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Air-stable Ambipolar Organic Thin Film Transistors Based on Copper Pthalocyanince Composites

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1. Introduction

The development of organic thin-film transistors (OTFTs) with a performance comparable or superior to that of a-Si:H TFTs is an important goal for organic electronics. In most silicon-based microelectronics, the use of complementary logic elements requires n- and p-channel (ambipolar) semiconductors. This complementary technology has enabled the construction of digital circuits, which operate with low power dissipation and a good noise performance. Organic CMOS logic circuits based on discrete n- and p-type transistors have also been reported.[1] On the other hand, the use of organic ambipolar transistors, which work as both p- and n-channel transistors, can simplify the design of organic CMOS integrated circuits. Very recently, CMOS inverter circuits were fabricated with organic ambipolar transistors based on heterogeneous blends of p- and n-semiconductors or a single semiconductor with a narrow band gap.[2-4] Furthermore, ambipolar devices were also demonstrated by using heterostructures of p- and n-type semiconductors.[5-8] However, ambipolar charge transport measurements were only performed in vacuum due to the oxidatively unstable nature of the organic materials used as n-type semiconductors, such as C_{60} and C_{60} derivatives such as [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) and *N,N'*-ditridecylperylene-3,4,9,10-teteracarboxylic diimide (PTCDI-$C_{13}H_{27}$), in air.[2-8] In this paper, we report on air-stable ambipolar transistors based on copper phthalocyanince composites.

2. Experimental

The molecular structures of F_{16}CuPc and CuPc used in this study are shown in Fig. 1, along with their relative energy levels and the OTFT device schematic structure [9-10] The OTFT device schematic structure is shown in the inset of Fig 1. A heavily n-doped Si substrate acts as the gate electrode with a 300 nm thermally grown SiO_2 layer (C_i ~10 nF/cm^2) as the gate dielectric. F_{16}CuPc thin films approximately 10 nm and CuPc thin films of approximately 30 nm were continually vacuum-deposited from two deposition sources. During deposition, the substrate temperature was set at 120 °C under a base pressure of less than 5×10^{-4} Pa. Film thicknesses and growth rates were monitored by a thickness and rate monitor (CRTM-6000, ULVAC). Finally, Au source and drain electrodes of approximately 100 nm were vacuum-deposited through a shadow mask with a channel width of 5 mm and a length of 70 μm. The characteristics of OTFTs were measured with a two-channel voltage current source/monitor system (R6245, ADVANTEST) under ambient laboratory air conditions.

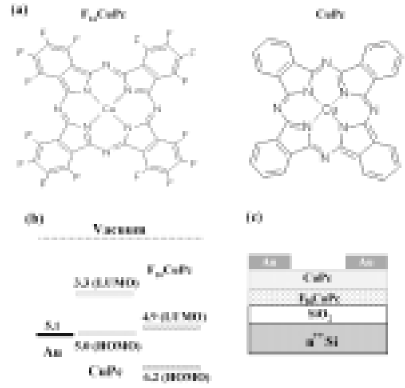

Fig. 1 (a) F_{16}CuPc and CuPc molecular structures, (b) energy levels (in electron voltages) of HOMO and LUMO of CuPc and F_{16}CuPc and (c) schematic structure of OTFT based on F_{16}CuPc/CuPc layers. The dimensions are not scaled.

3. Results and Discussion

Figure 2 displays the typical drain current-voltage (I_D - V_D) characteristics obtained for an F_{16}CuPc/CuPc TFT operating in the hole-enhancement and electron-enhancement modes, respectively. The p-channel operational characteristics of the ambipolar F_{16}CuPc/CuPc TFT are different from those of TFTs with only a CuPc layer. At negative gate voltages $|V_G|$<30, unusual characteristics were observed: I_D does not saturate and rapidly increases for $|V_D|$-$|V_G|$>10V, which can be explained by the contribution of drain-induced electrons. Similarly, at positive gate voltages $|V_G|$>30, n-channel operational characteristics of the ambipolar TFT identical to those of TFTs with only an F_{16}CuPc layer are observed. For $|V_G|$<30 V and $|V_D|$-$|V_G|$>30V, an increase in nonsaturated I_D could also be observed, which originates from drain-induced holes.

The electric parameters of the ambipolar F_{16}CuPc/CuPc TFT were estimated using the standard analytic theory of metal oxide semiconductor field-effect transistors (MOSFETs).[11] From the plots of $|I_D|^{1/2}$ vs V_G in Fig. 2, field-effect hole and electron mobilities of 3.27 x 10^{-3} cm^2/Vs and 3.10 x 10^{-3} cm^2/Vs for the ambipolar F_{16}CuPc/CuPc TFT, respectively, were derived in the saturation region.

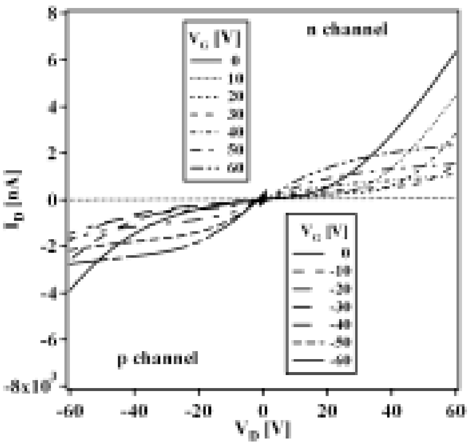

Fig. 2 Drain current-voltage (I_D - V_D) characteristics of ambipolar TFT operating in hole-enhancement mode and electron-enhancement mode.

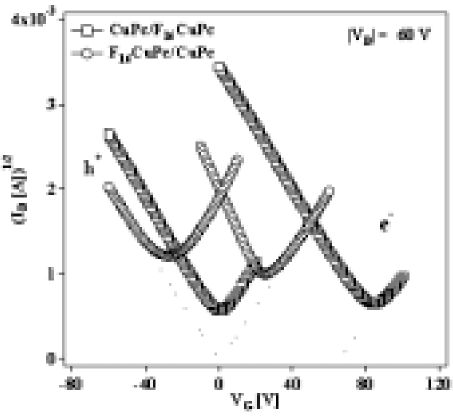

Fig. 3 $I_D^{1/2}$ vs V_G at fixed $|V_D|$ of 60 V for ambipolar TFTs based on F_{16}CuPc/CuPc and CuPc/F_{16}CuPc layers

Table I Summary of mobility and threshold voltage (V_T) for ambipolar TFTs based on copper pthalocyanince composites

Device		mobility (cm^2/Vs)	V_T (V)
F_{16}CuPc/CuPc	p	3.27×10^{-3}	-0.75
	n	3.10×10^{-3}	+1.19
CuPc/F_{16}CuPc	p	3.96×10^{-3}	+10.62
	n	2.28×10^{-3}	+66.09

On the other hand, the order of the two materials was reversed with CuPc deposited first. In such CuPc/F_{16}CuPc devices, good p-channel behavior was observed. However, for positive gate biases, only weak n-channel behavior was observable but ambipolar field-effect mobilities for a CuPc/F_{16}CuPc TFT derived from Fig. 2 had the same order of magnitude as shown in Table I.

F_{16}CuPc and CuPc have similar molecular shapes and sizes, and their thin-film *d*-spacings (d_{200}) are almost identical (1.42 nm and 1.29 nm, respectively) with both materials having the same crystal structure. The highly ordered polycrystalline thin films of both F_{16}CuPc and CuPc can be deposited on amorphous SiO_2 substrates under similar optimized growth conditions.[9,12] Unlike organic heterostructures, such as C_{60} and α-hexathienylene (α-6T) with completely different *d*-spacings, in which the structure of the second layer is completely disrupted by the first layer, highly ordered F_{16}CuPc and CuPc polycrystalline thin films can be continuously grown.[13-14] Therefore, these ambipolar mobilities are comparable to the unipolar mobilities of single-layer TFTs measured under ambient conditions. [9, 12] For CuPc/F_{16}CuPc devices, n-channel operation needs high gate biases due to highly p-doping of CuPc thin films.

4. Conclusions

We have demonstrated the fabrication and characterization of OTFTs based on copper pthalocyanince composites. These devices show ambipolar characteristics operating in both hole accumulation and electron accumulation depending on gate voltage. Although the performance of the device with F_{16}CuPc deposited first is prior to that of the device with CuPc deposited first, these ambipolar mobilities have the same order of magnitude, and are comparable to the unipolar mobilities of single-layer thin-film transistors.

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References

[1] B. Crone, A. Dodabalapur, Y.-Y. Lin, R. W. Filas, Z. Bao, A. LaDuca, R. Sarpreshkar, H. E. Katz and W. Li: Nature **403** (2000) 521.

[2] A. Bael, J. D. Wind and A. Jenekhe: Adv. Funct. Mater. **14** (2004)891.

[3] Y. Kunugi, K. Takimiya, N. Negishi, T. Otsuo and Y. Aso: J. Mater. Chem. **14** (2004)2840.

[4] E. J. Meijer, D. M. Deleeuw, S. Setayesh, E. Vanveenendaal, B. –H. Huisman, P. W. M. Blom, J. C. Hummelen, U. Scherf and T. M. Klapwijk: Nature Mater. **2** (2004)678.

[5] A. Dodabalapur, H. E. Katz, L. Torsi and R. C. Haddon: Science **269** (1995) 1560.

[6] A. Dodabalapur, H. E. Katz, L. Torsi and R. C. Haddon: Appl. Phys. Lett. **68** (1996)1108.

[7] C. Rost, D. J. Gundlach, S. Karg and W. Rieβ: J. Appl. Phys. **95** (2004)5782.

[8] T. D. Anthopoulos, D. M. De Leeuw, E. Cantatore, S. Setayesh and E. J. Meijer: Appl. Phys. Lett. **85** (2004)4250.

[9] Z. Bao, A. J. Lovinger and J. Brown: J. Am. Chem. Soc. **102** (1998) 207.

[10] I. G. Hill and A. Kahn: J. Appl. Phys. **84** (1998) 5583.

[11] S. M. Sze: *Physics of Semiconductor Devices* (Wiley, New York, 1981).

[12] K. Xiao, Y. Liu, G. Yu and D. Zhu: Appl. Phys. A, **77** (2003) 367.

[13] S. Heutz, R. Cloots and T. S. Jones: Appl. Phys. Lett. **77** (2000) 3938

[14] N. Nanai, M. Yudasaka, Y. Ohki and S. Yoshimura: Thin Solid Films **265** (1995) 1.