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High-performance solution-processed organic transistors with electroless-plated electrodes

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ABSTRACT

Electroless-plated gold and platinum films are used as source and drain electrodes in high-performance solution-processed organic field-effect transistors (OFETs), representing a promising large-area, near-room-temperature and vacuum-free technique to form low-resistance metal-to-semiconductor interfaces in ambient atmosphere. Developing non-displacement conditions using a Pt-colloidal catalyst for soft electroless plating, the electrodes are deposited on crystallized thin films of 2,9-didecyl-dinaphtho[2,3-b:2′, 3′-f]thieno[3,2-b]thiophene (C_{10}-DNTT) without significant damage to the semiconductor material. The top-contact OFETs show remarkable performance, with a mobility of 6.0 $cm^2 V^{-1} s^{-1}$. The method represents a practical fabrication technique to mass-produce circuitry arrays of nearly best-performing OFETs for the printed electronics industry.

Printed organic field-effect transistors (OFETs) are attracting considerable attention as active circuitry devices for next generation electronic technologies, with large-area and low-cost matrix back panels to be implemented in such products as flexible displays. In OFETs, the semiconductor channels are activated by two kinds of interfaces, semiconductor-to-insulator boundaries for charge accumulation and semiconductor-to-electrode junctions for charge injection. Therefore, the future printed electronics industry must be based on the performance of both of these interfaces. Thus far, developments in materials and film-growth methods for solution-based processes have given rise to pronounced advances in the quality of the semiconductor-to-insulator boundaries based on polymer and small-molecule semiconductors [1,2]. The highest mobility in such devices with vacuum-deposited electrodes has already exceeded 10 cm^2/Vs, by utilizing a simple fabrication technique of forming crystallized films from solution [3,4].

On the other hand, the development of reliable printing processes to form metallic electrodes on high-performance solution-processed organic semiconductors remains a challenge. Although it is highly desirable to establish good ohmic contacts near room temperature from solution without sacrificing the performance of recent printable OFETs, there have been few reports on successfully accomplishing this because of several fundamental difficulties. In order to fabricate good (ohmic) contacts to semiconductors, the "metal ink" needs to wet the organic semiconductor surface. However, such solvents that can adequately wet the organic semiconductor surfaces often damage the metal/semiconductor interface and induce interface trap states causing injection barriers. For recently reported water-based inks that do not damage the organic semiconductors, improved painting processes need to be developed [5]. There is a general concern that these methods of forming electrodes will degrade the organic semiconductors, because of the solubility in the organic solvent as well as stresses from either high temperatures or ultraviolet radiation used for curing processes. In addition, the annealing temperature of more than 200 °C, which is required for most "metal inks", is often too high for common organic substrates. Several high-mobility solution-processed organic semiconductors also suffer from structural phase

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transition below the typical annealing temperatures of 150–200 °C.

In this paper, we introduce the use of electroless plating, which is actually the most common technique used in practical electronics circuitries for wiring on plastic boards, to fabricate stable source and drain electrodes on solution-crystallized high-mobility organic semiconductors under atmospheric pressure [6], as demonstrated in this study. The method is advantageous in coating thin metallic films easily on any surface so long as catalyst particles are mounted to initiate the plating reaction. The method allows for highly efficient consumption of metals, and quicker processing than vacuum deposition. Furthermore, the purity of the metallic films is far greater than obtained by the usual methods of printing inks, securing reliability of the charge injection properties. By carefully choosing mild processing conditions using a water-based solution, we successfully demonstrated high-performance solution-processed OFETs reproducibly using both Au and Pt electrodes. The typical mobility of the device turned out to be as high as 6.0 $cm^2 V^{-1} s^{-1}$.

We constructed bottom-gate and top-contact OFET devices with electroless-plated electrodes, as shown in Fig. 1a, in the present experiments. The high-mobility crystalline organic-semiconductor films were prepared by a recently developed method enabling directional crystallization on the surface of 200-nm-thick thermally-oxidized SiO_2 gate-insulating layers on a doped-Si substrate [3,7]. The oxide surface was treated with self-assembled monolayers of trimethoxy[3-(phenylamino)-propyl]silane by a vapor-phase epitaxial method to reduce surface energy for wettability. We used a 0.08% solution of a recently developed material 2,9-alkyl-dinaphtho[2,3-b:2′,3′-f]thieno[3,2-b] thiophene (C_{10}-DNTT) (Fig. 1b) in tetraline, so that the process at 100 °C allows for the production of high-quality crystalline films reproducibly, as shown in Fig. 1c. In addition, a fluorine-based coating agent (CYTOP: ASAHI GLASS Co., Ltd.) was painted on the organic semiconductor film by an ink-jet technique to specify the channel area. The channel length was approximately 100 μm under CYTOP coverage, which did not damage the organic semiconductor and prevented adhesion of the plated metals.

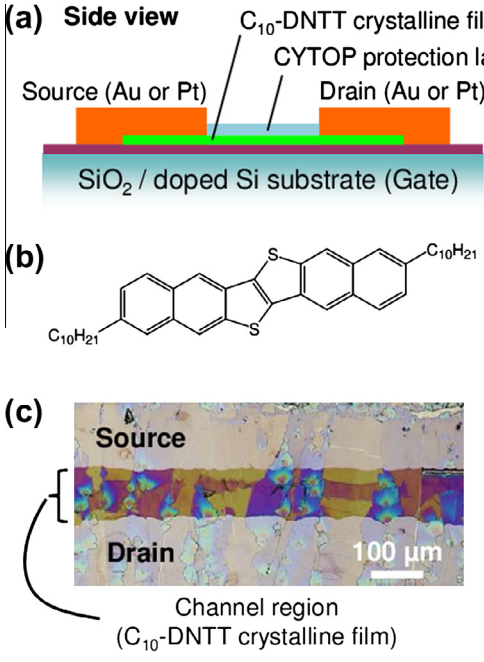

Fig. 1. (a) A schematic illustration of high-mobility organic transistors with solution-crystallized semiconductors and electroless plated electrodes. (b) The molecular structure of 2,9-alkyl-dinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophene (C_{10}-DNTT). (c) An optical top view of the high-mobility organic transistors with solution-crystallized semiconductors and electroless plated electrodes.

Gold electrodes were formed by electroless plating on the substrate using the following method to minimize damage to the surface of the organic semiconductor. As pretreatment, the substrate with the semiconductor layer was dipped in a 0.1% aqueous solution of trimethylstearylammonium chloride for 10 s. Next, the platinum colloid, which is the catalyst for the electroless gold plating, was adsorbed on the substrate. The substrates were then dipped in Pt-polyvinylpyrrolidone (PVP) colloid solution (Platinum 0.01%: TANAKA KIKINZOKU KOGYO K.K.) wherein the PVP acts as a protective agent of the platinum colloid. After rinsing in deionized water, the substrates were dipped in the electroless-gold-plating solution for a 60 s dip at 25 °C. This solution contains $HAuCl_4$:10 mM and H_2O_2:20 mM [2]. As a result, we obtained approximately 50-nm-thick gold plating films. Finally, the gold plating film in the channel area and outer circumference extra area was removed by laser ablation. We thus obtained OFET devices with gold electrodes as shown in Fig. 1c. Platinum electrodes were also fabricated similarly by adjusting the conditions appropriately. After the same processes of pretreatment and adsorption of platinum colloids under the same conditions, the substrates with the C10-DNTT films were dipped in an electroless-platinum-plating solution for 120 s at 25 °C. This solution contained $H_2[Pt(OH)_6]$: 5 mM, $(NH_4)_2SO_4$: 230 mM, L-Aspartic acid: 75 mM and NaOH: 110 mM. As a result, we obtained approximately 30-nm-thick platinum plating films. At the end, the plated platinum film in the channel area and outer circumference extra area was removed by laser ablation similarly.

Fig. 2a and b shows the typical characteristics of the OFET devices with the gold electrodes. The transfer and output characteristics suggest that the device could be operated successfully as a typical transistor. The narrow hysteresis observed is satisfactory for typical devices with vapor-deposited gold electrodes, indicating that the charge injection from the electroless plated gold indeed forms an electric connection to the organic semiconductor layer. The ohmic output characteristics in the low V_D area, as shown in Fig. 2b, further suggests that the gold-organic semiconductor junction did not induce significant interface traps. It should be noted that the channel dimensions are W = 3000 μm and L = 150 μm, and the mobility of the device is estimated to be approximately 6.0 $cm^2 V^{-1} s^{-1}$. By forming electrodes on solution-crystallized organic semiconductors by electroless gold plating, we were able to fabricate a high performance OFET device without using vacuum processes.