Organic Electronics 22 (2015) 1–4

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Letter

All solution-processed organic single-crystal transistors with high mobility and low-voltage operation

S. Sakai [a], J. Soeda [a], R. Häusermann [a], H. Matsui [a], C. Mitsui [a], T. Okamoto [a], M. Ito [a,b], K. Hirose [c], T. Sekiguchi [c], T. Abe [d], M. Uno [e], J. Takeya [a,e,*]

[a] Department of Advanced Materials Science, Graduate School of Frontier Science, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan
[b] Electroplating Engineers of Japan Ltd., 5-50 Shinmachi, Hiratsuka, Kanagawa 254-0076, Japan
[c] Toppan Forms Co., Ltd., 1-7-3 Higashi Shimbashi, Minato-ku, Tokyo 105-8311, Japan
[d] Asahi Glass Co., Ltd., 1-5-1 Marunouchi, Chiyoda-ku, Tokyo 100-8405, Japan
[e] Technology Research Institute of Osaka, 2-7-1 Ayumino, Izumi, Osaka 594-1157, Japan

ARTICLE INFO

Article history:
Received 23 January 2015
Received in revised form 10 March 2015
Accepted 10 March 2015
Available online 12 March 2015

Keywords:
Organic single crystal transistor
Solution process
Low voltage operation

ABSTRACT

High-mobility organic single-crystal field-effect transistors of 3,11-didecyldinaphtho[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]-dithiophene (C_{10}-DNBDT) operating at low driving voltage are fabricated by an all-solution process. A field-effect mobility as high as 6.9 $cm^2/V\,s$ is achieved at a driving voltage below 5 V, a voltage as low as in battery-operated devices, for example. A low density of trap states is realized at the surface of the solution-processed organic single-crystal films, so that the typical subthreshold swing is less than 0.4 V/decade even on a reasonably thick amorphous polymer gate dielectrics with reliable insulation. The high carrier mobility and low interface trap density at the surface of the C_{10}-DNBDT crystals are both responsible for the development of the high-performance all-solution processed transistors.

Due to their unique features of mechanical flexibility, lightweight and low manufacturing cost organic transistors have been attracting considerable interest for the use in fundamental electronic switches in an information society relying even more on complex communication and computation networks in the near future [1–3]. Since such products as displays, RFID tags and sensor circuitries can be attached easily to arbitrary shaped surfaces with low-price organic semiconductor circuits, they suit the concept of the "trillion sensors universe" with a highly connected informational network ranging from medical service, agriculture to logistics [4]. In this regard, the target in the development of organic transistors is achieving a high device performance at the end of simple low-cost fabrication processes to promote the prevailing of trillions of communicating sensor units.

Recently, remarkable progresses in material development increased the carrier mobility of solution-processed organic semiconductors to values above 1 $cm^2/V\,s$ for crystalline films [5–9], which is already a promising level to realize moderate-speed logic circuits. However, most of these high-mobility transistors are equipped with vacuum deposited metal electrodes and inorganic gate insulators, features which both need to be replaced in a desirable low-cost all-solution process. We therefore not only established a process of forming gate insulating layers and high-mobility crystalline semiconductor films from solutions but we also studied combinations of solvents and materials for forming gate and source–drain electrodes, both solution-processable. Note that solution-processable organic gate insulators usually require a thickness of more than a few hundred nanometers to prevent gate leakage, causing significant challenge to operate the transistors at low voltages. Consequently, some reports of all-solution-processed devices suffer from either low mobility or high operation voltage [10,11]. We emphasize, however, that lightweight and flexible devices absolutely have to operate at low voltages, by relatively low-power wireless transmission, without rigid and heavy batteries. In this paper, we disclose all-solution-processed organic single-crystal transistors with a high mobility up to 6.9 $cm^2/V\,s$ operated at a relatively low voltage within 5 V. The transfer curves show little hysteresis and an on/off ratio of 10^5.

To process all layers of organic transistors from solution, the choice of organic materials and solvents is crucial in order not to damage the previously coated layers. Therefore, we carefully selected the combination of solvents for organic, aqueous and fluorine compounds to complete the multilayered film deposition. Furthermore, the organic semiconductor material needs to be thermally stable in order not to deteriorate during the curing

* Corresponding author at: Department of Advanced Materials Science, Graduate School of Frontier Science, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan.
E-mail address: takeya@k.u-tokyo.ac.jp (J. Takeya).

http://dx.doi.org/10.1016/j.orgel.2015.03.015
1566-1199/

processes, and chemically stable in order not to react with the solution. Among reported organic semiconductor compounds with high mobility, 3,11-didecyldinaphtho[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene (C_{10}-DNBDT) is particularly suited due to its excellent chemical and structural stability; the material is highly resistive against oxidization because of the high ionization potential of 5.24 eV and no phase transition is detected up to a temperature of 200 °C due to steric hindrance against molecular rotation caused by the zigzag-shaped π-conjugated hard core as shown in Fig. 1(a) [12].

A powerful approach to achieve high mobility is to crystallize the molecules during the solution process. C_{10}-DNBDT is actually one of the most favored materials for this purpose. We note that another well-studied compound of C_8-BTBT has the drawback of a low phase transition temperature of approximately 100 °C that significantly restricts further process windows and conditions upon practical usage [13]. An additional advantage of using this stable compound is that we can employ the standard bottom-gate and top-source–drain-contact geometry, which allows for a stable deposition of the organic semiconductor layer on the well-defined single-component surface of the gate insulator layer. In contrast, using a bottom-contact device configuration generally leads to injection problems resulting in a large contact resistance and therefore unstable operation. Because of its chemical stability source and drain electrodes of gold are directly patterned on C_{10}-DNBDT by photolithography, a method reported in our previous study [14]. A schematic diagram of the present all-solution-processed bottom-gate top-contact transistor is shown in Fig. 1(b).

While choosing an appropriate material for the bottom gate electrode, a flat metal surface is favored whereas a gate insulating layer with a rough surface put directly on the gate electrode causes a significant reduction in mobility as the semiconductor layer is deposited on the insulator layer [15]. This sensitivity can be attributed to the fact that charge is accumulated at the very bottom of the semiconductor layer next to the insulator surface. A smoother surface of the gate electrode furthermore prevents gate leakage and minimizes the density of interface traps originating from the disordered molecular arrangement.

We employed a silver salt ink (Toppan Forms Co., Ltd.) for spin coating on a glass substrate [16]. Owing to the slow curing reaction and the thinness of the silver layer, the resultant surface was expected to be relatively smooth without gas-releasing holes.

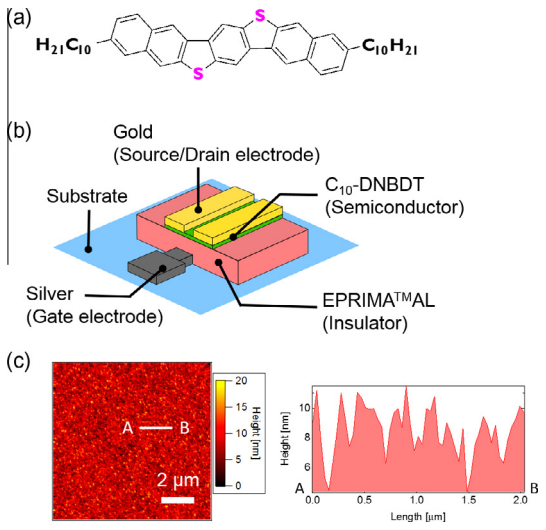

Fig. 1. (a) Molecular structure of C_{10}-DNBDT. (b) Schematic of the all-solution-processed C_{10}-DNBDT transistor. (c) Atomic-force-microscopy image of the solution-processed silver gate electrode and its cross-sectional profile.

Indeed, after baking in the oven at 150 °C for 30 min, the surface roughness was evaluated to be only ~5 nm as shows the atomic force microscopy image in Fig. 1(c). The silver film was patterned by a conventional photolithography process using a OFPR-800LB resist (Tokyo Ohka Kogyo Co., Ltd.). The silver film was etched with SEA-1 (Kanto Chemical Co., Inc.). It is anticipated that the silver gate electrode with its smooth surface helps to reduce the trap density at the interface between the insulator and the organic layer, contributing to realize a low-voltage transistor operation.

A fluorinated polymer (EPRIMA™AL; Asahi Glass Ltd.) was spin coated and baked on a hot plate at 150 °C for 30 min to form the gate insulating layer with a thickness of 320 nm, as measured by a stylus profiler. To minimize the interface traps, the use of water-repelling fluoro-polymer can be advantageous as reported in [17,18]. It is reported that the subthreshold swing *S* is particularly small for rubrene single-crystal devices on the highly hydrophobic surface of CYTOP™, being close to the theoretical fundamental limit of 0.06 V/decade. Since the surface of CYTOP™ itself does not accept aromatic solution coating, we employed a fluorinated polymer of EPRIMA™AL as a substitute on account of the wettability for the organic semiconductor solution.

An organic single-crystal layer of C_{10}-DNBDT was fabricated by "continuous edge cast" method, described in Ref. [19]; the solution of C_{10}-DNBDT was retained as a meniscus between the blade and the moving substrate, so that the organic single crystal layer was grown during the evaporation of the solvent. By adjusting the sweeping speed and temperature of the substrate, stable growth of the organic crystal layer was conditioned to fabricate inch-sized organic crystal films in ambient atmosphere. It is reported that crystal films of C_{10}-DNBDT show high mobility up to 16 $cm^2/V\,s$ and thermal stability even at 150 °C [12].

Besides the high mobility, we note that the relatively small subthreshold swing *S* of single-crystal transistors is another advantage for low-voltage operation; the required quantity of gate voltage to increase the drain current by one order of magnitude is a direct translation of the trap density. Since the surfaces of organic single crystals are highly ordered without dangling bonds, a low level of interface trap density of states and a small *S* can be expected in principle. Indeed, it is reported that rubrene single crystal transistors showed a remarkably small value of the subthreshold swing close to the theoretical limit [18,20].

To form arrays of organic transistors OScOR4000 (Orthogonal Inc.), which is a fluorine nega-type photoresist, was spin coated and patterned as a protective layer for the organic semiconductors. A fluorine solvent of OScOR4000, developer and remover solutions did not damage the C_{10}-DNBDT layer owing to the orthogonal property of the fluoro-based solvents. After the fabrication of the protective layer, *o*-dichlorobenzene was used to dissolve non-protected C_{10}-DNBDT to complete the patterning by removing the OScOR4000 by the fluorine solvent Novec™7100 (purchased from 3 M Japan Limited).

We then employed the method of electroless plating to achieve fair electric contacts on the high-mobility organic semiconductors as demonstrated in our previous study [21]. A gold layer was fabricated by electroless plating as described in Ref. [21]. For the surface pretreatment, a solution of 0.1 wt% trimethylstearylammonium chloride was first spin coated. The colloid catalyst of Au–Xi was then absorbed to the surfactants on the organic semiconductor layer. Finally, the substrate was dipped in the water-based plating solution (PRECIOUSFAB ACG3000WX; Electroplating Engineers of Japan Ltd.) at 60 °C, so that the gold film was plated on the semiconductor layer. Source and drain electrodes were patterned by OScOR4000 and partially etched by an iodine-based etchant following the method described in Ref. [14]; after the OScOR4000 patterning, the substrate was immersed in AURUM S-50790 (Kanto Chemical Co., Inc.) gold etchant to