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Low-voltage organic transistor with subfemtoliter inkjet source–drain contacts

Tomoyuki Yokota, Tsuyoshi Sekitani, Yu Kato, and **Kazunori Kuribara,** Department of Electrical Engineering and Department of Applied Physics, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan
Ute Zschieschang and **Hagen Klauk,** Max Planck Institute for Solid State Research, D-70569 Stuttgart, Germany
Tatsuya Yamamoto and **Kazuo Takimiya,** Department of Applied Chemistry, Graduate School of Engineering, Institute for Advanced Materials Research, Hiroshima University, Higashi-Hiroshima 739-8527, Japan
Hirokazu Kuwabara and **Masaaki Ikeda,** Nippon Kayaku Co., Ltd., Kita-ku, Tokyo 123-0865, Japan
Takao Someya, Department of Electrical Engineering and Department of Applied Physics, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan; Institute for Nano Quantum Information Electronics (INQIE), The University of Tokyo, Meguro-ku, Tokyo 153-8505, Japan

Address all correspondence to Takao Someya at **someya@ee.t.u-tokyo.ac.jp**

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Abstract

We have successfully achieved a transconductance of 0.76 S/m for organic thin-film transistors with 4 V operation, which is the largest value reported for organic transistors fabricated using printing methods. Using a subfemtoliter inkjet, silver electrodes with a line width of 1 µm and a channel length of 1 µm were printed directly onto an air-stable, high-mobility organic semiconductor that was deposited on a single-molecule self-assembled monolayer-based gate dielectric. On reducing the droplet volume (0.5 fl) ejected from the inkjet nozzle, which reduces sintering temperatures down to 90 °C, the inkjet printing of silver electrodes was accomplished without damage to the organic semiconductor.

Printing processes such as inkjet have attracted significant attention for the fabrication of thin-film transistors (TFTs)[1–4] and other active devices, potentially offering less material consumption and lower cost compared with more traditional device manufacturing methods.[5–8] Employing the combination of inkjet and surface modification[9] or electrohydrodynamic jet printing,[10] the spatial resolution of printing has been recently reduced down to 1 µm or less, and applied to the fabrication of organic TFTs.[9–11]

The main motivations to miniaturize dimensions of organic TFTs are reduction in power dissipation and increase in operation speed. The cutoff frequency, f_T, is formulated by $f_T = g_m/(2\pi C_G)$, where g_m and C_G represent transconductance and gate capacitance, respectively; thereby, it is important to increase g_m. For organic TFTs with a channel length of 90 nm, which were fabricated by electron beam lithography, g_m as high as 0.4 S/m,[12] was reported. Furthermore, D. Frisbie reported on ion-gel gated organic transistors with a large transconductance (0.5 S/m).[13]

In order to improve g_m in printed organic TFTs, it is important to simultaneously realize an increase in mobility and a decrease in device dimensions. In addition to improving g_m, the parasitic capacitance between gate and source/drain electrodes has to be minimized to increase f_T. This may be achieved by improving registration accuracy between electrodes and/or by reducing the line width of electrodes. For example, organic TFTs with a channel length of 1 µm and a contact line width of 2 µm were fabricated by a subfemtoliter inkjet.[11] However, the mobility of printed organic TFTs was small (0.03 cm^2/V s) when the channel length decreased to the micrometer regime due to the large contact resistance. Indeed, the printed silver electrodes usually require relatively high sintering temperatures (130 °C in Ref. 11), which degrade the interfaces between organic semiconductors and silver electrodes. To further increase g_m in printed organic TFTs, a better control of interfacial quality has to be achieved by ultrafine printing as described below.

Employing subfemtoliter inkjet printing, we report here the successful fabrication of a high-performance top-contact organic TFT using a self-assembled gate dielectric and silver contacts deposited by subfemtoliter inkjet printing with a contact line width of 1 µm and a channel length of 1 µm. By reducing the sintering temperature of printed silver electrodes down to 90 °C, the device exhibits a mobility of 0.2 cm^2/V s and a transconductance of 0.76 S/m at an operation voltage of 4 V. To the best of our knowledge, this is the highest transconductance reported for organic TFTs fabricated using printing.

The TFTs and circuits were manufactured on silicon substrates. The TFTs employ the top-contact geometry, which is similar to the one reported in Ref. 11, although the semiconductor is replaced by DNTT and the process conditions are optimized. A photograph of a printed and sintered silver nanoparticle contact is shown in Supplementary Fig. 1 online. The contacts had a line width of 1 µm and, because the droplet volume was less than 1 fl, could be printed with a line spacing (i.e., a channel length) as small as 1 µm. The 25-nm-thick aluminum gate electrodes were first deposited through a shadow mask onto the substrate. The surface of the aluminum was exposed to oxygen plasma to create a 4-nm-thick aluminum oxide (AlO_x) layer. The plasma power was 300 W and the duration of the plasma treatment was 30 min. The substrate was then dipped for 16 h in a 2-propanol solution containing 5 mM of *n*-tetradecylphosphonic acid to form a self-assembled monolayer (SAM) on the surface of the aluminum oxide layer.[14,15] Thus, the AlO_x/SAM gate dielectric had a total thickness of 6 nm and a capacitance per unit area (C_{diel}) of 700 nF/cm^2, which allowed the transistors and circuits to operate with voltages of 2–3 V. The 30-nm-thick films of dinaphtho-[2,3-*b*:2′,3′-*f*]thieno[3,2-*b*]thiophene (DNTT)[16] were vacuum deposited through shadow masks onto the gate dielectric as the organic semiconductors for the p-channel TFTs. Finally, silver nanoparticles (NPS-J-HP, Harima Chemical Co. Ltd., Japan) were deposited directly onto the organic semiconductors by subfemtoliter inkjet printing to form the source and drain contacts of the top-contact organic TFTs. After sintering the printed nanoparticles at a temperature of 90 °C for 5 h in nitrogen, the printed lines had a resistivity of about 20 µΩ cm, which was sufficiently low for the source and drain contacts of the organic TFTs.

Figure 1(a) shows a SEM image of a completed DNTT TFT. There was no scattering of ink in the transistor channel. Figure 1(b) shows cross-sectional TEM images of TFTs in which the silver contacts were deposited by picoliter inkjet printing (left) and subfemtoliter inkjet printing (right). As can be seen, when the nanoparticles were deposited by picoliter inkjet printing, the nanoparticle ink seeped into the organic semiconductor layer, while in the case of subfemtoliter inkjet printing, there was no visible damage to the organic semiconductor.

All of the electrical measurements were carried out in ambient air. Figure 2(a) shows the transfer characteristics of DNTT TFTs fabricated by subfemtoliter inkjet printing of the source and drain contacts with channel lengths ranging from 1 to 98 µm. Even for the shortest channel length of 1 µm, the transfer characteristics had negligible hysteresis, steep subthreshold slope (90 mV/decade), small off-state drain currents (<20 pA), and large on/off ratios (>10^7). The output characteristics of a

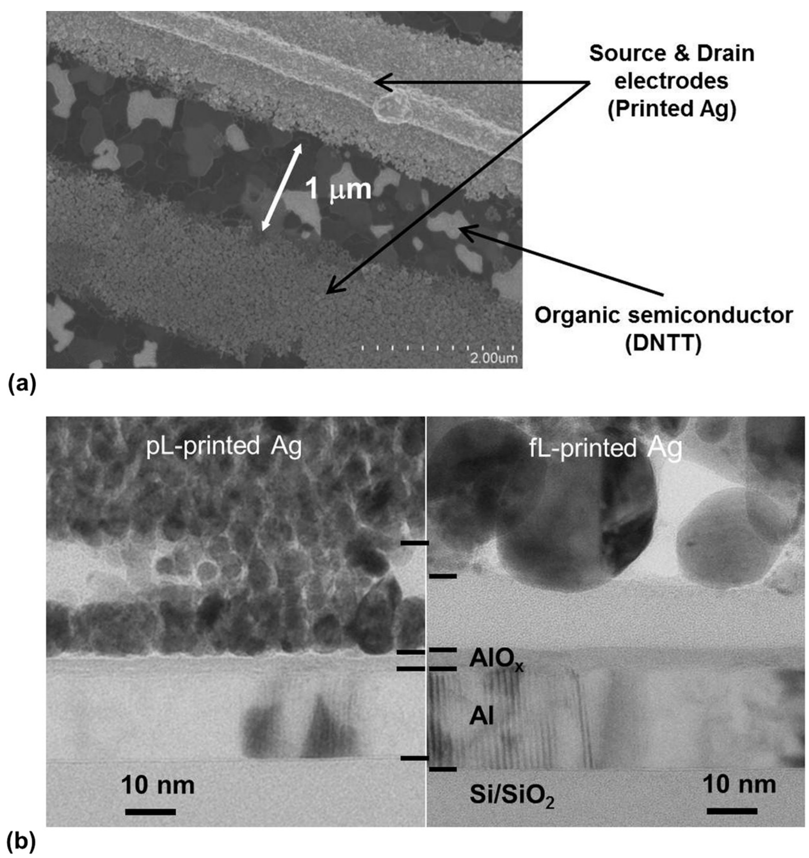

Figure 1. SEM and TEM images of organic transistors. (a) SEM image of a DNTT transistor. The line width of the inkjet-printed contacts and channel length are 1 µm. (b) Cross-sectional TEM images of DNTT transistors in which the silver nanoparticle contacts were deposited by picoliter inkjet printing (left) and subfemtoliter inkjet printing (right).

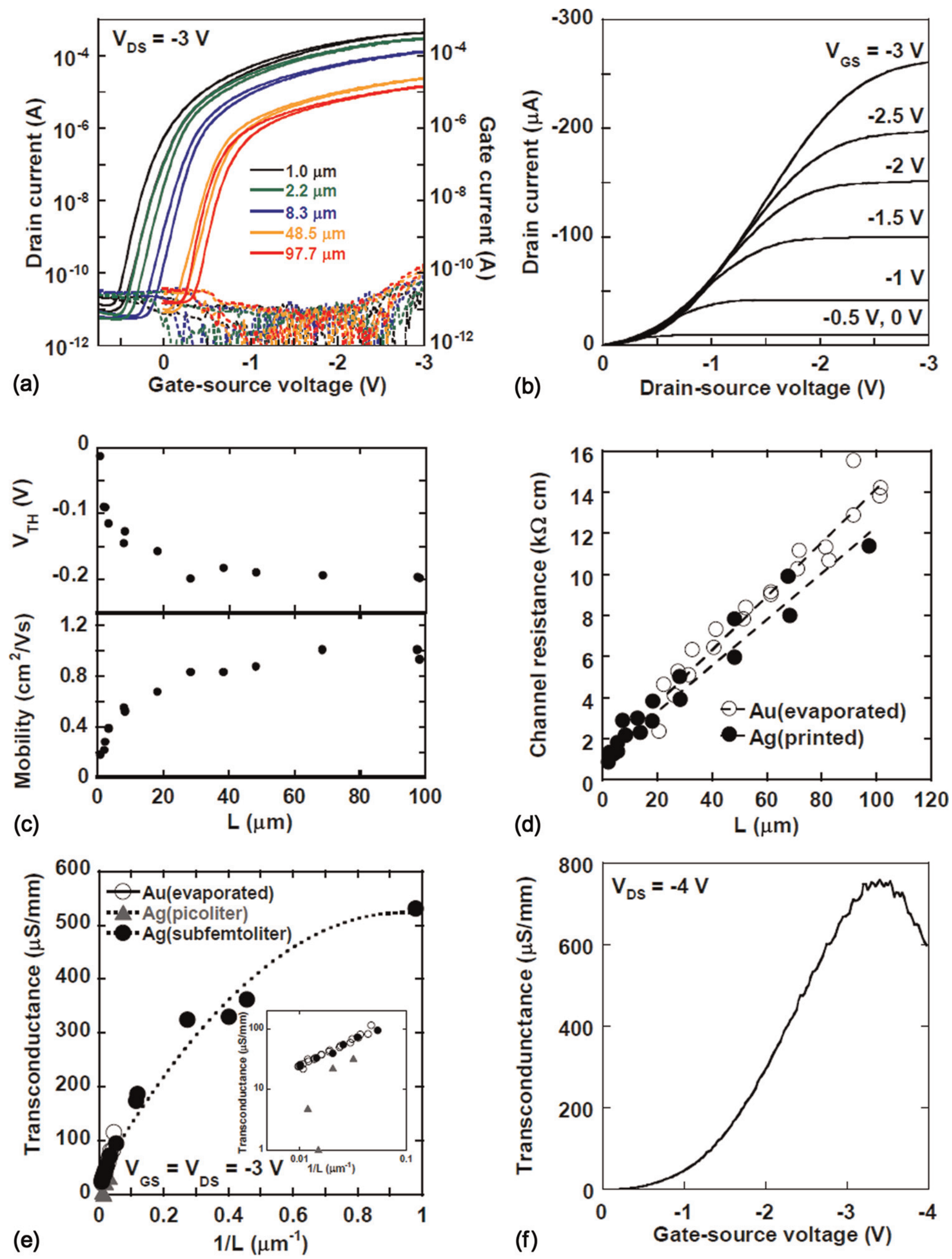

Figure 2. Electrical characteristics of DNTT p-channel TFTs. (a) Transfer characteristics of DNTT TFTs with channel lengths of 1, 2.2, 8.3, 48.5, and 97.7 μm (channel width is 500 μm for all devices). (b) Output characteristics of a DNTT TFT with a channel length of 1 μm and a channel width of 500 μm. (c) Dependence of the threshold voltage and apparent mobility of the transistors on the channel length. (d) Channel resistance of DNTT TFTs measured in the saturation regime as a function of channel length. Solid and open circles represent DNTT TFTs with silver nanoparticle contacts deposited by subfemtoliter inkjet printing and DNTT TFTs with evaporated gold contacts patterned using shadow masks, respectively. (e) Transconductance of DNTT TFTs as a function of inverse channel length. Solid and open circles and gray triangles represent DNTT TFTs with silver nanoparticle contacts deposited by subfemtoliter inkjet printing, DNTT TFTs with evaporated gold contacts patterned using shadow masks, and DNTT TFTs with silver nanoparticle contacts deposited by picoliter inkjet printing, respectively. (f) Transconductance of a TFT with a channel length of 1 μm plotted as a function of gate–source voltage ($g_m = \partial I_D / \partial V_{GS}$).

DNTT TFT with a channel length of 1 μm are shown in Fig. 2(b), showing reasonable saturation of the drain current.

When the channel length was reduced to 1 μm, the threshold voltage shifted toward more positive values [Fig. 2(c)]. The observed channel-length dependence of the threshold voltage is known as the threshold-voltage roll-off effect,[17] while the observed decrease in the apparent field-effect mobility is the result of the increasing impact of contact resistance on total device resistance as channel length (and hence channel resistance) is reduced.[18]

The channel resistance of TFTs was measured in the saturation regime with inkjet-printed silver nanoparticle source and drain contacts and the results were compared with those of TFTs with evaporated and shadow-mask-patterned gold source and drain contacts as a function of channel length [Fig. 2(d)]. By extrapolating the linear fit to a channel length of zero, the contact resistance can be determined.[18] The TFTs with inkjet-printed silver nanoparticle contacts had a contact resistance of 980 Ω cm, while the TFTs with evaporated gold contacts had a contact resistance of 970 Ω cm. Considering workfunctions of contact metals (silver: 4.4 eV; gold: 5.0 eV) and the ionization potential of DNTT (5.4 eV; see Ref. 16), a larger difference between the contact resistances would have been expected. A possible explanation for the surprisingly small contact resistance in the case of the silver nanoparticle contacts is that the workfunction of the printed nanoparticles was larger than that of bulk silver for exposure to oxygen[19,20] and/or the different morphology of the metal–organic semiconductor interface and its effect on the electrical properties of the transistors.

Because of the short channel length ($L = 1$ µm) in combination with the relatively large mobility (>0.1 cm^2/V s) and relatively small contact resistance (<1 kΩ cm), the transconductance ($g_m = \partial I_D/\partial V_{GS}$) normalized to the channel width (W) of the TFTs reached a value as high as 0.76 S/m at a drain–source voltage of −4 V [see Figs. 2(e), 2(f) and Supplementary Fig. 2 online]. On the other hand, the transconductance is 0.1 S/m for DNTT TFTs with source and drain contacts (channel length $L \sim 20$ µm) that were patterned by a shadow mask technique in the evaporation system, while it is 0.03 S/m for DNTT TFTs with printed source and drain contacts ($L \sim 30$ µm) by using a picoliter inkjet. The present transconductance of 0.76 S/m is the largest transconductance reported for organic transistors fabricated using printing methods. For a contact line width (ΔL) of 1 µm and a channel width of 500 µm, the calculated gate capacitance of these TFTs was about 10 pF ($C_G \sim C_{diel} \cdot (L + 2 \cdot \Delta L)W$), which suggests a theoretical cutoff frequency of about 6 MHz ($f_T \sim g_m/(2\pi C_G)$). This calculated cutoff frequency was similar to the cutoff frequency estimated by Noh et al. for polymer TFTs with a channel length of 200 nm and a self-aligned gate electrode.[9]

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Supplementary materials

For supplementary material for this article, please visit http://dx.doi.org/10.1557/mrc.2011.4

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Supplemental data

Figure S1. Optical microscopy image of the organic thin-film transistors with patterned Al gates, ultrathin AlO_x/SAM gate dielectric, vacuum-deposited DNTT as the semiconductor, and subfemtoliter inkjet-printed Ag nanoparticle source/drain contacts. The channel length is 1 μm.

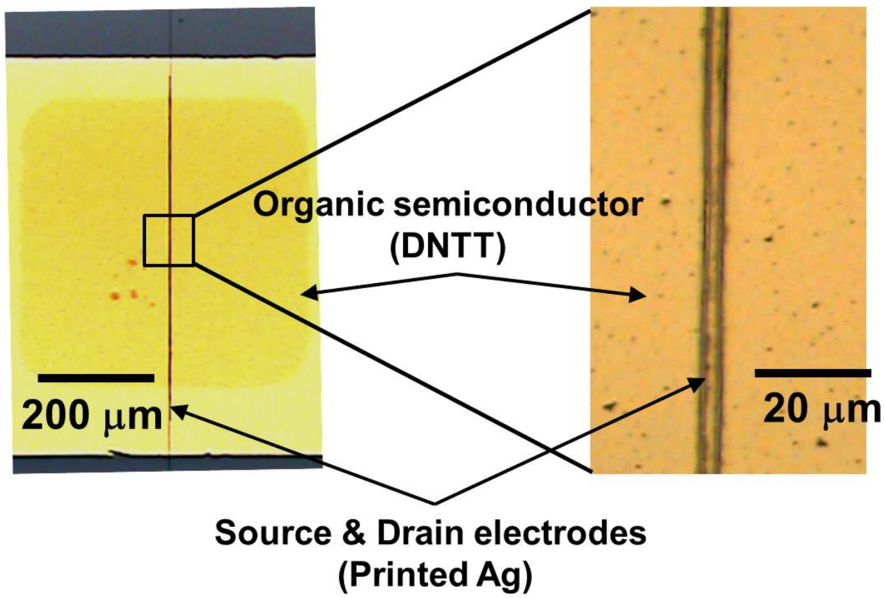

Figure S2. Electrical characteristics of DNTT TFTs with channel lengths of 1 μm (V_{DS} = -4 V) (a) Drain current as a function of gate-source voltage (b) Square root of drain current as a function of gate-source voltage.