.

Interface engineering, which focuses on the configuration of electrodes and organic semiconductors, is a key technology to decrease contact resistance, thereby promoting OFET performance.[5–10] In molecular electronics, tetrathiafluvalene (TTF) and tetracyanoquinodimethane (TCNQ) are the well-known molecules to form charge-transfer crystals because of their strong electron donating and accepting characteristics. For ambipolar OFETs, insertion of the electron-donating or -accepting organic layer should, respectively, promote or suppress carrier transport across the interface.[9,10]

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We have demonstrated the unipolarization of ambipolar OFETs using a composite consisting of polyhexylthiophene (PHT) and [6,6]-phenyl C61-butylic acid methyl ester (PCBM) (PHT:PCBM) by the simple insertion of a TTF or TCNQ thin film on Au electrodes. The characteristics of a CMOS inverter consisting of unpolarized ambipolar OFETs and, in particular, the I_t characteristics were compared with those of a CMOS inverter consisting of unipolar OFETs as well as one consisting of ambipolar OFETs.

TTF and TCNQ were purchased from Aldrich followed by sublimation *in vacuo*. PHT purchased from Aldrich was reduced with ammonia water and then subjected to soxlet extraction.[11,12] PHT supplied by Merck and PCBM supplied by Frontier Carbon were used as obtained. Homemade Si/SiO_2 wafers with a dried oxidation layer of 300 nm thickness were used as substrates and the surfaces were silanized with hexamethyldisilizane before use. PHT and PCBM were individually dissolved in dried chloroform in an amount of 0.2 wt %. Mixtures of PHT/chloroform and PCBM/chloroform with volume ratios of 1:3 were spin coated at 2000 rpm for 30 s, followed by 4000 rpm for 10 s, resulting in 60-nm-thick composite films being typically provided. PHT (80 nm) and PCBM (60 nm) films were also prepared in the same way. Two top Au electrodes of 30 nm thickness and 5 mm length were deposited after the TTF or TCNQ deposition *in vacuo* at less than 6×10^{-6} torr through a Ni shadow mask, with which a channel width of 2 mm and a channel length of 50 μm were obtained. One top electrode was connected to one of the other OFET electrode to form the CMOS inverter [Fig. 1(b)]. All the measurements were carried out *in vacuo*. Transfer and output characteristics were measured with an Advantest R6246 two channel source measurement unit. CMOS operation was analyzed with two Keithley 6517 electrometers. All the film thicknesses were measured with a Dektak 6M profiler.

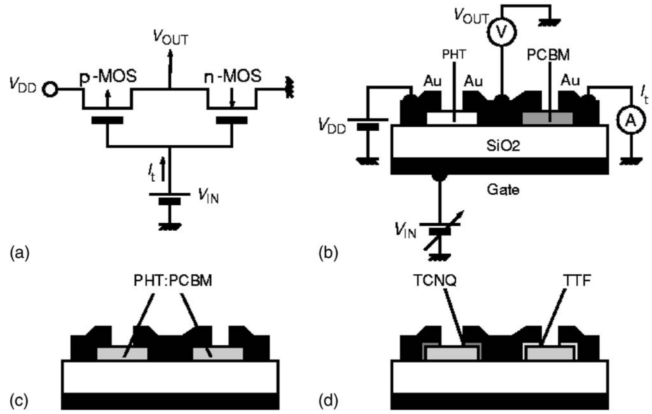

FIG. 1. (a) Equivalent circuit of CMOS inverter, (b) measurement setup, and [(c) and (d)] other CMOS configurations compared.

TABLE I. Semiconductor parameters of OFETs having various different channel layers.

Channel layer	μ_p (cm^2/V s)	μ_n (cm^2/V s)	$V_{th\text{-}p}$ (V)	$V_{th\text{-}n}$ (V)	S (V/decade)	On/off
PHT	2.1×10^{-3}	⋯	−19.5	⋯	24.0	1.8×10^{3}
PCBM	⋯	8.6×10^{-3}	⋯	43.0	5.5	1.5×10^{5}
Composite	4.1×10^{-5}	2.7×10^{-4}	−9.5	44.0	⋯	⋯
With TCNQ	5.0×10^{-5}	⋯	14.5	⋯	28.5	
With TTF	⋯	1.4×10^{-3}	⋯	37.0	10.0	1.4×10^{2}

Measured transfer characteristics of unipolar OFETs constructed with PHT or PCBM revealed hole and electron mobilities of 2.1×10^{-3} and 8.6×10^{-3} cm^2/V s, respectively. In the PHT:PCBM composite film, the mobilities were reduced to be of the orders of 10^{-5} and 10^{-4}. The output and transfer characteristics of ambipolar OFETs before and after buffer layer insertion are shown in Fig. 2. The ambipolar transport was clearly switched to p-type unipolar transport and n-type unipolar transport with insertion of TCNQ and TTF layers, respectively. The maximum currents were increased with the unipolarization, indicating that charge injection was promoted. All the device parameters obtained in this study are listed in Table I. The findings are essentially similar to those in the literature, although the reason for the decrease in mobility remains controversial.[2–4,13,14]

Since TCNQ is an electron acceptor, doping is possibly generated at TCNQ/PHT interface.[15] The channel conductivity of PHT was, however, found to be constant even for the case of a thin TCNQ coating formed over the whole PHT channel, unlike a case using F_4-TCNQ.[16] Absorption spectra of the PHT:TCNQ composite films did not show any new low-energy absorption features, except for an increase in the intensities of vibrational shoulders at 580 and 650 nm,[17] indicating that TCNQ probably does not dope PHT but instead promotes molecular-molecular interaction. Similar characteristics were also found for the mixture of PCBM and TTF.

The Fermi level (E_F) of the organic-metal electrode determines the barrier height for carrier transport.[9,18] For TCNQ/Au and TTF/Au electrodes, values of E_F of 4.8 and 4.2 eV, respectively, have been estimated by ultraviolet photoelectron spectroscopy.[19] Meanwhile, the highest occupied molecular orbital (HOMO) level of PHT and the lowest unoccupied molecular orbital (LUMO) level of PCBM have been reported as 4.9 and 4.2 eV.[14] The increased mobilities in unipolarized FETs denote a promotion of charge injection at the interface. The model of vacuum level matching, however, has difficulty explaining the intercept of single charge injection. Temporal doping (or charge transfer) triggered by the external field is another possible explanation for single carrier transport. Detailed investigations into this mechanism are still required.

Three types of CMOS(-like) inverters were compared (Fig. 3). Although all the CMOS inverters displayed clear inverter functions, I_t varies among the CMOS configurations. A clear inversion of output voltage (V_{out}) was found in the CMOS circuit consisting of p-type and n-type FETs. I_t appeared in a narrow potential region, corresponding to the

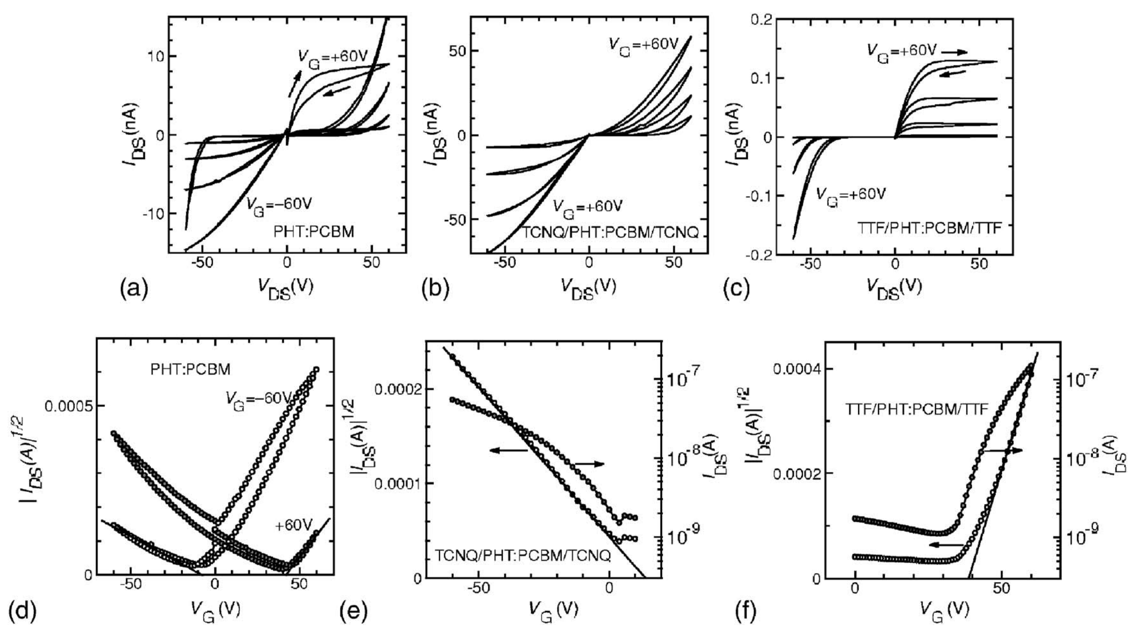

FIG. 2. Output characteristics of OFETs consisting of (a) the composite of PHT:PCBM in 1:3, (b) the composite with TCNQ buffer layer, and (c) the composite with TTF buffer layer; and transfer characteristics of OFETs consisting of (d) the composite, (e) the composite with TCNQ buffer layer, and (f) the composite with TTF buffer layer.

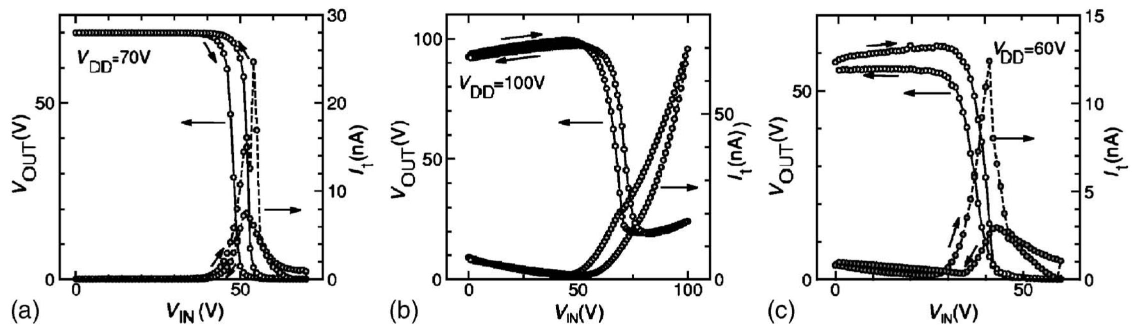

FIG. 3. CMOS output (solid line) and through current I_t (dashed line) as a function of input voltage (V_{in}) consisting of (a) PHT and PCBM layers, (b) composite of PHT:PCBM, and (c) composite of PHT:PCBM with TCNQ or TTF layer insertion.

subthreshold swing (S) of both types of FETs. Expansion of the subthreshold potential region broadens the switching potential, resulting in increased consumption of power and decreased switching speed.

The CMOS-like circuit consisting of ambipolar FETs showed a large I_t, indicating decreased output at high input voltage (V_{in}). Thus, a fundamental difficulty to construct a logic circuit with this CMOS-like circuit is found. As shown in Fig. 3(b), V_{out} could not reach zero even when the drive voltage (V_{DD}) was a high value of V_{in}. Large I_t prevents V_{out} from being zero due to the low impedance.

The CMOS inverter characteristics for unipolarized ambipolar FETs are shown in Fig. 3(c). The output characteristics are similar to those of ambipolar FETs, indicating that the fundamental performance of ambipolar FETs is conserved. The unipolarization clearly reduces I_t, particularly at high V_{in}. Of marked importance in the characteristics is that the output of voltages is the same as V_{in} at the two extremes, unlike the CMOS using ambipolar FETs. This indicates that unipolarized ambipolar OFETs can be used to construct a high-impedance logic circuit, similar to a CMOS using unipolar OFETs. To reduce the number of fabrication steps is still a key issue for the unipolarization procedure toward realizing a low-cost circuit.

The shift of switching potential toward high voltages for all the CMOS circuits is attributed to the large S in PHT FETs, as well as the mismatch in V_{th} between PHT and PCBM. Similar to the interfacial traps in the channel, a large distribution of molecular weight in PHT also causes to unsharpen the switching behavior. A decrease in the dispersion number is required to reduce S.[20]

In summary, unipolarization of ambipolar FET consisting of a mixture of PHT and PCBM has been demonstrated by insertion of TTF or TCNQ as a buffer layer. The sign of the unipolarization observed indicates that the TTF promotes electron injection into the ambipolar layer besides blocking hole injection, and the opposite effect is observed with TCNQ. This suggests that Fermi-level matching of electrodes to the HOMO and LUMO levels of PHT and PCBM, or temporal doping at the interface is possible, resulting in promotion of single carrier injection. The comparison of the CMOS characteristics clarifies a way of solving the problem of the lowered CMOS impedance with conventional ambipolar OFETs. Unipolarization is considered to be a key method for realizing the high-output impedance possibly embedded in logic circuits.

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