Influence of the contact metal on the performance of *n*-type carbonyl-functionalized quaterthiophene organic thin-film transistors

S. Schols,^{1,a),b)} L. Van Willigenburg,^{1,c)} R. Müller,¹ D. Bode,^{1,a)} M. Debucquoy,^{1,a)} S. De Jonge,¹ J. Genoe,¹ P. Heremans,^{1,a)} S. Lu,² and A. Facchetti^{2,d)}

¹IMEC v.z.w., SOLO/PME, Kapeldreef 75, B-3001 Leuven, Belgium

²Polyera Corporation, 8025 Lamon Avenue, Skokie, Illinois 60077, USA

(Received 18 July 2008; accepted 9 December 2008; published online 30 December 2008)

Organic thin-film transistors using 5, 5'''-diperfluorohexylcarbonyl-2,2':5',2'':5'',2'''-quaterthiophene (DFHCO-4T) as the electron conducting organic semiconductor are fabricated and the performance of these transistors with different top-contact metals is investigated. Transistors with Au source-drain top contacts attain an apparent saturation mobility of 4.6 cm²/V s, whereas this parameter is 100 times lower for similar transistors with Al/LiF top contacts. We explain this lower performance by the formation of a thin interfacial layer with poor charge injection properties resulting from a redox reaction between Al and DFHCO-4T. © 2008 American Institute of Physics. [DOI: 10.1063/1.3059556]

Driven by potential applications of complementary logic, the field of electron-channel (*n*-type) organic thin-film transistors (*n*-OTFT) and corresponding *n*-type materials has recently gained a lot of attention. Examples of such materials are fullerene,¹ naphthalene,² perylene,³ and oligothiophene⁴ derivatives. Recently, 5, 5'''-diperfluorohexylcarbonyl-2,2':5',2'':5'',2'''-quaterthiophene (DFHCO-4T) (Fig. 1) was shown to have an electron field-effect mobility of 1.7 cm²/V s.⁵ Top-contact geometry Au source and drain contacts were used in these devices. In the present letter, we compare the performance of DFHCO-4T transistors with different top-contact metals. While most *n*-OTFTs show good performance when using Al/LiF as top contact,^{6,7} we find that DFHCO-4T *n*-OTFTs only function properly with contacts that have a low chemical reactivity such as Au and Ag, and report mobilities as high as 4.6 cm²/V s for Au top-contact transistors. We explain the reduced performance with easily oxidizable metals such as Al and Yb as a consequence of an electron-transfer reaction occurring at the metal/DFHCO-4T interface.

The substrates used in this work are doped *n*⁺⁺-Si wafers with a 140 nm thick thermally grown SiO₂ layer (serving as the OTFT gate dielectric), covered with a 5 nm thick poly-(α -methylstyrene) layer (*P* α MS, standard 700.000, Fluka) prepared by spin-coating a solution of 0.1 wt % *P* α MS in toluene at 4000 rpm and drying on a hotplate at 120°C for 1 min.⁸ This procedure provides a high-quality, electron-trap free surface allowing excellent electron transport.⁹ Thin DFHCO-4T films were deposited on these substrates by thermal vacuum evaporation ($p=10^{-8}$ torr) of the material (available from Polyera Corporation under the trade name ActivInk™ N0800), which was used as received. Atomic force microscopy analysis of DFHCO-4T reveals

typical Stransky–Krastanov growth mode¹⁰ with the first few monolayers grown in a two-dimensional arrangement followed by a three-dimensional (3D) lattice. In the case of DFHCO-4T films, thick elongated needles (up to 100 nm long) are formed. Preliminary experiments indicated that this 3D growth can be suppressed by deposition at high substrate temperature and high deposition flux. Therefore, in this study we deposited DFHCO-4T at a flux of 4.5 Å/s and a substrate temperature of 70°C. Afterwards, the transistor structure was completed by metallic top-contact (100 nm Au, Ag or Yb or 0.8 nm LiF followed by 100 nm Al) evaporation onto the organic semiconductor through a shadow mask. The resulting device channel width is 2000 μ m and the channel length varies between 50 and 200 μ m. Immediately after their fabrication, the devices were transferred to a N₂-filled glove box (without exposure to air) for electrical characterization using an Agilent 4156C parameter analyzer. Thin-film mobilities were calculated from saturation,¹¹ using a total dielectric capacitance per area of 2.33 10⁻⁴ F/m², which was determined based on relative dielectric constant values of 3.9 for SiO₂ and 2.5 for *P* α MS, as obtained from capacitance-voltage measurements.

Figure 2(a) shows the output characteristics of a transistor with 130 μ m channel length and Al/LiF top contacts. For this device, an apparent field-effect electron mobility of 0.03 cm²/V s was calculated. This value is more than one order of magnitude lower than the electron mobility of DFHCO-4T previously reported using Au top contacts.⁵ In addition, the OTFTs show strongly nonideal characteristics, as apparent from a superlinear dependence of the current on the drain voltage at low bias, the saturation of the output current at a more or less fixed drain-to-source bias, and a decrease of the current at higher drain voltages. On the other hand, transistors fabricated under the same DFHCO-4T

FIG. 1. Chemical structure of DFHCO-4T and DFH-4T.

^{a)}Also at Katholieke Universiteit Leuven, Electrical Engineering Department, B-3001 Leuven, Belgium.

^{b)}Electronic mail: sarah.schols@imec.be.

^{c)}Also at University of Applied Science Utrecht, Oudenoord 700, 3513 EX, Utrecht, The Netherlands.

^{d)}Also at Northwestern University, Department of Chemistry and the Material Research Center, Evanston, Illinois 60208, USA.

FIG. 2. Output characteristics of DFHCO-4T transistors ($W/L=2000/130$) using (a) Al/LiF, (b) Au, (c) Yb, and (d) Ag top contacts.

growth conditions but with Au instead of Al/LiF source-drain top contacts exhibit much better-behaved output characteristics with much higher drain currents [Fig. 2(b)]. For Au top-contact transistors with 130 μm channel length, an apparent mobility of 4.6 cm^2/Vs is measured. Such remarkable mobility achieved with Au contacts is of high technological relevance because for use in complementary logic it is preferable to use a single type of source and drain metal for both the p -type and the n -type OTFTs. The reproducibility of the results is quite good. The average apparent mobility, calculated from transistors with channel lengths between 50 and 200 μm is 3.5 cm^2/Vs . These field-effect mobilities are higher compared to previously reported results⁵ and we attribute this to the different growth conditions used to deposit DFHCO-4T. The fact that electrons can be efficiently injected from Au into DFHCO-4T despite an injection barrier of ~ 1 eV is not fully understood yet. The deep lowest unoccupied molecular orbital (3.96 eV) (Ref. 12) of DFHCO-4T and the fact that in a top-contact geometry there is a high gate-field that supports the injection of charges in a large source-gate overlap area¹³ might be a possible explanation for this experimental observation.

The low apparent field-effect mobility (i.e., low output currents) and the nonideal characteristics of DFHCO-4T transistors with Al/LiF top contacts compared to Au top contacts point to the presence of a current-limiting contact problem in the former. A plausible cause of this is the occurrence of a redox reaction between the n -type semiconductor and the Al metal contact. In fact, it is well known that ketone groups—present in the DFHCO-4T chemical structure—are easily reduced into their radical anions according to the reaction scheme shown in Fig. 3(a).¹⁴ The electron transfer reaction is driven by the oxidation of a reactive metal, as for example Mg, Al, Fe, and Zn [depicted in Fig. 3(b) for Al]^{15,16} and the reduction of DFHCO-4T. The standard free energy (ΔG° , Gibbs free energy) of the overall redox reaction depicted in Fig. 3(c) is given by Eq. (1),¹⁷ where n is the overall number of electrons exchanged between the oxidizing and reducing agents for the balanced redox equation,

FIG. 3. (a) Reduction of a ketone, (b) oxidation of Al, (c) redox reaction between a ketone and Al, (d) complexation of Al^{3+} by F^- , and (e) dimerization of a ketone radical anion.

F the Faraday constant [96 485 J/(V mol)], and E° the standard cell potential (the difference in standard electrode potentials (SEPs) of both electrochemical couples)

$$\Delta G^\circ = -nFE^\circ. \quad (1)$$

For the Al/ Al^{3+} couple the SEP in aqueous solution is -1.662 V versus the normal hydrogen electrode (NHE),¹⁸ which is about -1.90 V versus the reference saturated calomel electrode (SCE).¹⁹ Published value for the first reduction potential of DFHCO-4T in tetrahydrofuran is -0.88 V versus the SCE.¹² Inserting this potential difference into Eq. (1), with $n=3$ [Fig. 3(c)], gives $\Delta G^\circ = -296$ kJ/mol. This indicates that the reaction between Al and DFHCO-4T is highly exergonic and thus thermodynamically spontaneous.

Similar reductions of organic layers by evaporation of strongly reducing metals have been reported in literature. The reaction of Al evaporated on films of tris(hydroxyquinoline) aluminum (Alq_3),^{20–23} copper hexadecafluorophthalocyanine (F_{16}CuPC),²⁴ and 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA),²⁵ for example, were experimentally proven. The reduction of DFHCO-4T by evaporated Al [Fig. 3(c)] in our case takes furthermore advantage of some follow-up reactions. One of these reactions is the complexation of the Al^{3+} cation by fluoride ions (F^-) originating from an ultrathin (0.8 nm) LiF layer on top of the DFHCO-4T. In fact, F^- anions are well known to form stable complexes [$\text{AlF}_n^{(3-n)+}$ with $n=1–6$, Fig. 3(d)] with Al^{3+} cations.²⁶ Furthermore, ketone radical-anions readily dimerize affording the corresponding acyloinic species [Fig. 3(e)].¹⁵ Such additional processes will enforce the DFHCO-4T/Al redox reaction [Fig. 3(c)] toward the right side according to Le Chatelier's principle.

The products of the reactions displayed in Figs. 3(c)–3(e), an ionic salt and possibly dimerized ketone species, will form a thin interfacial layer between the unreacted DFHCO-4T and Al layers, hindering electron injection. In the case of Au this kind of reaction is impossible: the SEPs of the couples involving oxidation of Au are so high ($+1.692$ V versus NHE for Au/Au^+ and $+1.492$ V versus NHE for Au/Au^{3+}) (Ref. 18) that a reaction with DFHCO-4T would be highly endergonic

($\Delta G^\circ = +225$ kJ/mol in the case of Au/Au⁺ and +619 kJ/mol for Au/Au³⁺).

In order to show the relevance of the ketone-group, we investigated transistors fabricated with Al/LiF electrodes and *a, ω*-diperfluorohexyl-quaterthiophene (DFH-4T, Fig. 1),⁴ an *n*-type material of similar structure, but missing the electron-attracting ketone group. In this case, no significant difference in apparent electron mobilities could be observed between DFH-4T transistors with Al/LiF (~ 0.15 cm²/Vs) and Au (~ 0.1 – 0.2 cm²/Vs) (Ref. 4) top contacts.

To find additional proof supporting the chemical reaction between Al and DFHCO-4T, we fabricated transistors using DFHCO-4T as the organic semiconductor but with two other top-contact metals: Yb and Ag. The standard free energies for possible reactions between DFHCO-4T and Yb indicates that this kind of reaction is highly exergonic and thus spontaneous, independently if the Yb/Yb²⁺ couple (SEP: -2.76 V versus NHE,¹⁸ corresponding to $\Delta G^\circ = -409$ kJ/mol) or Yb/Yb³⁺ couple (SEP: -2.19 V versus NHE,¹⁸ corresponding to $\Delta G^\circ = -449$ kJ/mol) is considered. The corresponding value for the reaction of DFHCO-4T with Ag (SEP: $+0.7796$ V versus NHE¹⁸ for Ag/Ag⁺) is $+139$ kJ/mol, indicating that this reaction is impossible. The output characteristics of Yb and Ag top-contact transistors with $130\ \mu\text{m}$ channel length are shown in Figs. 2(c) and 2(d). Transistors with Yb top contacts show similar output characteristics and low apparent field-effect mobility (0.06 cm²/Vs) as Al/LiF transistors, whereas the output characteristics of Ag top-contact transistors are much better. When Ag is used as top metal contact an apparent mobility of 1.7 cm²/Vs was measured. These results are in agreement with our argumentation and give further evidence that a redox reaction occurs at the interface between DFHCO-4T and easily oxidizable metals, similar to Hirose *et al.*'s report that PTCDA reacts with Al, but not with Au and Ag.²⁵

In summary, DFHCO-4T transistors with Au top contacts exhibit an average apparent field-effect electron mobility of 3.5 cm²/Vs, whereas the mobility of similar transistors fabricated with easily oxidizable top-contact metals is far lower. The reduced transistor performance of Al/LiF and Yb top-contact transistors is attributed to an electron-transfer reaction between the ketone group(s) of DFHCO-4T and Al or Yb, respectively, leading to an insulating interfacial layer. Since Au and Ag—in contrast to Al and Yb—do not react with the semiconducting material, the use of these inert metals is beneficial to achieve high-performance DFHCO-4T-based *n*-OTFTs.

This work is supported by the EU-funded Project OLAS (Contract No. 015034). S. Schols acknowledges the FWO Vlaanderen for financial support.

- ¹P. H. Wöbkenberg, J. Ball, D. D. C. Bradley, T. D. Anthopoulos, F. Kooistra, J. C. Hummelen, and D. M. de Leeuw, *Appl. Phys. Lett.* **92**, 143310 (2008).
- ²H. E. Katz, A. J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y.-Y. Lin, and A. Dodabalapur, *Nature (London)* **404**, 478 (2000).
- ³P. R. L. Malenfant, C. D. Dimitrakopoulos, J. D. Gelorme, L. L. Kosbar, T. O. Graham, A. Curioni, and W. Andreoni, *Appl. Phys. Lett.* **80**, 2517 (2002).
- ⁴A. Facchetti, M. Mushrush, M. Yoon, G. R. Hutchison, M. A. Ratner, and T. J. Marks, *J. Am. Chem. Soc.* **126**, 13859 (2004).
- ⁵M. Yoon, C. Kim, A. Facchetti, and T. J. Marks, *J. Am. Chem. Soc.* **128**, 12851 (2006).
- ⁶D. J. Gundlach, K. P. Pernstich, G. Wilckens, M. Grüter, S. Haas, and B. Batlogg, *J. Appl. Phys.* **98**, 064502 (2005).
- ⁷T. D. Anthopoulos, B. Singh, N. Marjanovic, N. S. Sariciftci, A. M. Ramil, H. Sitter, M. Cölle, and D. M. de Leeuw, *Appl. Phys. Lett.* **89**, 213504 (2006).
- ⁸K. Myny, S. De Vusser, S. Steudel, D. Janssen, R. Müller, S. De Jonge, S. Verlaak, J. Genoe, and P. Heremans, *Appl. Phys. Lett.* **88**, 222103 (2006).
- ⁹L. Chua, J. Zaumseil, J. Chang, E. C. Ou, P. K. Ho, H. Sirringhaus, and R. H. Friend, *Nature (London)* **434**, 194 (2005).
- ¹⁰J. A. Venables, G. D. Spiller, and M. Hanbucken, *Rep. Prog. Phys.* **47**, 399 (1984).
- ¹¹J. Zaumseil and H. Sirringhaus, *Chem. Rev.* **107**, 1296 (2007).
- ¹²M. Yoon, S. A. DiBenedetto, A. Facchetti, and T. J. Marks, *J. Am. Chem. Soc.* **127**, 1348 (2005).
- ¹³J. Zaumseil, C. L. Donley, J. Kim, R. H. Friend, and H. Sirringhaus, *Adv. Mater. (Weinheim, Ger.)* **18**, 2708 (2006).
- ¹⁴J. Grimshaw, *Organic Electrochemistry: An Introduction and a Guide*, 4th ed. (Carbonyl Compounds, New York, 2000), Chap. 10, pp. 411–434.
- ¹⁵H. G. O. Becker, R. Beckert, G. Domschke, E. Fanghänel, W. D. Habicher, P. Metz, D. Pavel, and K. Schwetlick, *Organikum*, 21st ed. (Wiley, Weinheim, 2001), Chap. D.7, pp. 586–587.
- ¹⁶M. Hulse and T. Lavaute, *Tetrahedron Lett.* **29**, 525 (1988).
- ¹⁷J. C. Kotz and K. F. Purcell, *Chemistry and Chemical Reactivity*, 2nd ed. (Saunders, Philadelphia, 1991), Chap. 21, pp. 851–899.
- ¹⁸*CRC Handbook of Chemistry and Physics*, 85th ed., edited by D. R. Lide (CRC, Boca Raton, 2004), pp. 8.23–8.33.
- ¹⁹A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed. (Wiley, New York, 2001), p. 809.
- ²⁰Q. T. Le, L. Yan, Y. Gao, M. G. Mason, D. J. Giesen, and C. W. Tang, *J. Appl. Phys.* **87**, 375 (2000).
- ²¹M. G. Mason, C. W. Tang, L. S. Hung, P. Raychaudhuri, J. Madathil, D. J. Giesen, L. Yan, Q. T. Le, Y. Gao, S. T. Lee, L. S. Liao, L. F. Cheng, W. R. Salaneck, D. A. dos Santos, and J. L. Brédas, *J. Appl. Phys.* **89**, 2756 (2001).
- ²²C.-I. Wu, G.-R. Lee, and T.-W. Pi, *Appl. Phys. Lett.* **87**, 212108 (2005).
- ²³C. Shen, A. Kahn, and J. Schwartz, *J. Appl. Phys.* **89**, 449 (2001).
- ²⁴C. Cheng, A. Kahn, and J. Schwartz, *J. Appl. Phys.* **90**, 6536 (2001).
- ²⁵Y. Hirose, A. Kahn, V. Aristov, P. Soukiasian, V. Bulovic, and S. R. Forrest, *Phys. Rev. B* **54**, 13748 (1996).
- ²⁶M. S. Corbillion, M. A. Olazabal, and J. M. Madariaga, *J. Solution Chem.* **37**, 567 (2008).