

Letter

Jet-printed electrodes and semiconducting oligomers for elaboration of organic thin-film transistors

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Abstract

A new oligomer of bithiophene and substituted fluorene has been successfully synthesized, exhibiting good FET performance. Our results show that devices can be obtained from inkjetted OTFTs and elaborated by direct writing without any particular pre-patterning or self-alignment techniques. We have also demonstrated the possibility to fabricate inexpensive OTFTs by direct writing paving the way toward using inkjet printing as the key technology for such applications in plastic electronics. The ease of this technique allows charts a clear path to flexible electronics.

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Here we describe the direct inkjet printing of transistors that utilize a semiconducting layer formed from the oligomers of bithiophene and the substituted fluorene and source and drain electrodes formed from gold nanoparticles. Organic materials are promising candidates to make organic thin-film transistors (OTFTs) active components for the fabrication of low-cost devices for applications such as radio frequency identity (RFID) tags [1], polymer electronics [2], and OTFT display backplanes [3]. However, the carrying out of OTFTs does not

attain the low-cost expected. Inline mass production, where the global process is made in continuous by one machine as fast as possible, fills this requirement. That is to say the integration of processes like spin-coating, photolithography, e-beam lithography, or vacuum thermal evaporation (VTE) steps [4] will become too expensive.

Direct printing techniques are mentioned to be one of the key-technologies [5] to complete such plastic electronics devices. The first existing technique consists of a pad printing technique in continuous processing [6]. The second approach is based on flexography technique which requires, as a preceding step to processing, the fabrication of a solid master by photolithography [7]. The last approach

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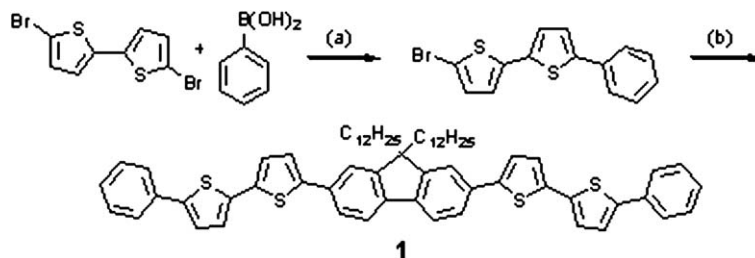
is based on drop on-demand inkjet printing (DOD-IJP) technique. This latter process allows the elaboration of OTFTs, even without (i) patterning through a shadow- or photo-mask, (ii) drops self-alignment thanks to a pre-patterning made by photolithography [8], (iii) etching and cleaning steps. Nonetheless, the materials used in DOD-IJP must be present in solution and potentially have high electrical properties.

Based on the work of Fréchet et al. [9], we selected well-defined oligomers rather than polymers as the subunit for the semiconducting layer. We utilized the oligomers of fluorene and bithiophene because their polymers [10] and other related oligomers [11] have been used extensively in electrical devices [10,11]. Oligomers present many advantages over polymers. For example, a higher degree of purity in oligomers should allow for a better opportunity to control the molecular arrangement. In addition the oligomers are easily processed due to their solubility and low viscosity.

Scheme 1 shows the synthesis of our target organic semiconductor (**1**). The synthesis involves two sequential Suzuki coupling reactions [12]. The

first coupling differentiates the two bromine atoms of the bithiophene by reaction with phenylboronic acid, and the second coupling joins two of these pieces to the diboronic acid of 9,9-didodecylfluorene (Scheme 1).

To test **1** for its efficacy in thin film transistors, we have fabricated thermally evaporated thin films of it and used a metal mask to define the source and drain electrodes. The doped silicon wafer serves as a global back gate for the devices. We deposited 50 nm of **1** followed by the Au electrodes, again by vacuum evaporation. The channel length (L) was 75 μm and the electrode width (W) was 2 mm. Fig. 1a and b show the transconductance and transistor output for a typical device. The mobility ($8 \times 10^{-3} \pm 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and threshold voltage (below -20 V) are calculated by plotting $|I_{\text{DS}}|^{1/2}$ versus V_{G} , using the formula [13]: $I_{\text{DS}} = (\mu WC_i/2L) \cdot (V_{\text{G}} - V_{\text{TH}})^2$ with the capacitance $C = 11.3 \text{ nF/cm}^2$ for the gate dielectric layer [14]. The gate dielectric capacitance (300 nm of SiO_2 and a monolayer of HMDS) comes from measurements over a range of frequencies [13] and is what would be expected for a 300 nm thick silicon oxide layer



Scheme 1. Reagents and conditions: (a) K_2CO_3 , $\text{Pd}(\text{PPh}_3)_4$, toluene/ H_2O , reflux, (b) 9,9-didodecylfluorene-2,7-diboronic acid, K_2CO_3 , $\text{Pd}(\text{PPh}_3)_4$, toluene/ H_2O , reflux.

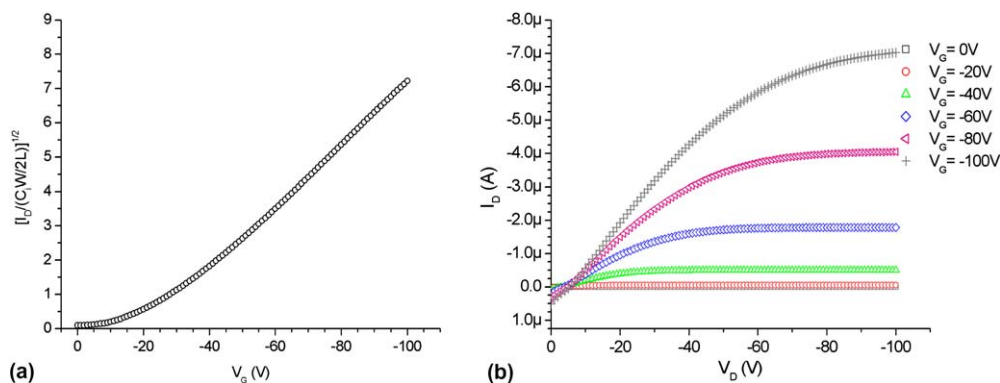


Fig. 1. (a) Transconductance at $V_{\text{DS}} = -100 \text{ V}$ and (b) output characteristics for OTFTs from **1** deposited by thermal vacuum evaporation (dots in each figure are experimental data).

with few defects [14]. These unoptimized results are consistent with the performance of fluorene-bithiophene based polymeric semiconductors [15,16].

Next we focus on printing the source and drain electrodes. Here we use nanoparticles of Au [18,19] and print them on clean silicon wafers coated with an HMDS self-assembled monolayer. We filtered a solution of capped gold nanoparticles (3 wt.%) diluted in toluene/ α -terpineol mixing (1.5/1 v/v) and then printed them with the inkjet setup described in the experimental section. Wafers were heated at 40 °C during the deposition process and the printed lines were subsequently annealed at 130 °C for \sim 1 h under ambient conditions to enhance the conductivity of the gold lines. We can notice shortest anneal times can be addressed for Au nanoparticles capped with shorter alkane-thiols chains [18]. The spatial control of features goes down to 30 μ m without pre-patterning the wafer or conductor self-alignment techniques [8,10,15]. The cross section of a line is not uniform in thickness due to a splash-effect. The printed lines are 1 mm long, 120 μ m wide and 200 nm thick. Fig. 2 shows an optical microscopy image of inkjet printed gold lines.

Fig. 3 shows the results of simple two-probe measurements comparing the conductivity from thermally evaporated gold lines and the inkjet printed lines. The conductivity of printed lines were lower by around a factor of 3 (from 3×10^4 S/cm and 9×10^4 S/cm) and similar to the results of others who have printed gold lines from gold nanoparticles [17,18].

Using these printed lines, we next turned our attention to printing the oligomer that was synthe-

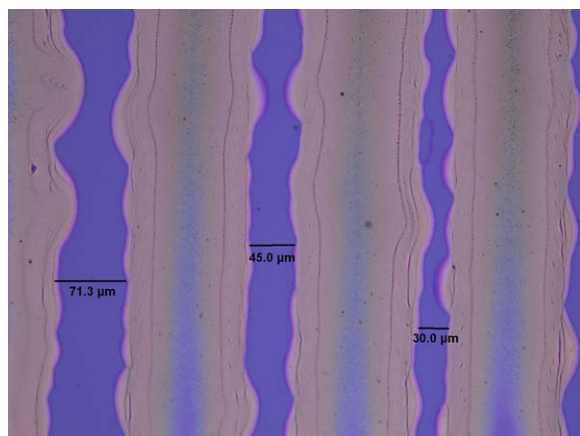


Fig. 2. Optical microscopy image of inkjet printed gold lines separated by 71.3 μ m, 45 μ m and 30 μ m, respectively without pre-patterning or self-alignment on substrates.

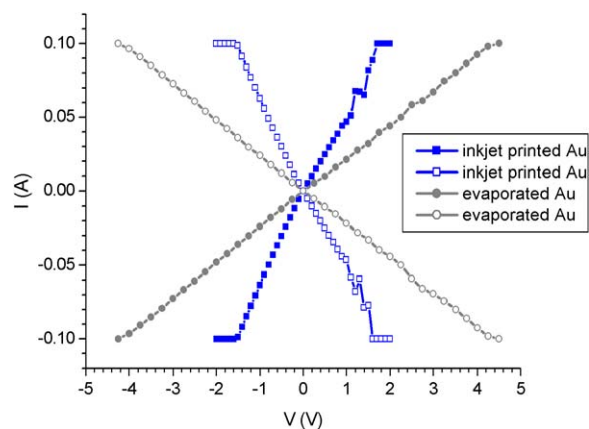


Fig. 3. Two-probe conductivity measurements of inkjetted and evaporated gold lines.

sized and tested above. We first filter (MilliporeTM, 200 nm pore diameter) a solution of **1** in 1,2,4 trichlorobenzene (5 mg/mL) and print this between gold lines that define the source and drain of the transistor (Fig. 4a). The material was annealed at 140 °C for 30 min under an argon atmosphere. The printed OTFTs have a channel length (L) of 45 ± 5 μ m and channel width (W) of 270 μ m. The device exhibits an average field effect mobility of 5.4×10^{-4} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and an on/off current ratio of 6×10^3 at $V_{\text{DS}} = -100$ V (Fig. 4b). The output characteristics show good saturation and no sign of significant contact resistance (Fig. 4c). The threshold gate voltage is below -30 V (Fig. 4b).

In conclusion, a new oligomer has been successfully synthesized, exhibiting good FET performance. Our results show that devices with good performance can be obtained from an all-inkjetted OTFT elaborated by direct writing without any particular pre-patterning or self-alignment techniques [8,10,15]. We have also demonstrated the possibility to fabricate inexpensive OTFTs by direct writing paving the way toward using inkjet printing as the key technology for such applications in plastic electronics. The ease of this technique and the possibility of organic semiconductor engineering with better electrical performances allow charts a clear path to flexible electronics.

Experimental section

The devices made by VTE were measured under daylight and ambient conditions using an HP4156C semiconductor analyzer, and exhibiting a field-effect mobility of 8×10^{-3} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ with

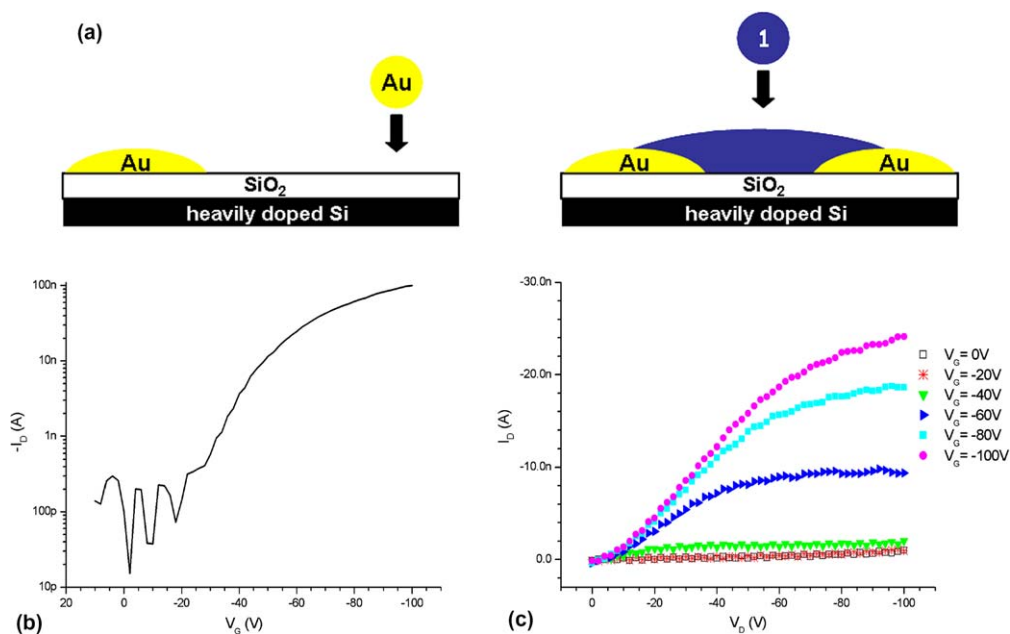


Fig. 4. (a) Schematic description of OTFT fabrication by printing (DOD-IJP): source, drain (gold nanoparticles) electrodes and **1** as semiconductor, (b) transconductance at $V_{DS} = -100$ V and (c) output characteristics of all-inkjet printed OTFTs on insulated silicon wafer.

an on/ off current ratio of 6×10^3 at $V_{DS} = -100$ V (Fig. 1a).

The synthesis of gold nanoclusters were first reported by Murray [19]. 1.5 g of tetraoctylammonium bromide was mixed with 80 mL of toluene and added to 0.31 g of $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ in 25 mL of deionized water. AuCl_4^- was transferred into toluene and the aqueous phase was removed.

The DOD-IJP experiment used in the present study is a custom-build setup, composed of three parts: (i) DOD-IJP assembly, (ii) X–Y translation stages, and (iii) a computing system, which commands both the DOD-IJP dispensing device and the X–Y stages, simultaneously. MicroJet™ print-heads, drop-on-demand dispensing devices, provided by Microfab Inc. were employed. The Piezoelectric DOD used in this apparatus is suited for dispensing droplets with a diameter of 50 μm from a range of solvents including water and many organic solvents. Waveform dispensing controller generates bipolar pulses which avoids the formation of satellites droplets during jetting. X–Y translation stages are driven by a stepper-motor with a resolution of 1 μm over which is mounted a hotplate used to heat the predeposited droplets, and to enhance the continuity of the printed lines. The DOD-IJP experiment was undertaken in a standard labora-

tory environment at under ambient conditions, with no temperature or humidity control.

References

- [1] T.W. Kelley, P.F. Baude, C. Gerlach, D.E. Ender, D. Muyres, M.A. Haase, D.E. Vogel, S.D. Theiss, *Chem. Mater.* 16 (23) (2004) 4413.
- [2] 'Field of technology in which polymers and/or oligomers assume an electrical and/or electronic function': J. Ficker, A. Ullman, W. Fix, H. Rost, W. Clemens, *J. Appl. Phys.* 94 (2003) 2638.
- [3] L. Chabinye, W.S. Wong, K.E. Paul, R.A. Street, *Adv. Mater.* 15 (2003) 1903.
- [4] W. Kelley, P.F. Baude, C. Gerlach, D.E. Ender, D. Muyres, M.A. Haase, D.E. Vogel, S.D. Theiss, *Chem. Mater.* 16 (2004) 4413.
- [5] J. Mills, Printed Electronics Conference (New Orleans, USA), 2004.
- [6] A. Knobloch, A. Manuelli, A. Berndts, W. Clemens, *J. Appl. Phys.* 96 (2004) 2286.
- [7] U. Zschieschang, H. Klauk, M. Halik, G. Schmid, C. Dehm, *Adv. Mater.* 15 (2003) 1147.
- [8] H. Sirringhaus, T. Kawase, *Science* 290 (2000) 2123.
- [9] P.C. Chang, J. Lee, D. Huang, V. Subramanian, A.R. Murphy, J.M.J. Fréchet, *Chem. Mater.* 16 (23) (2004) 4783.
- [10] N. Stutzmann, R.H. Friend, H. Sirringhaus, *Science* 299 (2003) 1881.
- [11] H. Meng, Z. Bao, A.J. Lovinger, B.-C. Wang, A.M. Majsce, *J. Am. Chem. Soc.* 123 (2001) 9214.
- [12] N. Miyaura, A. Suzuki, *Chem. Rev.* 95 (1995) 2457.

- [13] Q. Miao, M. Lefenfeld, T.-Q. Nguyen, T. Siegrist, C. Kloc, C. Nuckolls, *Adv. Mater.* 17 (2005) 407.
- [14] S.M. Sze, *Physics of Semiconductor Devices*, Wiley-Interscience, New York, 1969.
- [15] T. Kawase, T. Shimoda, C. Newsome, H. Sirringhaus, R.H. Friend, *Thin Solid Films* 438 (2003) 279.
- [16] K.E. Paul, W.S. Ong, S.E. Ready, R.A. Street, *Appl. Phys. Lett.* 83 (2003) 2070.
- [17] Y. Wu, Y. Li, B.S. Ong, P. Liu, S. Gardner, B. Chiang, *Adv. Mater.* 17 (2005) 184.
- [18] D. Huang, F. Liao, S. Molesa, D. Redinger, V. Subramanian, *J. Electrochem. Soc.* 150 (2003) G412.
- [19] M.J. Hostetler, J.E. Wingate, C.J. Zhong, J.E. Harris, R.W. Vchet, M.R. Clark, J.D. Longdono, S.J. Green, J.J. Stokes, G.D. Wignall, G.L. Glish, M.D. Porter, N.D. Evans, R.W. Murray, *Langmuir* 14 (1998) 17.