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## Vertical polyelectrolyte-gated organic field-effect transistors

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Short-channel, vertically structured organic transistors with a polyelectrolyte as gate insulator are demonstrated. The devices are fabricated using low-resolution, self-aligned, and mask-free photolithography. Owing to the use of a polyelectrolyte, our vertical electrolyte-gated organic field-effect transistors (VEGOFETs), with channel lengths of 2.2 and 0.7  $\mu\text{m}$ , operate at voltages below one volt. The VEGOFETs show clear saturation and switch on and off in 200  $\mu\text{s}$ . A vertical geometry to achieve short-transistor channels and the use of an electrolyte makes these transistors promising candidates for printed logics and drivers with low operating voltage. © 2010 American Institute of Physics. [doi:10.1063/1.3488000]

Organic thin-film transistors, which promise low-cost and solution-processed circuits for printed electronics, have attracted much attention in recent years. Due to the low mobility of organic semiconductors, in comparison to their inorganic counterparts, it is important to reduce the transistor channel length in order to achieve a high cutoff frequency and high currents, which are crucial in applications such as signal processing and addressing. Many fabrication techniques have been explored to achieve organic transistors with short channels, for example, self-aligned inkjet printing,<sup>1</sup> selective laser sintering,<sup>2</sup> hot embossing,<sup>3</sup> UV-nanoimprinting,<sup>4</sup> electron-beam lithography,<sup>5</sup> and underetching.<sup>6</sup> However, the processing complexity of high-resolution manufacturing equipment typically prevents large-area and high-volume production. One possible option to achieve small channel dimensions is to stack metal/insulator/metal layers to define the source-channel-drain configuration in a vertical manner.<sup>7,8</sup> In such a configuration, the channel length is tuned by simply varying the insulator layer thickness. The source-channel-drain materials stack can easily be printed, and the vertical edge, defining the transistor channel, can be provided in reel-to-reel production by use of, e.g., laser ablation or liftoff.<sup>9</sup>

Another important requirement for printed electronics is to lower the transistor operating voltage to a range that facilitates operation using printed batteries or electromagnetic induction. Transistor gating via ultrathin organic dielectric has been explored to reach driving voltages on the order of 1 V.<sup>10,11</sup> Recently, electrolyte-gated organic field-effect transistors (EGOFETs) (Ref. 12) have also been used to achieve operation at voltages of around 1 V.<sup>13–20</sup> The former approach is typically not compatible with printing techniques while electrolyte-gated devices have been manufactured using different reel-to-reel (compatible) printing techniques.<sup>15,21</sup> In EGOFTs, low-voltage operation is possible thanks to the high capacitance in the thin electric double layers (EDLs) at the gate-electrolyte and electrolyte-semiconductor interfaces, which are formed independently of

the electrolyte thickness, thus enabling printed transistors with a thick electrolyte layer.

In this work, we demonstrate that a short channel can be combined with low-voltage operation in a device that is manufacturable using printing or other reel-to-reel methods. To achieve this, we employ a polyelectrolyte in a vertical channel transistor configuration. The resulting vertical EGOFT (VEGOFET) has a (sub)micrometer vertical channel, operates below 1 V and shows clear saturation in the output characteristics.

The VEGOFETs were produced according to the following procedure [Figs. 1(a) and 1(c)]. First, a 90 nm thick Au/Cr layer was thermally evaporated through a shadow mask in vacuum to form the source bottom electrode on a Si/SiO<sub>2</sub> wafer. After spin-coating a positive photoresist layer, another 40 nm thick Au/Cr layer was evaporated

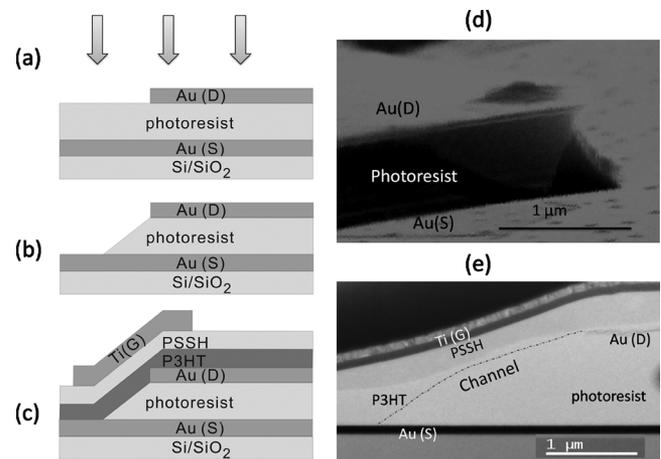


FIG. 1. Sketches of the manufacturing steps for the VEGOFET; (a) the top electrode is used as a mask for the lithography to self-align the drain and source. (b) Vertical source-drain electrodes obtained after developing and rinsing. (c) The final structure after deposition of semiconductor, polyelectrolyte, and gate. (d) Cross-sectional SEM image with vertical drain/insulator/source structure confirms the channel length of group (i) to be 0.7  $\mu\text{m}$ . (e) TEM image of the full structure of transistor group (ii). The interface between photoresist and P3HT was identified by high angle annular dark field scanning TEM, as indicated by dashed lines, showing a 2.2  $\mu\text{m}$  channel length.

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through a shadow mask to define the drain top electrode. The photoresist was then exposed to UV light, using the top Au layer as the mask, developed, and then rinsed to achieve the vertical source-insulator-drain electrode structure, see Fig. 1(b). The exposure time and developing time were both carefully chosen in order to form the desired slope of photoresist. Global layers of 80 nm thick regioregular poly(3hexylthiophene) (P3HT) and 280 nm thick polyelectrolyte poly(styrenesulfonic acid) (PSSH) films were sequentially spin coated onto the device. Finally, a titanium gate electrode was thermally evaporated in vacuum through a shadow mask to finalize the transistor structure. A cross section of the resulting structure is shown in Fig. 1(c). Except for the vacuum processes, all manufacturing of the VEGOFETs was done in ambient atmosphere and at room temperature.

Transistors with two different channel lengths were manufactured by using two different photoresists as follows: Shipley 1805 for group (i) and Shipley 1813 for group (ii). The different slope and thickness of the photoresists resulted in transistors with different channel lengths. The cross-sectional architecture was imaged using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), see Figs. 1(d) and 1(e). From SEM and TEM images, we found resulting channel lengths of 0.7  $\mu\text{m}$  [group (i)] and 2.2  $\mu\text{m}$  [group (ii)], respectively.

The electrical characterization was performed in ambient atmosphere using a Keithley 4200-SCS parameter analyzer. As evident from the output characteristics shown in Fig. 2(b), the transistor with 2.2  $\mu\text{m}$  channel length shows typical transistor behavior with pronounced saturation. The saturation is less distinct for the 0.7  $\mu\text{m}$  channel length device, see Fig. 2(a), suggesting channel length modulation.<sup>22</sup> Interestingly, the pinch-off effect is still relatively much stronger for our 0.7  $\mu\text{m}$  channel VEGOFET compared to vertical P3HT OFETs with 0.9  $\mu\text{m}$  channel length gated via an organic dielectric insulator.<sup>8</sup> The electrical double-layer capacitance of the proton-conductive electrolyte PSSH has previously been measured<sup>13</sup> and is found to be 20  $\mu\text{F}/\text{cm}^2$ . By plotting the square root of the drain current ( $I_D^{1/2}$ ) versus gate voltage ( $V_G$ ), the mobility is estimated to be 0.003  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  and the threshold voltage ( $V_T$ ) is  $-0.08 \text{ V}$ .

When considering short-channel transistors, a major issue is the absence of saturation in the output characteristics, the so-called short-channel effect. To prevent this, the transversal electric field  $E_T$  has to be much larger than the longitudinal electric field  $E_L$  induced by drain-source potential.<sup>22,23</sup> In our 0.7  $\mu\text{m}$  transistor,  $E_L$  can be estimated to 1 V/0.7  $\mu\text{m}$ =1.4 MV/m. The transversal electric field is independent of the thickness of the insulator since the relevant distance that determines the electric field is the separation distance between the planes of ions in the electrolyte and the countercharges planes. To quantify  $E_T$ , we model the electrolyte as two capacitors connected in series.<sup>24</sup> Capacitance I corresponds to the Helmholtz EDL formed at the gate metal–electrolyte interface while capacitance II is associated with the EDL at the electrolyte–semiconductor interface. We assume a small separation between electrolyte protons and the metal surface in capacitance I, on the order of a few angstroms; and an approximately ten times larger separation between the polyanions and the charged semiconductor

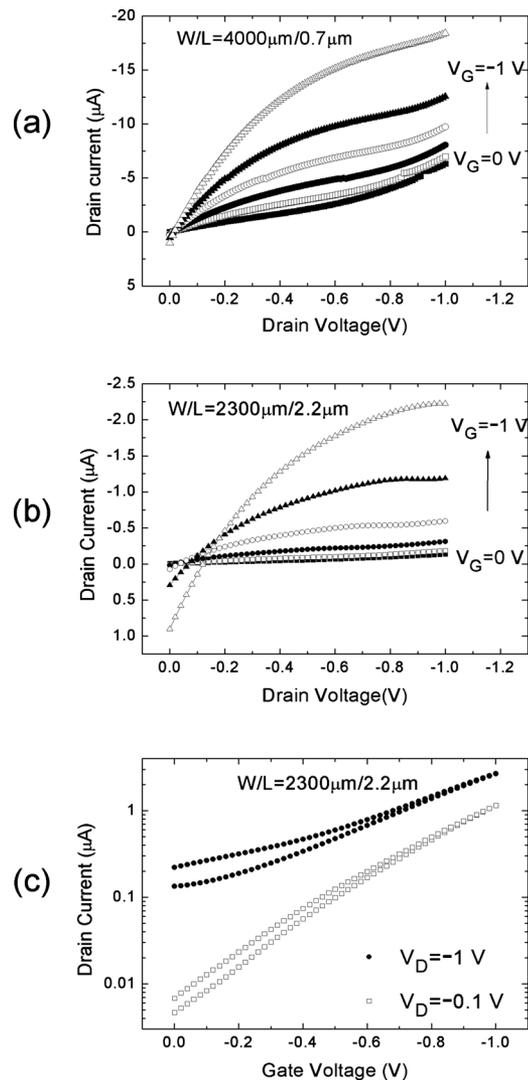


FIG. 2. Electrical characterization of VEGOFETs. (a) Output characteristics of devices with 0.7  $\mu\text{m}$  channel length, (b) output, and (c) transfer characteristics of devices with 2.2  $\mu\text{m}$  channel length.

channel (on the order of 2 nm). Assuming similar permittivity in the two EDLs,  $E_T$  can be calculated by  $E_T = (V_G - V_T)/d$ , where  $d$  is the accumulated thickness of two EDLs. For  $V_G = 1 \text{ V}$ ,  $E_T$  is estimated to be 450 MV/m, which is about 300 times larger than  $E_L$ . Note that despite the saturation character, a space-charge limited current (SCLC) flowing through the bulk of the semiconductor<sup>22</sup> is observed and visible as the superlinear shape of the output curves at high drain voltages ( $V_D$ ). This behavior is less pronounced for the longer channel transistor, seen in Fig. 2(b).

The transfer characteristics of the VEGOFET with 2.2  $\mu\text{m}$  channel length [Fig. 2(c)], indicate an on/off ratio of around 500 at  $V_D = -0.1 \text{ V}$  and 22 at  $V_D = -1 \text{ V}$ . The low on/off ratio is due to the high off-state current which we attribute to SCLC through the bulk of the semiconductor, and possibly also oxygen doping of P3HT (Ref. 25) and residual water electrolysis between drain and gate.<sup>26</sup> To improve the on/off ratio, semiconductor thickness has to be minimized and inert atmosphere is required during device fabrication and characterization. Replacing the electrolyte protons with other cations is also thought to result in lower off-currents.<sup>26</sup>

Transient response characteristics were measured for the 2.2  $\mu\text{m}$  channel length VEGOFET by applying a 100 Hz

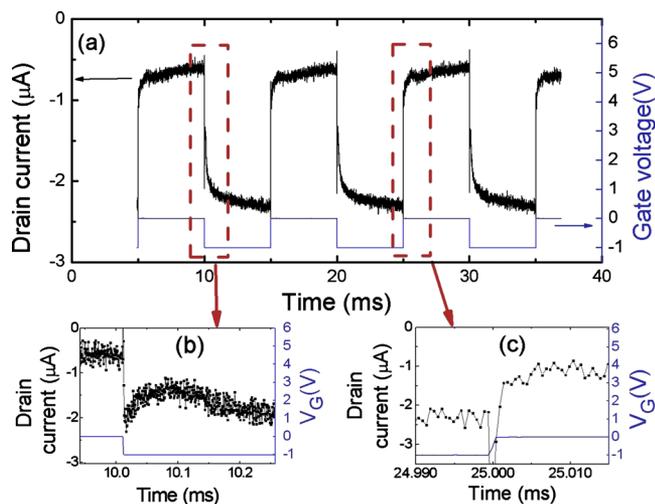


FIG. 3. (Color online) (a) Transient characteristics of VEGOFET with  $2.2\ \mu\text{m}$  channel length. (b) and (c) indicates the turn on and turn off response times to be  $200\ \mu\text{s}$  and  $5\ \mu\text{s}$ , respectively.

square-shaped (0 to  $-1\ \text{V}$ ) voltage pulse to the gate electrode while recording the effective drain current, at  $V_D = -1\ \text{V}$ , as can be seen in Fig. 3(a). Details of this measurement setup and procedure can be found in a previous publication.<sup>16</sup> Representative values for the 90% rise and fall time were  $200\ \mu\text{s}$  and  $5\ \mu\text{s}$ , respectively [see Figs. 3(b) and 3(c)], with the  $5\ \mu\text{s}$  off switch time being the fastest reported value for this class of transistors. The switching speed is significantly improved compared to other EGOFETs (Refs. 13, 15, and 27) with longer channels, and is comparable to EGOFETs having a  $200\ \text{nm}$  short channel.<sup>16</sup> Generally, the response time of EGOFETs is limited by semiconductor mobility or electrolyte polarization.<sup>24</sup> The latter plays a dominant role in short-channel EGOFETs (typically when  $L < 9\ \mu\text{m}$ ), since the ion relaxation time in the polyelectrolyte is longer than the hole transit time through the channel. Thus an electrolyte with increased ion conductivity is needed to further improve the transistor response. Note that the ionic conductivity is found to decrease exponentially with temperature,<sup>28</sup> thus a slower transistor response is expected at low temperature operation.

In summary, a vertical channel electrolyte-gated OFET is reported. (Sub)micrometer channel lengths were achieved using a photoresist manufacturing process excluding lithographic masks. A polyelectrolyte acid is used as gate insulator to promote large capacitance in the transistor, as well as high transversal electric fields to suppress short-channel effects. The combination of the vertical transistor configuration and the polyelectrolyte gating results in the VEGOFET, a transistor that runs at low voltages ( $< 1\ \text{V}$ ), switches on and off in  $200\ \mu\text{s}$ , and exhibits clear pinch-off behavior for channel lengths longer than  $2\ \mu\text{m}$ . We believe that by optimizing the device layout and the materials, the VEGOFET performance can be further improved, particularly in terms of off-currents. Importantly, the fact that neither ultrathin organic layers, nor submicrometer lateral patterning is needed

means that this architecture is a candidate for fully reel-to-reel manufacturable organic short-channel transistors.

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