Organic thin film transistor by using polymer electrolyte to modulate the conductivity of conjugated polymer

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This work presents an organic thin film transistor using double polymer layers, polymer electrolyte/conjugated polymer, i.e., poly(diallyldimethylammonium chloride) (PDDA)/poly(diphenylamine) (PDPA) structure. The single mobile anions (Cl\(^-\)) pending on the PDDA are stuffed into the conjugated polymer to dope the nitrogen atoms (imine) by applying the gate bias, resulting a higher drain current under the same source-drain voltage. The PDDA/PDPA polymer structure working in the enhancement mode which operates under atmospheric conditions as a typical p-channel transistor is demonstrated. © 2006 American Institute of Physics. [DOI: 10.1063/1.2398896]

Electrochemical devices were recently presented by Kruger et al.\(^1\) and Rosenblatt et al.\(^2\) in which a salty solution was used as a gate material, thereby enhancing the source-drain current by orders of magnitude. However, although the performance of the device looks promising, the use of liquid materials in the devices presents practical problems in real electronic applications. Chao et al. fabricated a microelectrochemical transistor by using a solid-state polymer electrolyte (PEO\(_{16}\)·LiCF\(_3\)SO\(_3\)) instead of salty liquid.\(^3\) However, the devices showed good performance only at 95 °C in a N\(_2\) atmosphere. At low temperature, the solid-state oxidation/reduction of the poly(3-methylthiophene) is not well defined, which is consistent with the low ionic conductivity of PEO or poly(3-methylthiophene). Here, we present a different, single mobile anion of poly(diallyldimethylammonium chloride) (PDDA)/poly(diphenylamine) (PDPA) structure for organic thin film transistors (OTFTs). The replacement of the salty solution with a polymeric solid electrolyte material (PDDA) can also lead to the achievement of good device performance at room temperature under atmospheric conditions and can prevent the problems from the liquid materials in the devices. Comparing PDDA with PEO, the differences are the former has single mobile anions and the latter has both mobile positive ions and anions. The pendant positive ions along the polymer chain do not migrate to the PDPA compared with the two mobile ions of the PEO-salt system under an electric field.

Many organic semiconductor materials with small molecules are rather rigid and possess planar structures which are generally insoluble in common organic solvents. These are very difficult to incorporate into electronic devices. On the other hand, some conjugated polymers, with their longer molecular chains, are good alternatives for processing in solutions. However, most conjugated polymers such as polyaniline are also insoluble owing to the stiffness of its backbone which further restricts its applications. One approach to increase its solubility is to modify the conductive polymer structure. PDPA is one of the derivatives of polyaniline with excellent solubility in common organic solvents.\(^3,6\)

The possibility of using a polymer electrolyte in the gate of a transistor was demonstrated over a decade ago for redox-active semiconductors, such as polythiophene, as well as for p-type crystalline silicon. More recently, Siddons et al. have reported carbon nanotube field effect transistors that have been gated and doped by polymer electrolytes.\(^7\) In accordance with these results, an additional nanoscale polymer electrolyte, PDDA, is introduced in this work to provide ions in/out the conjugated polymers, as well as to further control electrical performance. Figure 1 shows the chemical structures of the emeraldine base of PDPA and the PDDA.

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![Figure 1](image.png)

**FIG. 1.** Chemical structures of PDDA and PDPA.

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The conductivity of the emeraldine base of PDPA is very low due to the electron localization along the backbone of polymer structure. Hence, the additional polymer electrolyte, PDDA, can provide anions to dope the emeraldine base of PDPA to form the emeraldine salt of PDPA, resulting in the electronic delocalization along the backbone of the polymer. This electronic delocalization provides the “highway” for charge mobility along the backbone of the polymer chain and further control the electric performance of the device.

A schematic structure of the organic thin film transistor is shown in Fig. 2. Device fabrication began with a thin Al film (~1000 Å) deposited on the Si surface of a SiO2/Si(100) substrate (SiO2~2000 Å) as the gate electrode and was annealed in N2 under 400 °C for 90 s. In the front side, the polymer electrolyte PDDA (wt=5%) was spun on the SiO2 layer under 4000 rpm for 1 min and was baked on a hot plate under 150 °C for 30 min. Then the conjugated polymer PDPA was spun on the PDDA layer under 4000 rpm for 1 min and was baked on a hot plate under 150 °C for 30 min. Next, a thin Au layer (~1000 Å) was sputtered through a shadow mask to define the source and drain patterns. The channel length of this mask is 50 μm, and the area for both the source and the drain is 2 × 2 mm².

The current-voltage (I-V) characteristics were measured as those done in metal oxide semiconductor field effect transistors (FETs) by HP4156B. Gate voltage is from 0 to −100 V with −20 V per step, and drain voltage is from 0 to −40 V. Figure 3 shows the I-V characteristics of the OTFTs operating at different gate voltages. The inset shows the transconductance $g_{ms} = dI_{ds}/dV_{gs}$ taken at $V_{sd} = −40$ V. The used conjugated polymer is emeraldine base form of PDPA which shows low drain current under $V_{gs} = 0$ V. When a negative gate bias is applied, the drain-source current scales with the gate voltage, which is similar to the typical gate modulated p-channel FET behavior. The “doping-dedoping” of conjugated polymers, with associated control of the electrical conductivity from insulator to semiconductor, can be accomplished either by chemical doping or by electrochemical doping. Based on these results, we propose a mechanism that the PDPA undergoes anions (Cl⁻) doping with applying the gate bias. PDPA was synthesized with HCl or H2SO4. Since PDPA was doped by Cl⁻ anions from HCl, the state of PDPA has been transformed into “emeraldine salt.” Then PDPA was neutralized with the ammonia, and the Cl⁻ anions bound with nitrogen atoms were removed. At present, the PDPA is in the “emeraldine base” state and possesses lower conductivity. This is because the charge carriers have been localized in the nitrogen atoms. In order to make the localized electrons in the nitrogen atoms delocalized and “hop” along the conjugated bonds of PDPA, the Cl⁻ anions were introduced from PDDA into PDPA. At this time, the PDPA is under the emeraldine salt state and with higher conductivity. As negative voltage is applied to the gate electrode, the Cl⁻ anions from the polymer electrolytes (PDDA) are stuffed into the interface between the conjugated polymer (PDPA) and the polymer electrolytes (PDDA) by the electric field, thereby doping the PDPA and transforming the PDPA into emeraldine salt form (Fig. 2). The conjugated polymer at the semiconductor/electrode interface is emeraldine base or emeraldine salt form of PDPA during charge injection. The charges move by the “hopping” of polarons or bipolarons from one molecule to another. The doped conjugated polymer offers more free carriers than undoped one and presents a high drain current under the same source-drain voltage. The p-channel FET operates in an enhancement mode when a negative bias is applied to the gate electrode. Therefore, $I_{ds}$ will increase due to the increased concentration of holes. The electric performance of the device with the solid-state polymer electrolyte is not as good as that with liquid electrolyte. The absence of saturation at high $V_{ds}$ could be due to the slow movement of ions during the doping process. Although the anions move slowly in the solid, PDPA is doped by Cl⁻ anions, in fact, to form the channel, resulting in the transistor behavior as obviously shown in Fig. 3. Gate voltage is from 0 to −100 V with −20 V per step, while drain voltage is from 0 to −40 V. When $V_{gs}$ is swept from −100 to 0 V, the $I_{ds}$ becomes smaller than measured from 0 to −100 V, which is probably due to the surface states and mobile ions in the device. The magnitude of hysteresis was also observed in inorganic metal-insulator semiconductor devices.
The on/off ratios [ratio between the current at a given gate voltage (−100 V) and zero gate voltage] are in the range of 2–30. The effective electrical field mobility was calculated as follows:

\[ I_{ds} = \frac{(W/L)}{\mu} C_i (V_g - V_0 - V_{ds}/2) V_{ds} + I_{\Omega}, \]

where \( I_{ds} \) is the source-drain current, \( W \) and \( L \) are the channel width and channel length, respectively. \( \mu \) is the field effect mobility of devices. \( C_i \) is the capacitance per unit area of the insulating layer. \( V_g \) and \( V_0 \) are the gate and threshold voltages. \( I_{\Omega} \) is the Ohmic current that flows through the conjugated polymer film. The effective electric field mobility is \( \sim 10^{-2} \text{ cm}^2/\text{V s} \).

In order to probe the role of the PDDA, devices based on undoped PDPA without PDDA were fabricated. Figure 4 shows the \( I-V \) characteristics of the devices based on undoped PDPA. The source-drain currents are increased slightly as a result of increasing electric field as the gate voltages are from 0 to −100 V. When the larger voltage is applied to the gate, the more carriers are induced to the interface between the PDPA and the SiO\(_2\). Owing to PDPA in the emeraldine base, the carriers induced by the electric field are fewer than those doped by the electrochemical doping mechanism. Obviously, the drain current of the PDPA/PDDA is much higher than that without the PDDA. The function where the conjugated polymer, PDPA, is doped by Cl\(^-\) anions from the polymer electrolyte, PDDA, is demonstrated. However, the undoped PDPA of the device based on the PDPA acts like the insulator in spite of the applied \( V_g \). In comparison with the traditional polymer field effect transistors, the use of the PDDA provides Cl\(^-\) anions to dope PDPA. The concentrations of Cl\(^-\) anions can be modulated by the applied gate voltage. As the \( V_g \) voltages increase (from 0 to −40 V), the concentration of the Cl\(^-\) doped in PDPA is likewise increased. This in turn leads to an increased conductivity of the PDPA and shows the enhancement of the \( I_{ds} \) current. Moreover, the \( I-V \) characteristic of the device is investigated under atmospheric conditions without avoiding the presence of neither oxygen nor moisture. Generally, oxygen and moisture will be adsorbed onto the organic film just like organic light emitting diode. Qie et al.\(^9\) also reported the effect of moisture on the stability of pentacene-based organic field effect transistors. In the present study, the \( I-V \) characteristics of the devices exhibit promising performance in the presence of oxygen and moisture.

In summary, an organic thin film transistor comprising of polymer electrolyte, PDDA, and conjugate polymer, PDPA, was fabricated. The “doping-dedoping” of anions to PDPA can be achieved by applying the gate bias to control the Cl\(^-\) anions from PDDA in/out PDPA to form the emeraldine salt/base, resulting in electron delocalization/localization to modulate the electric conductivity. Accordingly, the electrical characteristics of the PDDA/PDPA structure with SiO\(_2\) gate dielectric organic thin film transistor demonstrated that the device behaves as a typical \( p \)-channel transistor working in an enhancement mode, even though it operates under atmospheric conditions at room temperature.

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