Modified poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) source/drain electrodes for fully printed organic field-effect transistors consisting of a semiconductor blend


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Modified poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) source/drain electrodes for fully printed organic field-effect transistors consisting of a semiconductor blend


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The performance of organic field-effect transistors (OFETs) can be changed and improved considerably by special treatments of the source/drain electrodes. Treatment methods are either the implementation of self-assembled monolayers (SAMs), post-treatment with specific solvents, or usage of plasma with the main goal to minimize the energy barriers between the electrodes and the organic semiconductor for an efficient charge injection and extraction. Most of the research groups working on the development of OFETs use metals. These electrodes are very insensitive against organic solvents or highly energetic fields of plasma with the main goal to minimize the energy barriers between the electrodes and the organic semiconductor for an efficient charge injection and extraction. Most of the research groups working on the development of OFETs use metals. These electrodes are very insensitive against organic solvents or highly energetic fields of plasma. When using organic materials, like poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) or polyaniline, which can be used as cheap and printable alternatives for all electrodes, these conventional surface treatment techniques using SAMs or plasma are not applicable.

Nevertheless, there are possibilities to change the surface properties of conductive polymers for performance increase and other purposes (e.g., stability issues) as well. However, the mechanism behind the change is quite different. PEDOT:PSS can be used in very different compositions and formulations with PEDOT to PSS ratios depending on the application. Furthermore, the PEDOT to PSS ratio at the surface can significantly vary as a result of the manufacturing technologies, e.g., drying and humidity conditions, leading to large variations of the conductivity and the work function of the material. Thus, PEDOT:PSS can be used for manifold applications, e.g., as hole injection or hole extraction layer in organic light emitting diodes (OLEDs) or solar cells, respectively. While most publications describe the modification of PEDOT:PSS formulations, e.g., by adding secondary dopants to the dispersion itself, only a few groups show results of post-processing treatments.

Kim et al. describe the modification of PEDOT:PSS used as indium tin oxide (ITO) substituent in solar cells by means of treatment with ethylene glycol or dimethyl sulfoxide to increase conductivity. Wang et al. used ethanol or methanol to change the work function of PEDOT:PSS as hole injection layer in OLEDs.

In this paper, we present the post-press treatment of printed PEDOT:PSS source/drain electrodes with ethylene glycol and demonstrate the positive effects of this modification on the performance of fully printed organic field effect transistors based on a new semiconductor blend consisting of the small molecule 6,13-bis(cyclopropyldiisopropylsilyl)ethynyl) pentacene and poly(triarylamine) (PTAA). Semiconductor blends are an interesting alternative to pure crystalline materials, because of their simpler processability while keeping field effect mobility high.

As a basis for all experiments, source/drain electrodes made with “Cyflex” technology were used on flexible PET foil. The channel length was ~20 µm. This technology is a combination of flexography and gravure printing, which makes use of self alignment processes of liquids on surfaces with heterogeneous surface energy, described elsewhere. The prestructuring layer was made of CYTOP (Asahi Glass) and a special PEDOT:PSS formulation on basis of Clevios P (PEDOT:PSS-ratio 1:2.5, Heraeus) was used for the electrodes. After printing, the structures were dried in-line at 130 °C for 20 s.

Before applying the semiconductor, post-press treatment was carried out. Source/drain electrodes were covered with ethylene glycol for 2 min. Afterwards, the remaining solution was removed through spin-coating at a spin speed of 3000 rpm and dried for 2 min at 110 °C in a conventional oven. For comparison, samples without ethylene glycol treatment were further processed as well. To increase wetting properties of the Cyflex-structures, CYTOP was wiped off using perfluorodecalin as well-working CYTOP solvent.
Subsequently, the semiconductor was applied by means of gravure printing. As semiconductor, a blend consisting of CP-DIPS (3M) and PTAA (FS0025, Flexink) was chosen. Both materials were solved in a mixture of toluene and 1,2,3,4-tetrahydronaphthalene to achieve good wetting behavior and good film forming properties. Screen printing was used for the realization of a ~2 μm thick dielectric layer made of the low-k material CYTOP. Finally, gate electrodes including contact pads to source and drain were flexo printed with a copper particle ink (Eckart), defining a channel width of 30 mm. All process steps were performed under ambient laboratory conditions in air. For a better overview, the whole setup is depicted in Fig. 1, including a photograph of printed devices.

For determining the PSS to PEDOT ratio and work function before and after the post-process treatment, XPS and UPS analysis were performed. For details of the experimental and measurement methods, see the supplemental online material.

To analyze the effect of ethylene glycol treatment on the geometry and conductivity of source/drain electrodes, thickness and cross-sectional area as well as the resistivity of the electrodes were measured with a profilometer (Veeco Dektak 8) and two-point measurements (Keithley 2612, 6 mm distance between pins) directly on top of the source and drain fingers, respectively. The cross-sectional area was measured to be (14.7 ± 1.7) μm² and (11.7 ± 1.4) μm² before and after treatment (Fig. 2(a)). Since the lateral dimensions—length and width of the source/drain electrodes—remained constant because of the prestructuring layer, made of hydrophobic CYTOP located around these structures, the treatment led to a real reduction of the PEDOT:PSS volume. This observation can be explained by two main reasons: (i) the removal of material because of the manufacturing process and (ii) a morphological change, described in the following.

In accordance with Kim et al., the conductivity of ethylene glycol treated source/drain electrodes increased from 75 S/cm to 172 S/cm. The reason for this result can be found in the reduction of the PSS amount at the surface, which was confirmed by XPS analysis, and an improved alignment of the PEDOT chains in the PEDOT:PSS film. Fig. 2(b) clearly shows the difference of the sulphur XPS features, assigned according to Crispin et al. While the signal peak for PSS remains nearly constant, the signal peak for PEDOT increases for the treated sample. When comparing the area values, a PSS to PEDOT surface ratio of 3.8:1 and 3.0:1 without and with treatment can be calculated, respectively.

Besides good conductivity, which is necessary to lower the series resistance of source/drain contacts, it is even more important to have good interaction of electrodes and semiconductor in OFETs. Therefore, the work function of the PEDOT:PSS electrodes was analyzed by UPS (Fig. 2(c)). For samples with and without ethylene glycol treatment, a work function of (5.39 ± 0.10) eV and (5.65 ± 0.15) eV was measured, respectively. The difference could be explained by the change of the PEDOT to PSS ratio at the surface, but the values are relatively high compared to literature. A reason for that might be the influence of the drying procedure, which is completely different for a very fast roll-to-roll process in contrast to a conventional oven or hot plate. While powerful roll-to-roll drying systems need seconds only to

![FIG. 1. (a) 3D model of top gate OFET setup and (b) photograph of fully printed OFETs.](image)

![FIG. 2. Analysis of printed PEDOT:PSS source/drain electrodes. (a) Profile scan, (b) XPS S (2p) spectra, and (c) UPS measurements on ethylene glycol treated and untreated samples. Vertical bars mark the secondary electron cutoff positions.](image)
dry water-based inks like the PEDOT:PSS formulation used here with the support of strong air blow, it takes minutes for conventional systems without strong air circulation at the same temperature level. Additionally, considerable differences occur when drying in vacuo or in air. Assuming a highest occupied molecular orbital (HOMO) level of 5.1 eV for the semiconductor PTAA, which preferably creates the contact to the PEDOT:PSS electrodes due to phase separation of the blend, good hole injection can be expected for source electrodes with and without treatment. In contrast, hole extraction into the drain contact is expected to be improved for treated PEDOT:PSS electrodes due to the lower work function.

15 transistors per sample were electrically characterized by sweeping the gate voltage \( V_{gs} \) from + 60 to −60 V with a constant source/drain voltage of \( V_{ds} = −10 \) V and −60 V (transfer curve) and by sweeping the source/drain voltage \( V_{ds} \) from 0 to −60 V for different constant gate voltages \( V_{gs} \) from 0 to −60 V (output curve) under ambient conditions. The mobility in linear and saturation regimes was determined from the slope of the transfer curve by means of a standard procedure. Fig. 3 shows typical output and transfer curves of fully printed OFETs with and without ethylene glycol treatment. Both types are working well in linear and saturation regimes, indicating good hole injection and extraction from the PEDOT:PSS electrodes into the semiconductor blend and back. With a mean mobility of 0.2 cm²/Vs devices with ethylene glycol treatment achieve one of the highest field effect mobilities for fully mass printed devices reported so far. Former publications using mass printing technologies only achieved mobilities, which were at least one order of magnitude below the values of this work. A summary of the most important values and their standard deviation is given in Table I. These results indicate relatively small device to device deviations due to using a semiconductor blend instead of a purely crystalline small molecule, which is extremely difficult to manufacture by means of solution based processes and especially fast mass printing technologies. Furthermore, it shows the good process stability of all other printing steps, despite using different mass printing technologies and manual handling of the samples between the printing steps. Besides these superior results, our OFETs offer an on/off-current ratio between approximately 250 and 300, which is a typical value for fully printed devices on the basis of PEDOT:PSS source/drain electrodes, but lower in comparison to OFETs with a similar semiconductor blend realized on the basis of gold electrodes and made with the help of non-printing techniques, like lithography and spincoating. We attribute this difference to the relatively thick dielectric layer of ~2 μm, leading to a short channel effect, and the execution of all process steps in air, both resulting in an increased off-current.

Hence, when comparing samples with and without treatment, it becomes obvious that OFETs with treatment outperform their counterparts. This can be attributed to measured differences in conductivity and work function of the PEDOT:PSS source/drain electrodes.

On the basis of OFETs with ethylene glycol treatment, diode type inverters and 7-stage ring oscillators were realized (Fig. 4). Therefore, the channel width of the drive OFET was increased to 45 000 μm whereas the channel length of the load OFET was 5400 μm. Although inverters show relatively small voltage swing of ~25 V at a supply voltage of \( V_{DD} = −60 \) V, which is a well-known problem for unipolar inverters, stable oscillation of the ring oscillators could be demonstrated with a frequency of 1.0 kHz and 1.7 kHz at a supply voltage of \( V_{DD} = −60 \) V and −80 V, respectively. This is an approximately fifty-fold higher value in comparison to our former results for fully mass printed OFETs owing to the strongly improved mobility of the semiconductor. Ring oscillators were still working down to a supply voltage of \( V_{DD} = −48 \) V. For further improvement of the frequency and reduction of the supply voltage, the challenging tasks of reducing the gate overlap and increasing the gate capacitance while keeping the high mobility of the semiconductor have to be addressed in continuative studies.

![Image](https://example.com/image.png)

**FIG. 3.** OFET characteristics: (a) Output curves \((V_{gs} = −20, −40, \text{and } −60 \) V) and (b) transfer curve \((V_{ds} = −60 \) V) of OFETs with and without ethylene glycol treatment of PEDOT:PSS source/drain electrodes.

![Image](https://example.com/image.png)

![Image](https://example.com/image.png)

**TABLE I.** Electrical parameters of fully mass printed OFETs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>( \mu_{lin} ) (cm²/Vs)</th>
<th>( \mu_{sat} ) (cm²/Vs)</th>
<th>( V_{th} ) (V)</th>
<th>( I_{on}/I_{off} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Yes</td>
<td>0.20 ± 0.03</td>
<td>0.21 ± 0.02</td>
<td>−13.1 ± 1.7</td>
<td>268 ± 124</td>
</tr>
<tr>
<td>2</td>
<td>No</td>
<td>0.14 ± 0.01</td>
<td>0.15 ± 0.02</td>
<td>−13.8 ± 0.7</td>
<td>289 ± 39</td>
</tr>
</tbody>
</table>

\(^{a}\)At \( V_{ds} = −60 \) V.
In conclusion, we reported on the development of fully mass printed OFETs and ring oscillator with strongly improved performance. A field effect mobility of 0.2 cm²/Vs could be achieved by the introduction of an additional treatment step for our printed PEDOT:PSS source/drain electrodes with ethylene glycol, leading to increased conductivity and reduced work function. Furthermore, a new small molecule-amorphous polymer blend was used. Printed ring oscillators with an oscillation frequency of more than 1 kHz were demonstrated. All manufacturing steps are roll-to-roll compatible, which is essential for continuous and highly efficient production in the future.

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14See supplementary material at http://dx.doi.org/10.1063/1.4819394 for detailed information about the experiments.