Blending of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) with poly(ethyleneimine) as an active layer in depletion-mode organic thin film transistors

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The conjugated polymer poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS) is usually applied in fabricating electrodes of devices. In this work, the applications to organic thin film transistor with the introduction of poly(ethyleneimine) (PEI) into the PEDOT-PSS are investigated. The conductivity of PEDOT-PSS can be reduced by incorporating PEI into PEDOT-PSS, which can be applied as an active layer instead of electrodes for devices application. Based on the PEDOT-PSS blended with PEI, the fabricated devices possess a depletion-mode transistor behavior with the on/off ratio of about $10^3$ is used. Meanwhile, the role of PEI in PEDOT-PSS to modulate the channel conductivity is discussed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2824381]

With its high potential in terms of flexibility, easy process, and low cost, conjugated polymer has been developed for organic thin film transistor (OTFT) applications. Doped poly(3,4-ethylenedioxythiophene) (PEDOT) displays conductivities ranging from 1 to 100 S/cm depending on the counter ions. With poly(styrene sulfonic acid) (PSS) as the counter ion, the conductivity is typically 10 S/cm. PEDOT-PSS are heavily exploited as charge injection layers, optically transparent electrodes in polymer light-emitting diodes, as well as conducting elements in organic transistors. However, no other reports can be found for the modulation of conductivity as transistor active layers.

The possibility of realizing transistors based on the electrochemical switching of organic materials has been demonstrated by several researchers. Compared to their study’s results, we demonstrate an organic field effect transistor based on PEDOT-PSS as an active layer by incorporating poly(ethyleneimine) (PEI) to modulate the conductivity for field-effect transistor applications. Unlike other groups which employed PEDOT-PSS in the active layer, the blending of PEDOT-PSS with PEI as an active layer in the OTFT can be implemented with the depletion mode transistor behavior. This opens an alternative for device applications.

Figure 1 shows the schematic diagram of the proposed OTFT on a Si (100) substrate based on PEDOT-PSS with PEI. First, the active layer materials were prepared by mixing PEI in PEDOT-PSS (high conductivity, solid concentration=1.34%, Alfa Chemicals) in a 1:1 ratio. The conductivities of the active materials without PEI are about 20 S/cm and that with PEI are about $10^{-4}$ S/cm.

Figure 2 illustrates the current-voltage (I-V) characteristics of OTFT measured by a semiconductor parameter analyzer HP4156B under the atmosphere at room temperature. Under $V_{gs}=0$ V, the drain current ($I_{ds}$) rises with the drain voltage ($V_{ds}$) and shows a large current because the active layer made of high doping of PSS in PEDOT leads to a high conducting state. The observation of the field effect in conducting materials is an entirely unusual phenomenon due to the large density of charge carriers in the conductors. The electric field should have been screened on the atomic scale and should not have penetrated the sample at all. For the conducting polymer, the charge concentration could be up to $\sim 10^{20}$ cm$^{-3}$ and the Debye length could be a few nanometers. When a positive voltage is applied to the gate, the currents of the source and drain are decreased. The decreased current for PEDOT-PSS-PEI OTFT is related to the tendency of $SO_3^{-}$ groups of PSS linking with $NH_3^{+}$ of PEI at the applied positive gate voltage as shown in Fig. 3(a). When a positive bias is applied to the gate and induces the electric field in the channel, the linked matters (PEI and PSS) are removed from the PEDOT [Fig. 3(b)] and possess low conductivity. This is because the charge carriers have been localized in the sulfur atoms. Therefore, the source-drain current of PEDOT-PSS-PEI-based OTFT is lower than that based on the doped PEDOT under the same source-drain voltage. The stronger the electric fields applied, the more PSS were removed. In other words, applying larger voltages...
to the gate lowers the presence of source-drain currents. At last, the source-drain currents decreased to $10^{-7}$–$10^{-8}$ A under $V_{gs}=100$ V (i.e., the OTFTs based on PEDOT-PSS with PEI operating as depletion-mode transistors), as shown in Fig. 2. The on/off ratios are about $10^3$ under the $V_{gs}$ ranging from 0 to 100 V. Field-effect mobility and subthreshold slope were evaluated to be about 1.94 cm V$^{-1}$ s$^{-1}$ and 0.8 V/decade, respectively. As compared to the materials reported in TFT applications such as poly(3-hexylthiophene) (field-effect mobility of 0.1 cm V$^{-1}$ s$^{-1}$, on/off ratio of $10^8$, and subthreshold slope of 1.2 V/decade), poly[5,5′-bis(3-dodecyl-2-thienyl)-2,2′-bithiophene]-12 (0.1 cm V $^{-1}$ s$^{-1}$, 10$^8$, 2.0 V/decade),$^8$ and a-Si: H (1 cm V $^{-1}$ s$^{-1}$, 10$^8$, 0.8 V/decade),$^9,10$ the presented results in this work are with lower on/off ratio and worse subthreshold slope except the field-effect mobility. It indicates the room to improve the transistor behavior, especially to reduce the leakage current. However, as compared to the similar type transistors (PEDOT-PSS), as listed in Table 1,$^5,7$ the proposed transistor still has the advantage of higher drain current density, comparable on/off ratio. The higher drain current density may be applied to other circuit applications instead of display pixels.

In order to investigate the role of PEI, devices based on PEDOT-PSS were fabricated. Figure 4 shows the $I$-$V$ characteristics of devices without PEI. It is obvious the $I$-$V$ characteristics have a resistor instead of a transistor behavior. Compared with the $I$-$V$ characteristics of devices without PEDOT-PSS with PEI, the source-drain currents of devices without PEI were larger. The low source-drain current for PEI/PEDOT-PSS-PEI based on OTFT was attributed to the SO$_3$H$^+$ groups of PSS, which were electrostatically linked with the NH$_3^+$ groups of PEI as the PEI was mixed with PEDOT-PSS. The charge carriers were localized in the sulfur atoms.

In the presented work, PEI plays an important role in modulating the conductivity of PEDOT-PSS. When the ratio of PEI/PEDOT-PSS was raised, the cutoff currents of the source-drain were reduced. In other words, a higher ratio of PEI/PEDOT-PSS will lead to a higher on/off ratio. However, the blending ratio of PEI and PEDOT-PSS is limited to the materials’ nature. When the ratio of PEI/PEDOT-PSS is higher than 1, the PEDOT-PSS-PEI becomes a jellied state, which is very difficult to process. The OTFT with the ratio of PEI/PEDOT-PSS in 1.5 was fabricated. Because of the jellied materials, the device shows poor performance, as depicted in Fig. 5. The low source-drain currents of the device with a ratio of PEI/PEDOT-PSS in 1.5 could be observed. The low source-drain current of the device is attributed to more PEI mixed with PEDOT-PSS, which in turn results in more PSS linking with PEI, as well as more electrons being localized in the sulfur atoms of the PEDOT main chain. The jellied PEDOT-PSS-PEI makes the thick film by spinning. Due to these thick films, large electric fields should be applied to cut off the channel. This makes low on/off ratios even under $V_{gs}=100$ V. When comparing the dc characteristics of the ratio of PEI/PEDOT-PSS with 0, 1, and 1.5, the optimal ratio is about 1.

In summary, the depletion mode of OTFTs based on PEDOT-PSS with PEI has been demonstrated. As compared to the transistors with similar materials, the proposed transistors with larger current density (1.2 mA/mm) and comparable on/off ratio ($10^3$) can be obtained. Field-effect mobility and subthreshold slope were evaluated to be about

![FIG. 2. I-V characteristics of the proposed PEDOT-PSS with PEI OTFT.](image)

![FIG. 3. (a) The synthesized structure of PEDOT-PSS with PEI. (b) Operation mechanism of the depletion-mode OTFT.](image)

![FIG. 4. I-V characteristics of OTFT based on PEDOT-PSS without PEI. It only indicates the resistor.](image)

<table>
<thead>
<tr>
<th>Channel width (μm)</th>
<th>Material</th>
<th>$I_{ds}$ ($V_{gs}$=0 V, $V_{gs}$=10 V) (μA)</th>
<th>Density (mA/mm)</th>
<th>$I_{on}$/I$_{off}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PEDOT-PSS</td>
<td>~150</td>
<td>10$^2$</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>PEDOT-PSS</td>
<td>~7</td>
<td>2×10$^3$</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>PEDOT-PSS</td>
<td>~3</td>
<td>1×10$^4$</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>PEDOT-PSS-PEI</td>
<td>~120</td>
<td>1.2</td>
<td>10$^3$</td>
<td>this work</td>
</tr>
</tbody>
</table>

TABLE I. Performance comparison with the reported transistors using PEDOT-PSS.
1.94 cm s\(^{-1}\) and 6.67 V/decade, respectively. Without the incorporation of PEI in PEDOT-PSS, a very high conductivity can be observed which only indicates the resistor behavior. The role of the PEI in the PEDOT-PSS is found to be the key issue in modulating the layer conductivity. By increasing the blending ratio of PEI in PEDOT-PSS, the conductivity of PEDOT-PSS can be modulated as an active layer for field effect transistor applications. However, the blending ratio of PEI with PEDOT-PSS is limited by the material’s nature.

The jelly state of PEDOT-PSS-PEI can be observed by increasing the ratio of PEI/PEDOT-PSS ratio up to 1.0 and leading the poor performance for the OTFT operation. The optimal blending ratio of PEDOT-PSS/PEI as the active layer is found to be 1.0.

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