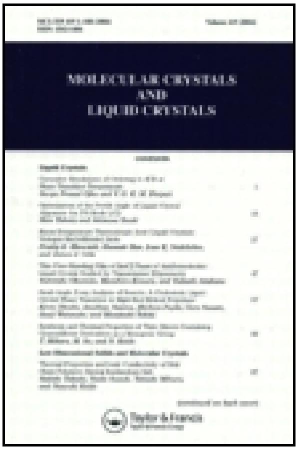

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n-Channel Organic Field-Effect Transistors Based on Boron-Subphthalocyanine

Takeshi Yasuda [a] & Tetsuo Tsutsui [a]

[a] Department of Applied Science for Electronics and Materials, Graduate School of Engineering Science, Kyushu University, Kasuga, Fukuoka, Japan

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n-Channel Organic Field-Effect Transistors Based on Boron-Subphthalocyanine

Takeshi Yasuda
Tetsuo Tsutsui
Department of Applied Science for Electronics and Materials,
Graduate School of Engineering Science, Kyushu University,
Kasuga, Fukuoka, Japan

We fabricated organic field-effect transistors (OFETs) consisted of vacuum-sublimed boron-subphthalocyanine film. The device characteristics were evaluated in a glove box (O_2<1 ppm, H_2O<1 ppm) condition. The OFETs showed typical n-type characteristics and the field-effect electron mobilities were estimated to be $5.4 \times 10^{-5}\,cm^2/V \cdot s$ for Ca source-drain electrodes and $1.2 \times 10^{-5}\,cm^2/V \cdot s$ for Au source-drain electrodes. In the case of the OFET with Au source-drain electrodes exposed to ambient air for a few minutes, a clear conversion from n-type to p-type behavior was also observed.

Keywords: electron transport material; mobility; n-channel; organic field-effect transistor; organic semiconductor

1. INTRODUCTION

As a result of intensive research on organic semiconductors for organic field-effect transistors (OFETs), the device performance has been significantly increased. Recent advances, especially, in p-type organic semiconductors have fulfilled many of the requirements for use in OFET applications [1–3]. However, n-type organic semiconductors, needed for complementary circuits, continue to present challenges, such as low mobilities, instability in air and large barriers to electron injection [4]. From these viewpoints it is important to explore and study new n-type organic semiconductors.

Address correspondence to Takeshi Yasuda, Department of Applied Science for Electronics and Materials, Graduate School of Engineering Science, Kyushu University, Kasuga, Fukuoka 816-8580, Japan. E-mail: yasuda@asem.kyushu-u.ac.jp

In our previous work, by using Ca source-drain electrodes to lower the electron injection barrier and, at the same time, eliminating extrinsic traps, n-channel conduction was successfully demonstrated even in OFETs with thin film of copper-phthalocyanine (CuPc) that has been considered p-type semiconductors [5]. In this study, we focused subphthalocyanines for new organic semiconductors, because they, like phthalocyanines, often exhibit unusual optical and electrical properties due to their structure and aromaticity [6]. We fabricated OFETs of a vacuum-sublimed boron-subphthalocyanine (BsubPc) film as an active layer utilizing low work function metal, calcium for source-drain electrodes for the purpose of reducing electron injection barrier. In addition, all the procedures of device fabrication and measurements of device characteristics were performed under an oxygen-free condition without exposing ambient air. We were successful in observing well-defined n-channel OFET characteristics.

2. EXPERIMENTAL DETAILS

2.1. Material

BsubPc, as depicted in Figure 1(a), was purchased from Aldrich and purified by train sublimation before use. The ionization potential (*IP*) of BsubPc was determined to be 5.7 eV by photoemission spectroscopy (AC-2, Rikenkeiki). Optical energy band-gap (*Eg*) of BsubPc was calculated to be 1.9 eV from the absorption spectra edge, and the electron affinity (*EA*) of BSubPc was estimated to be 3.8 eV from the equation $EA = IP\text{-}Eg$.

2.2. Fabrication of Organic Field-Effect Transistors

We fabricated OFETs having a top source-drain contact geometry shown in Figure 1(b). Onto a cleaned glass substrate, an Au gate

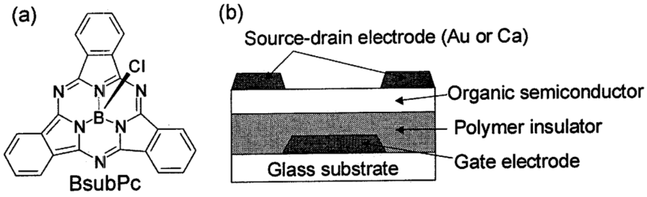

FIGURE 1 (a) Molecular structure of boron-subphthalocyanine (BsubPc) and (b) schematic cross section of the organic field-effect transistor in this study. The poly-chloro-*p*-xylylene (Parylene-C) for the insulator was deposited by a thermal chemical vapor deposition.

electrode was sputtered through a shadow mask to form a 5 mm-wide and 30 nm-thick stripe. Poly-chloro-*p*-xylylene (diX-C, Daisankasei Co. Ltd.) was subsequently deposited by thermal chemical vapor deposition (Parylene-C coating) at a thickness ranging from 810 to 1040 nm [7]. The substrate with the Au gate electrode and the diX-C insulator film was placed in a glove box ($O_2 < 1$ ppm, $H_2O < 1$ ppm), followed by transferring into a vacuum evaporation chamber through a gate valve without exposing to ambient air. BsubPc was vacuum-evaporated at 2×10^{-6} Torr at the deposition rate of 0.05 nm/s with thickness of 40–50 nm onto the substrate. The thickness was determined with a Sloan Dektak 3 profilometer in all cases. A shadow mask with an interdigitated configuration was attached onto the film in the glove box and the substrate with the mask was transferred again in the vacuum chamber to form Au source-drain electrodes or Ca source-drain electrodes with an Ag overlayer. The channel length L and width W were 75 µm and 5 mm, respectively. Finally, the fabricated device was placed in the glove box and OFET characteristics were examined using an Agilent 4156C precision semiconductor parameter analyzer.

3. RESULTS AND DISCUSSION

3.1. n-Channel Organic Field-Effect Transistors

On the application of positive bias to the gate electrode, a typical n-type behavior was observed under N_2 atmosphere. On the other hand, upon application of negative bias to the gate electrode, a typical characteristic in p-type behavior was not observed. The source-drain current (I_D)-voltage (V_D) relationships in the gate voltage (V_G) range from 0 to 100 V for the OFET with Ca source-drain electrodes are shown in Figure 2(a). For use as a reference, OFETs with Au source-drain electrodes instead of Ca source-drain electrodes were also fabricated. The output characteristic is shown in Figure 2(b). The n-channel OFET operates in the accumulation mode upon application of a positive bias to the gate electrode, as the concentration of electrons contributing to I_D increases. Above the threshold voltage, the field-effect mobility can be calculated from the slope of the plot of $|I_D|^{1/2}$ versus V_G. From the plot in Figure 3, the field-effect electron mobility was calculated to be $5.4 \times 10^{-5}\,\mathrm{cm^2/V \cdot s}$, when the threshold voltage was 11 V for the OFET with Ca source-drain electrodes. On the other hand, the field-effect electron mobility was calculated to be $1.2 \times 10^{-5}\,\mathrm{cm^2/V \cdot s}$, when the threshold voltage was 45 V for the OFET with Au source-drain electrodes.

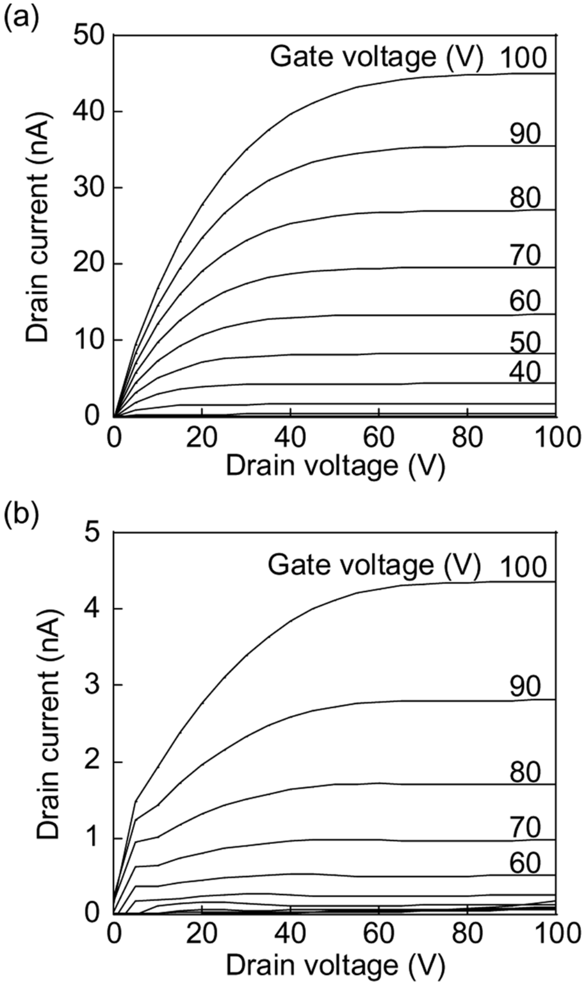

FIGURE 2 (a) Output characteristics of n-channel OFET using vacuum evaporated BsubPc films and Ca source-drain electrodes in a glove box condition. (b) Output characteristics of n-channel OFET using vacuum evaporated BsubPc films and Au source-drain electrodes in a glove box condition.

The experimentally extracted field-effect mobility has been known to be strongly dependent on the injection barrier from a source electrode to an organic semiconductor. We found a large dependency of field-effect mobilities on the choice of source-drain contact metals in CuPc, pentacene and conjugated polymers OFETs [5,8–10]. The experimental results have shown that a large injection barrier from

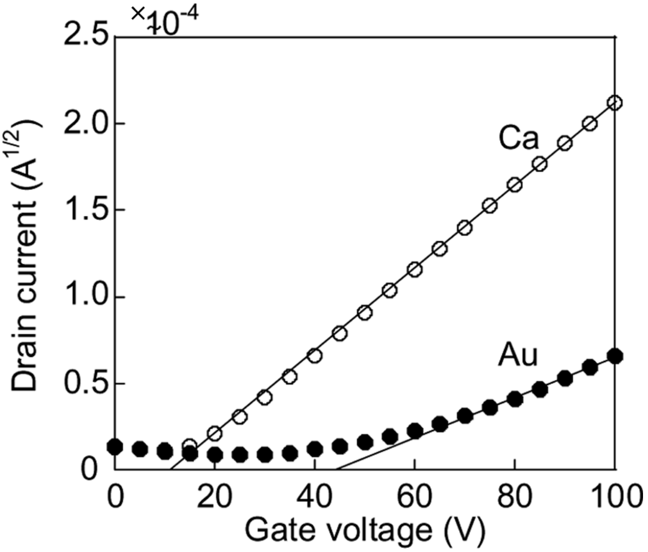

FIGURE 3 Dependence of transfer characteristics on the metal electrodes with different work function (Ca or Au).

the source electrode to organic semiconductors causes large decrease in the field-effect mobility. The 5 times of magnitude decrease in the field-effect electron mobility in the BsubPc FETs with Au source-drain electrodes over the case of the Ca source-drain electrodes is apparently due to the large barrier for electron injection from Au to *EA* of BsubPc.

3.2. p-Channel Organic Field-Effect Transistors

In the case of the OFET with Au source-drain electrodes exposed to ambient air for a few minutes, typical n-type characteristics of the OFET became undetectable and a clear conversion from n-type to p-type behavior was observed. At large negative gate voltages, hole injection becomes dominant and the device shows p-type unipolar behavior as shown in Figure 4. From the saturation regimes, the field-effect hole mobility is evaluated to be $7.5 \times 10^{-7}\,\mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s}$. It has been known that an oxygen-induced conversion of transport property from n-type to ambipolar was observed in the thin film of titanyl-phthalocyanine (TiOPc) and fullerene (C_{60}) [11,12]. Drastic decrease of a field-effect electron mobility in vacuum-sublimed naphthalene derivatives due to absorbed oxygen has been also observed [13]. These results by other

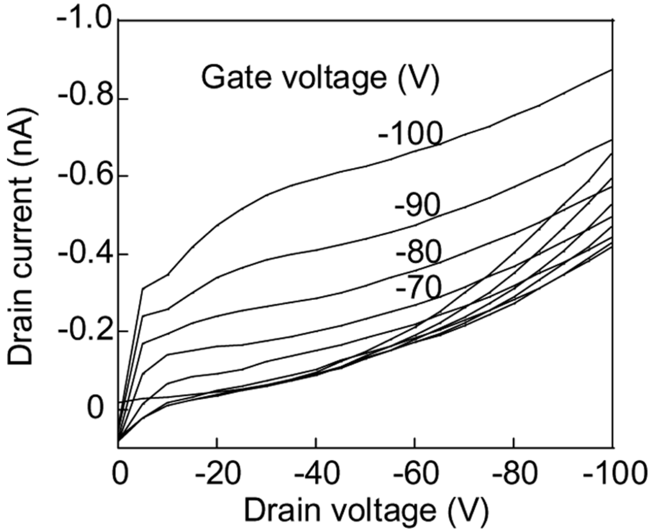

FIGURE 4 p-Channel output characteristics of the OFET with Au source-drain electrodes after exposed to ambient air for a few minutes.

groups and our experimental results show the possibility of electron trapping centers and a practical hole doping by the oxygen adsorption.

4. CONCLUSIONS

In conclusion, by eliminating extrinsic traps in BsubPc film, n-channel OFET was successfully demonstrated and characterized. The OFETs showed typical n-type characteristics and field-effect electron mobilities were estimated to be $5.4 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$ for Ca source-drain electrodes and $1.2 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$ for Au source-drain electrodes. In the case of the OFET with Au source-drain electrodes exposed to ambient air for a few minutes, typical n-type characteristics of the OFET became undetectable and a clear conversion from n-type to p-type behavior was observed. Our experimental results indicate the intrinsic electron transport in BsubPc film is easily obstructed under ambient air.

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