Organic Electronics 13 (2012) 244–248

Contents lists available at SciVerse ScienceDirect

Organic Electronics

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

Electrical characteristics of ink-jet printed, all-polymer electrochemical transistors

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ARTICLE INFO

Article history:
Received 27 July 2011
Received in revised form 10 November 2011
Accepted 17 November 2011
Available online 2 December 2011

Keywords:
Organic ElectroChemical Transistor
PEDOT:PSS
Ink-jet printing

ABSTRACT

We report on the fabrication and characterization of inkjet-printed, all-Organic Electro-Chemical Transistors (OECTs) entirely realized by a conducting polymer, namely poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonic acid) (PEDOT:PSS). The transistors utilized saline as the electrolyte and exhibited output characteristics typical for operation in depletion regime. The transfer characteristics could be tuned on the basis of device geometry, with the ratio between the area of the channel and the area of the gate electrode determining the transconductance. This work paves the road for the low-cost, print-on-demand fabrication of circuits for applications in bio-sensors and disposable electronics.

1. Introduction

Organic semiconductors offer the possibility of implementing innovative, large area, flexible and low-cost applications, concerning devices such as light emitting diodes [1], photovoltaic cells [2], and organic transistors. Among the latter, two classes of devices may be found: namely Organic Field-Effect Transistors (OFETs) [3] and Organic ElectroChemical Transistors (OECTs) [4]. OECTs exploit the ability of organic semiconductors to conduct ionic in addition to electronic charge and are of great interest for chemo-sensing and bio-sensing applications as they can operate in liquid environment [5]. They are also used for the fabrication of simple circuitry that, if fabricated at low enough cost, could become disposable [6]. OECTs have a simpler geometry than OTFTs, as they may have a planar, monolayer structure, composed by a channel, usually made of poly(3,4-ethylenedioxythiophene) doped with poly (styrene sulfonic acid) (PEDOT:PSS), and a gate contact realized close to the channel, that can be fabricated employing a variety of conducting materials [5]. The gate contact can also be made by PEDOT:PSS, thus enabling an even simpler structure (as only one material is used) that can be printed, as PEDOT:PSS inks are commercially available.

Recently [7], Kaihovirta et al. presented all-polymer electrochemical transistors and memory elements fabricated by means of flexography, which is a roll-to-roll manufacturing technique. This is an extremely interesting example of OECT realized with a high throughput manufacturing technique. However, ink-jet printing offers a great flexibility in the choice of the substrates to print. A first example of an ink-jet printed OECT was presented by Mannerbro et al. [8] who adapted a conventional desktop thermal ink-jet printer to the deposition of an aqueous dispersion of PEDOT:PSS onto photo-paper. The present work deals with the realization of Organic ElectroChemical Transistors made with a piezoelectric, drop-on-demand, ink-jet printing technique that, in principle, has looser constraints than thermal printing in terms of ink composition and properties [9].

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doi:10.1016/j.orgel.2011.11.010

The goal of the present work, focused on the realization of devices entirely made of PEDOT:PSS, is: (i) to show that inkjet printing is a simple and reliable printing procedure for obtaining robust working devices and (ii) to demonstrate that their working range (i.e. the gate voltage range in which they can operate) may be predictably varied by changing the ratio between the gate and the channel areas.

With this aim, we fabricated all-organic, semitransparent devices by ink-jet printing PEDOT:PSS electrodes on plastic substrates. Thanks to a treatment with Ethylene Glycol (EG), that can be done as a final fabrication step after the printing, not only a clear increase in the conductivity, but also a significant improvement in the mechanical robustness of the final PEDOT:PSS films was achieved. In this way, several runs of measurements can be performed on the same device without problems of delamination, which is typical for PEDOT:PSS devices when measured in liquid environment.

2. Materials and methods

All-PEDOT:PSS OECTs were fabricated on transparent and flexible 175 μm thick poly(ethyleneterephthalate) (PET) sheets by means of inkjet printing. Substrates were cleaned by subsequent 15 min ultrasonic baths both in acetone and in isopropyl alcohol, then washed in deionized water and finally dried under nitrogen flow. The devices have been entirely ink-jet printed in air by means of Fujifilm Dimatix Material Printer (DMP) 2800, a piezoelectric, drop on demand, ink-jet printer widely used for organic electronic applications, using a DMC-11610 cartridge. This cartridge contains 16 nozzles with a diameter of 21.5 μm and each nozzle generates 10 pl drops of ink. For all electrodes, we employed an aqueous dispersion of PEDOT:PSS (Clevios P Jet HC provided from H.C. Starck), made of sub-micrometer sized gel particles, which after solvent drying and thermal annealing, form a continuous and transparent conducting film. Before filling the cartridge, PEDOT:PSS-based ink has been sonicated for 15 min and then filtered with a 0.2 μm nylon filter to avoid nozzle clogging. During printing, substrates have been kept at a constant temperature of 60 °C to help fast solvent evaporation. Electrodes were fabricated superimposing 2, 3 or 4 printed layers, waiting for 60 s in printing two subsequent layers with a drop spacing of 20 μm in order to minimize ink spreading on the substrate. After printing, samples were annealed on a hot plate at 60 °C for 8 h. After annealing, EG was deposited on the structure by means of spin coating, then the devices were dried in an oven at 60 °C for 12 h. Between gate and source-drain electrodes, a 6 μL drop of aqueous PBS (Phosphate Buffered Saline) 0.01 M electrolytic solution (NaCl – 0.138 M; KCl – 0.0027 M provided by Sigma–Aldrich) was deposited only a few seconds before the electrical characterization was performed. The electrical measurements were carried out in air, at room temperature, using two Keithley 2600 SourceMeters controlled by Labview software.

3. Results and discussion

We have first carried out a complete characterization of printed PEDOT:PSS lines, in order to establish printing quality, electrical conductivity properties and optical transparency.

By printing PEDOT:PSS ink with a suitable choice of drop spacing, it is possible to obtain uniform layers formed by the superposition of several single drops (Fig. 1a and b) being the total thickness on one layer about 200 nm (Fig. 1c). With three printed layers (including the final post treatment with EG), more than 80% of radiation in the range between 400 and 800 nm is transmitted through the PEDOT:PSS layer (Fig. 2a), thus ensuring a high level of transparency of the final devices. This value is comparable with that of a spin-coated layer with a similar thickness according to the datasheet of the PEDOT:PSS compound. Transparency is useful for bio-sensing applications as it could allow to optically inspect devices with conventional optical transmission microscopy. As for the conductivity, our results show the typical resistive behavior [10] displayed by a conducting polymer as shown in Fig. 2b by a R vs. T curve.

After this initial characterization step, we proceeded with the fabrication of all-PEDOT:PSS OECTs. As mentioned, the printed structures have been treated with Ethylene Glycol (EG), after the printing process. A direct mixing of EG into the PEDOT:PSS ink has been attempted but it had a detrimental effect to the quality of the printed

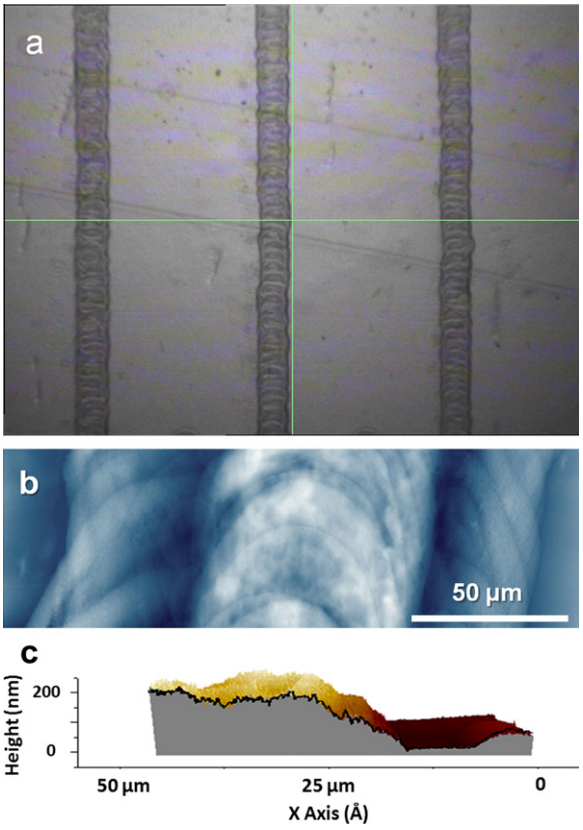

Fig. 1. (a) Optical image of PEDOT:PSS lines ink-jet printed on top of a PET substrate. (b) AFM image of a double layer of PEDOT:PSS printed on top of a PET substrate. (c) The profile of a single layer of PEDOT:PSS obtained with a drop spacing of 20 μm.

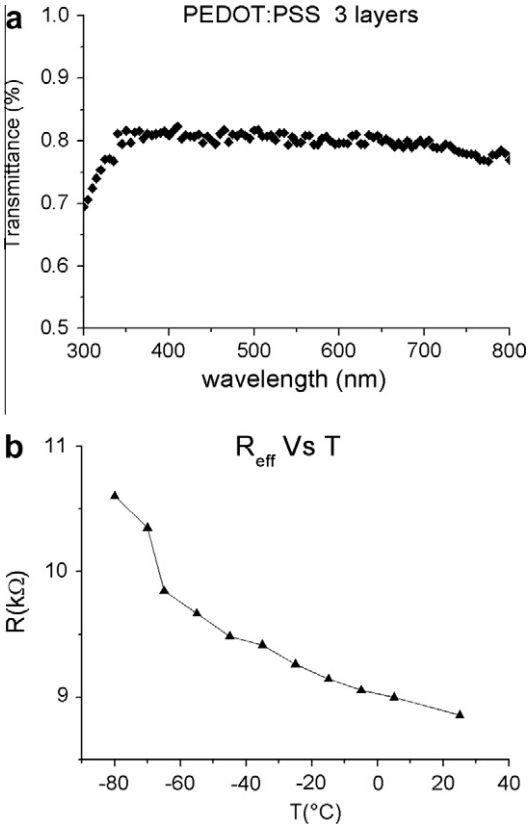

Fig. 2. (a) Transmittance of a triple layer of PEDOT:PSS printed on a PET substrate. The values are normalized with respect to PET. More or less 80% of the radiation is transmitted for all wavelengths in the visible range. (b) Resistance vs. temperature of a printed line with three layers.

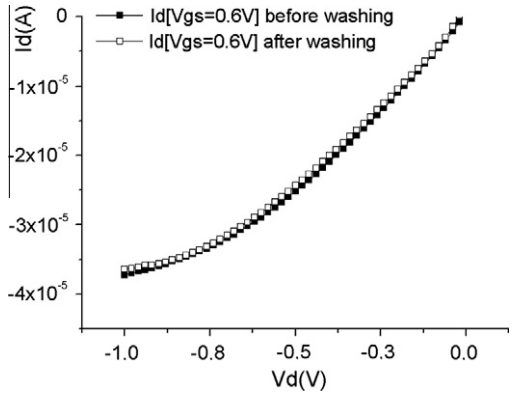

Fig. 3. The effect of washing on the behaviour of a device printed with PEDOT:PSS and then treated with Ethylene Glycol. It is clear that the current of the device is perfectly stable and no difference is appreciable between measurements before and after washing.

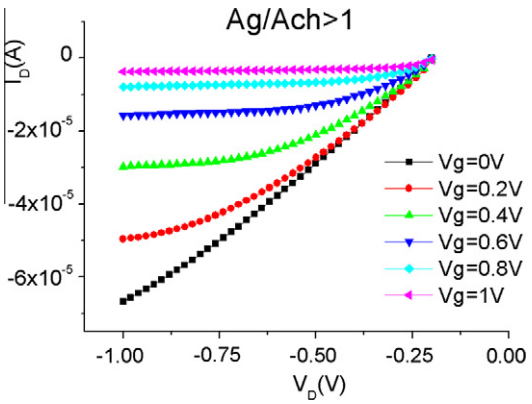

Fig. 4. I_d vs. V_d curves taken on a device with the gate area larger than the channel area.

layers. The treatment with EG is known to increase the conductivity of PEDOT:PSS [11] and also contributes to increasing the robustness of the printed devices. As a matter of fact, printed devices tend to delaminate from plastic substrates (as PET) or at least to severely degrade even after one operation. This does not occur for EG-treated devices as shown in Fig. 3 where it is evident that the current vs. drain voltage curve does not change at all before and after washing with deionized water, and drying under nitrogen flow.

Fig. 4 shows an output curve, i.e. I_d vs. V_d, measured in one of these devices. The current modulation due to the applied voltages is explained according to the usual operational model [4]: the drain current is due to hole drift in the PEDOT:PSS channel, induced by the drain voltage. When a positive gate voltage (V_g) is applied, cations from the electrolyte enter into the channel, de-dope it and reduce the drain current. After a certain value of V_g, called V_{off}, the channel current drops to zero (off-state) indicating a complete de-doping of the channel.

The effect of the device geometry may be observed in Fig. 5A that reports two measurements of I_d vs. V_g taken on the same asymmetric structure (see the top portion of the figure), by exchanging channel and gate. Currents are normalized with respect to the channel width. Basically, in the type 1 configuration (top left portion of Fig. 5A), the smallest structure is taken as the channel and the largest as the gate (therefore Ag/Ach > 1) while in the type 2 configuration (top right), the largest structure is taken as the channel and the smallest as the gate (therefore Ag/Ach < 1). It is clear that the transconductance (fitting lines in the bottom portion of Fig. 5A) is different in the two devices, showing that it is possible to tune the transistor characteristics (i.e. not only current by also the operative voltage range) by tuning device geometry. This feature is further confirmed in Fig. 5B, where the curves of three different devices with the same channel dimensions and different gate dimensions are shown. This feature is very useful in the design of biosensors, where the transconductance relates to sensitivity, as well as in the design of electronic circuitry. It should also be noted that the device may be operated also with negative value of V_g and the channel current continues to increase in this regime. This indicates that the application of negative V_g leads to further doping of the PEDOT:PSS in the channel. When a certain (negative) value of V_g is reached, the drain current saturates. This may be because on one hand, the channel reaches its maximum

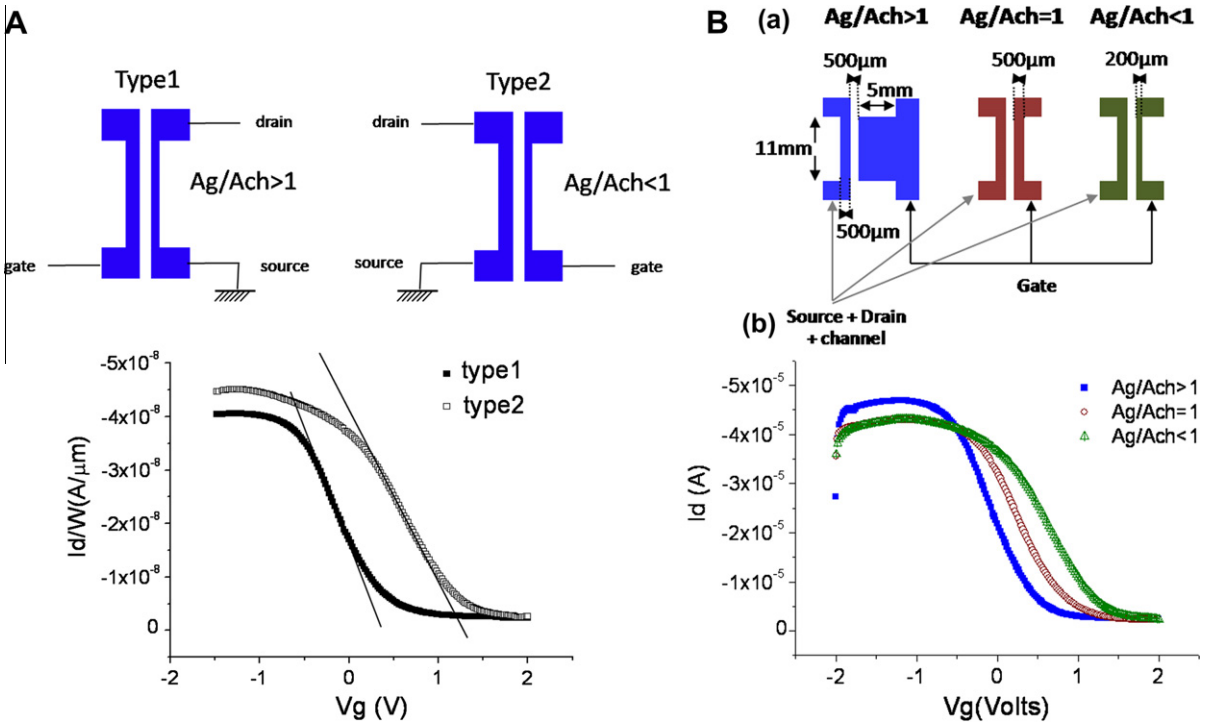

Fig. 5. (A) Schematic representation of the employed asymmetric geometry in which by exchanging the channel and the gate it is possible to modify the Ag/Ach ratio (top); I_d vs. V_g curves taken on the same device by exchanging the channel and the gate (bottom). The solid lines define the different transconductances exhibited in the two cases. The dimensions of gate width are 500 and 200 μm for type 1 and type 2 devices, respectively. (B) The effect of three different geometries on the transfer characteristic curve of the device. The channel dimension is always the same, while the gate dimension is changing.

doping limit and on the other hand, because the gate itself is dedoped and a fraction of the gate voltage is dropped across the gate electrode rather than being applied across the solution. The effect of saturation is more defined in type 1 devices. It is also noticeable that no permanent degradation is caused on the device by the cyclic application of this voltage range (see Fig. 6).

Previous studies showed that OECTs utilizing Pt gates (operated with positive gate voltages), showed a similar dependence of transfer characteristics on geometry, while OECTs utilizing Ag/AgCl gates did not [12]. This was attributed to the fact that the potential drop at the interface between a polarizable electrode like Pt and an electrolyte varies with the area of the electrode. In an OECT with a large gate and a small channel, the potential applied at the gate will drop mainly at the electrolyte/channel interface and result into efficient gating, hence a large transconductance. The opposite is true when the channel is larger than the gate. On the other hand, in OECTs with a gate electrode that is non-polarizable (such as Ag/AgCl), the potential applied at the gate always drops at the electrolyte/channel interface. Our results indicate that PEDOT:PSS is closer to the first limit, hence it exhibits characteristics similar to those of a polarizable electrode. However, it should be noted that ions are able to penetrate into electrode PEDOT:PSS film (after all, this is the basis of the OECT operation), hence an "effective" capacitance model is appropriate for the gate electrode/electrolyte interface, with a capacitance larger than that of a polarizable electrode [4].

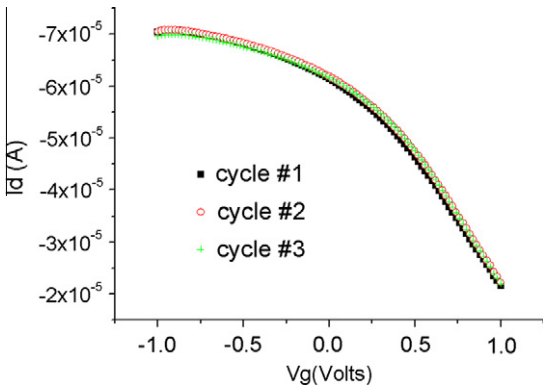

Fig. 6. Effect of multiple cycles of application of V_{gs}, also in the negative range. As it can be noticed, the curves are perfectly identical.

4. Conclusion

In conclusion, we demonstrated the possibility of using inkjet printing to fabricate all-PEDOT:PSS Organic Electro-Chemical Transistors, that are reproducible and robust enough for biosensors and low-cost circuitry. We also demonstrated that the working range of such devices can be controlled by varying the device geometry (i.e. the ratio between the gate and the channel areas) as in the case of structures with the gate acting as a polarizable electrode.

Acknowledgments

The authors acknowledge financial support by the European Commission, under the VII FP Project "Roboskin", Contract # 231500. PC acknowledges Regione Autonoma della Sardegna (RAS) for funding his research activity under the PO Sardegna FSE 2007–2013, L.R.7/2007, CRP Prot. No. 1399/207.

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