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Cite as: Appl. Phys. Lett. **99**, 163304 (2011); <https://doi.org/10.1063/1.3652912>

Submitted: 28 July 2011 . Accepted: 25 September 2011 . Published Online: 19 October 2011

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## High speed and high density organic electrochemical transistor arrays

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(Received 28 July 2011; accepted 25 September 2011; published online 19 October 2011)

A generic lithographic process is presented that allows the fabrication of high density organic electrochemical transistor arrays meant to interface with aqueous electrolytes. The channels of the transistors, which were  $6\ \mu\text{m}$  long, were made of the conducting polymer poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) and were in direct contact with phosphate buffered saline. Source and drain electrodes and interconnects were insulated by parylene C, a biocompatible material. The transistors operated at low voltages and showed a response time of the order of  $100\ \mu\text{s}$ . © 2011 American Institute of Physics. [doi:10.1063/1.3652912]

Interfacing transistors with aqueous electrolytes is of interest to the development of biosensors. Work on silicon-based ion-sensitive field-effect transistors, for example, has yielded biosensors for a variety of applications, ranging from the detection of metabolites like glucose to the monitoring of the activity of living cells.<sup>1</sup> In these devices, the gate dielectric (usually silicon oxide) separates and protects the silicon channel from the aqueous environment. A key advantage of transistors compared to other transducers lies in their miniaturization, which can yield high density arrays that enable the simultaneous detection of multiple analytes. Advances in the field of organic electronics are making available an alternative family of materials for field-effect transistors, based on conjugated small molecules and polymers.<sup>2</sup> The interfacing of these organic field-effect transistors (OFETs) with aqueous electrolytes is a rather recent endeavor. Examples include OFETs in which the organic semiconductor is separated from the electrolyte by an ultra-thin dielectric<sup>3</sup> (and which are, therefore, qualitatively similar to their silicon cousins mentioned above) as well as OFETs in which the organic semiconductor is in direct contact with water.<sup>4,5</sup> The latter are either gated through a bottom gate, separated from the organic semiconductor by a dielectric,<sup>4</sup> or gated through a metal electrode immersed in water, that is, deionized in order to minimize ion penetration in the organic and maintain a field-effect mechanism of operation.<sup>5</sup>

Organic electrochemical transistors (OECTs), developed in 1984 by White *et al.*,<sup>6</sup> provide an alternative to field-effect transistors. These devices utilize an electrolyte as an integral part of the device structure: In the usual configuration, they consist of a conducting polymer film (channel) brought in contact with an electrolyte. A gate electrode is immersed in the latter, while source and drain electrodes measure the current that flows through the channel (drain current,  $I_d$ ). The application of an appropriate bias at the gate (gate voltage,  $V_g$ ) causes ions from the electrolyte to enter the polymer film and dedope it, thereby decreasing the drain current.<sup>7</sup> As

such, OECTs act as ion-to-electron converters,<sup>8</sup> in which an ionic current in the electrolyte causes a change in the (electronic) drain current. Owing to the high conductivity of both the electrolyte and the channel, these devices operate at low voltages and are hence compatible with aqueous electrolytes, where voltages of the order of 1 V can cause electrolysis. OECTs have been used in biosensors, for the detection of ions<sup>9,10</sup> and metabolites such as glucose and lactate.<sup>11,12</sup> The vast majority of OECTs developed today are based on poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS), a commercially available polymer with high conductivity, which is also biocompatible. This latter fact enabled some very creative uses of these devices: Bolin *et al.*<sup>13</sup> cultured epithelial cells on the channel of a PEDOT:PSS OECT and was able to spatially control cell adhesion by adjusting the bias applied to the gate and the drain. Lin *et al.*<sup>14</sup> used an OECT as a sensor that monitors the attachment of cancer cells and fibroblasts, cultured directly on its PEDOT:PSS channel.

To take this work a step further, it is important to miniaturize OECTs and explore the impact of this process on their characteristics. An obvious target would be to reduce the channel of OECTs to cellular dimensions ( $1\text{--}10\ \mu\text{m}$ ), which would enable interfacing with single electrically active cells.<sup>15</sup> The fabrication of high-density array architectures is highly desirable in this case, as it increases the likelihood that, in a culture, a cell will be found directly on top of the channel of a transistor. These challenges have not been tackled to date and the limits of performance of OECTs have not been explored. Toward this goal, we developed a generic process for miniaturizing OECTs and developing high-density arrays using photolithography. As a proof-of-principle, arrays consisting of 64 OECTs with channels lengths of  $6\ \mu\text{m}$ , capable of responding to a gate pulse with a time constant of  $100\ \mu\text{s}$ , are demonstrated.

The overall architecture of the transistor array is shown in Figure 1(a), with a micrograph of a single OECT in Figure 1(b) and the fabrication process in Figure 1(c). The OECTs are arranged in a  $85\ \mu\text{m}$  center-to-center distance from each other, with each one of them having a PEDOT:PSS channel

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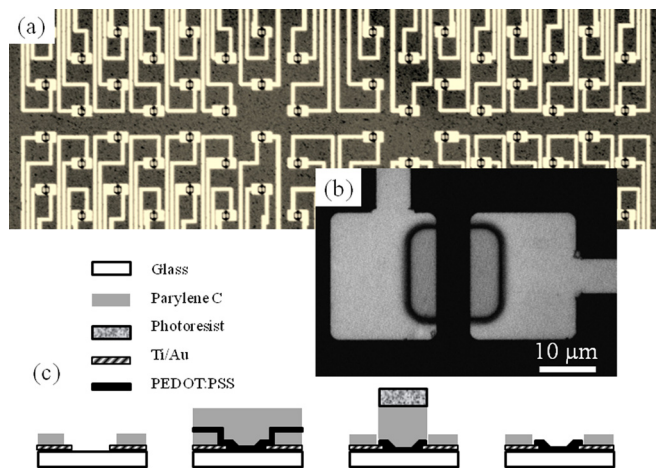


FIG. 1. (Color online) The overall architecture of the OEET array (a), a micrograph of a single OEET (b), and the fabrication process (c).

that is  $6\ \mu\text{m}$  long and  $15\ \mu\text{m}$  wide. Au was used to define source and drain electrodes and interconnects. The fabrication began with depositing an Au film anchored with Ti on a glass slide using a standard lift-off process. The sample was then coated with a  $2\ \mu\text{m}$  thick parylene C film, which ended up being the insulator layer. Parylene C is an obvious choice due to its good dielectric properties and its biocompatibility. The area where the PEDOT:PSS was deposited was defined using a second lithography step followed by dry etching. The PEDOT:PSS film was then spin coated from dispersion (PH-500 from H.C. Starck) and annealed at  $140\ ^\circ\text{C}$  for 60 min to yield a  $80\ \text{nm}$  thick film. To improve the conductivity of the resulting PEDOT:PSS films, 5 ml of ethylene glycol and  $50\ \mu\text{l}$  of dodecyl benzene sulfonic acid (DBSA) were added per 20 ml of PEDOT:PSS dispersion. Additionally, 0.25 g of the crosslinker 3-glycidoxypropyltrimethoxysilane was added to the above dispersion to prohibit PEDOT:PSS dissolution. The samples were then coated with a sacrificial parylene C film which protected the conducting polymer channel from the subsequent process steps. Final photolithography and etching steps defined the PEDOT:PSS regions on the sample. The fabrication ended with immersion in deionized water, which removed the sacrificial layer of parylene C film on top of the PEDOT:PSS patterned layer and subsequent thorough rinsing in deionized water.

Before testing, a reservoir made of polydimethylsiloxane (PDMS) was attached to the array and was used to contain phosphate buffered saline (PBS). The tip of a Pt wire with a diameter of  $250\ \mu\text{m}$  was immersed in the PBS and was used as a gate electrode. Out of 64 transistors fabricated on the same glass slide, 60 had a resistance value for the channel that varied less than 10% from the mean value, while the other 4 were open circuited due to incomplete Au lift-off. The mean channel resistance was  $670\ \Omega$ , corresponding to a conductivity of  $75\ \text{S/cm}$  for the PEDOT:PSS film. This value is four times lower than that specified by the manufacturer for PH-500 ( $\sim 300\ \text{S/cm}$ ), and we found the difference to arise mainly due to the addition of the crosslinker and due to the final washing step (presumably due to the removal of low molecular weight dopants).

Figure 2(a) shows the output characteristics of an OEET in the third quadrant, with negative bias at the drain ( $V_d$ ),

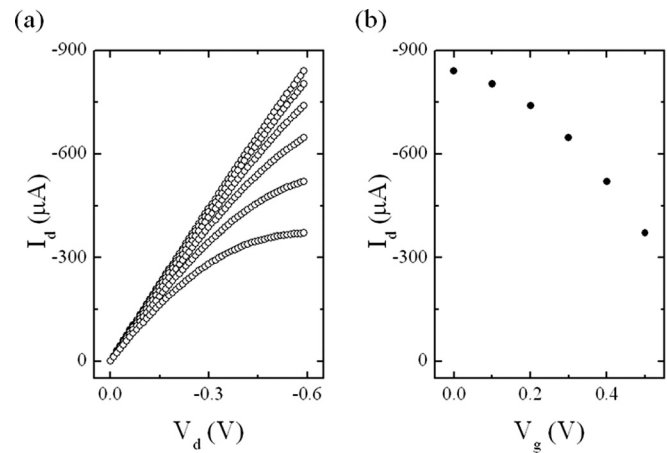


FIG. 2. Output characteristics for  $V_g$  varying from 0 V (top curve) to 0.5 V (bottom curve) (a) and transfer characteristics of an OEET for  $V_d = -0.5\ \text{V}$  (b).

and  $V_g$  varying from 0 V to 0.5 V. These characteristics show the typical low voltage operation which is the hallmark of OEETs, and are consistent with operation in the depletion regime, as described by Bernards and Malliaras.<sup>7</sup> The time delay between sourcing  $V_d$  and  $V_g$  and measuring  $I_d$  was 150 ms, which was found to be long enough for the drain current to reach steady-state. The gate current, also measured after the same delay, was 15 nA for  $V_d = -0.6\ \text{V}$  and  $V_g = 0.5\ \text{V}$ . The transfer characteristics are shown in Figure 2(b) for a drain voltage of  $-0.5\ \text{V}$ . PEDOT:PSS consists of a semiconducting polymer chain (PEDOT), which is degenerately doped *p*-type, with the anions on the PSS playing the role of acceptors. When a positive bias is applied on the gate, cations from the electrolyte enter the PEDOT:PSS film, compensate the anions on the PSS, and decrease hole density on the PEDOT, which is reflected in the decrease of the drain current seen in Figure 2(b). This process is analogous to compensation doping in traditional semiconductors, e.g., when an *n*-type dopant is implanted in *p*-type silicon. It should be noted that more efficient gating (a more significant reduction of the drain current for the same value of gate voltage) can be obtained by using a larger Pt electrode,<sup>16</sup> but the increased capacitance of the gate can degrade the time response of the transistor. Alternatively, a Ag/AgCl gate electrode can be used to yield more efficient gating, at the cost of a larger gate current.<sup>16</sup>

OEETs integrate the ionic current in the electrolyte: The change in the drain current reflects the total number of ions from the electrolyte that were “implanted” in the channel. The higher the ionic flux in the electrolyte, the faster the drain current will reach its steady-state. As such, their response time depends on the gate current.<sup>7</sup> In organic transistor literature, however, transistor speed is quantified by measuring response to a gate bias pulse. Accordingly, Figure 3 shows the time response of the drain current of an OEET to a 0.4 V pulse applied at the gate. The bias at the drain was  $-0.5\ \text{V}$ . The OEET was connected in series with a  $100\ \Omega$  resistor, and the voltage drop across the latter (from which the drain current was calculated) was measured with an oscilloscope. The line is a fit to an exponential decay with a time constant of  $101\ \mu\text{s}$ . This is the fastest response recorded in an

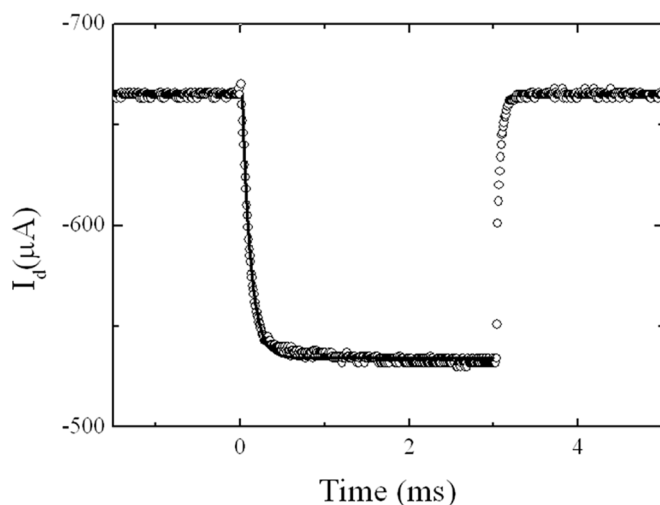


FIG. 3. Temporal response of the drain current of an OEECT to a 0.4 V pulse applied at the gate ( $V_d = -0.5$  V). The line is a fit to a single exponential decay with  $\tau = 101 \pm 1$   $\mu$ s.

OEECT, and it is a consequence of miniaturization of the OEECT channel. It is fast enough to allow accurate recording of action potentials from neurons, which have a duration in the millisecond range.<sup>15</sup> It should be mentioned that when the values of drain and gate voltage were corrected for the presence of the series resistor, the values of drain current recorded during the transient experiment correspond well to the steady-state output characteristics of Figure 2(a), therefore the transistor reaches steady-state within the duration of the gate pulse.

In conclusion, we presented a lithographic process that allows the fabrication of high density organic electrochemical transistor arrays. The transistors were based on PEDOT:PSS, had a channel length of 6  $\mu$ m, and used an aqueous electrolyte as integral part of their structure. Source and drain contacts and interconnects were insulated from the solution with the biocompatible material parylene C, making

the arrays suitable for integration with living cells. Together with a low operating voltage and a response time of 100  $\mu$ s, these features make OEECTs excellent candidates for interfacing with single electrically active cells as well as for a variety of biosensing applications.

This work was supported by the ANR through the project MUSIC, and by a Marie CURIE Fellowship. The authors acknowledge funding from the Partner University Fund (a program of French American Cultural Exchange). We would like to thank Cyril Calmes and Thierry Camilloni for technical support during fabrication.

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