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# Tuning of threshold voltage of organic field-effect transistors by space charge polarization

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We demonstrate a tunable threshold voltage in an organic field-effect transistor (OFET) using an ion-dispersed gate dielectric. By applying an external electric field ( $V_{ex}$ ) to the gate dielectrics, the dispersed ions in the gate dielectric are separated by electrophoresis and form space charge polarization. The drain current of the OFET increases more than 1.9 times, and the threshold voltage ( $V_{th}$ ) decreases by 22 V (from  $-35.1$  to  $-13.1$  V). The direction and the magnitude of  $V_{th}$  shift are tunable with the applied  $V_{ex}$ . The origin of the  $V_{th}$  shift is attributed to the polarization of the gate dielectric. © 2009 American Institute of Physics. [DOI: 10.1063/1.3086277]

In recent years, organic field-effect transistors (OFETs) using organic semiconductors have attracted much research interest due to their unique advantages, including a variety of molecular designs, light weight, low-cost fabrication, and mechanical flexibility. In particular, research interest in the gate dielectrics is recently increasing since the choice of the gate dielectrics directly affects the electric properties of the OFETs.<sup>1</sup> For example, high- $k$  gate dielectrics or very thin gate dielectrics can reduce the operation voltage of the OFETs.<sup>2,3</sup> The threshold voltage ( $V_{th}$ ) of the OFETs can be tuned by using polar self-assembled monolayers inserted at the surface of the gate dielectrics<sup>4,5</sup> and by using ferroelectric gate dielectrics, where the origin of the shift is due to remnant polarization of the gate dielectrics.<sup>6,7</sup> Controlling  $V_{th}$  was also realized by using the polarized gate dielectric with charged electrets.<sup>8</sup> These reports indicate that  $V_{th}$  is significantly affected by the surface or bulk polarization of gate dielectrics. In other words, tuning  $V_{th}$  may be realized by controlling the polarization of gate dielectrics.

Recently, we have reported that the polarization of gate dielectrics can be achieved by the alignment of carbonyl groups of polyurea chains.<sup>9</sup> The polarization of the gate dielectrics induced charged carriers in an active layer (pentacene) at the active layer/dielectric interface and  $V_{th}$  shifted toward a lower voltage. In this case,  $V_{th}$  of the OFETs decreased by 6 V compared to that of the OFETs using nonpolarized gate dielectrics. However, the decrease in  $V_{th}$  was limited by the amount of the polarization, a limitation which was caused by the difficulty of aligning carbonyl groups in the solid dielectric film. Indeed, the ratio of the aligned permanent dipoles was estimated to be 0.25% of total number of the permanent dipoles. For a further decrease in  $V_{th}$ , a larger amount of polarization will be necessary.

The polarization ( $P$ ) of dielectrics is expressed by two terms,  $P = \langle \delta \rangle N$ , where  $\langle \delta \rangle$  is the mean dipole moment averaged over the net direction of each dipole in the dielectrics.<sup>10</sup>  $N$  is the number of dipoles per unit volume. The magnitude of an individual electric dipole moment is expressed by two terms,  $\delta = qR$ , where  $R$  is the separation distance between the positive charge ( $+q$ ) and the negative charge ( $-q$ ). These equations suggest that there are two effective approaches to

increase  $P$ . One is to increase  $\langle \delta \rangle$  by aligning the individual dipoles in the dielectric. The other is to increase the magnitude of  $\delta$  by increasing the distance  $R$  between two charges ( $\pm q$ ).

Here, we report that a large  $P$  can be obtained by using the ion-dispersed gate dielectrics, where  $N$  can be controlled by the amount of added ions.  $R$  can be increased by ion migration (electrophoresis) in the dielectrics, where the negative ions and the positive ions migrate in opposite directions by applying an external electric field. The direction of the polarization would be aligned parallel to the external electric field. In this case, the magnitude and the direction of the polarization are adjustable depending on the external voltage used for the electrophoresis.

Figure 1(a) shows the device structure of the OFETs used in this study. Indium tin oxide (ITO) on a glass substrate was used as the gate electrode. Polymethylmethacrylate (PMMA) was used as a matrix polymer of the gate dielectric. The ionic compound dispersed in the gate

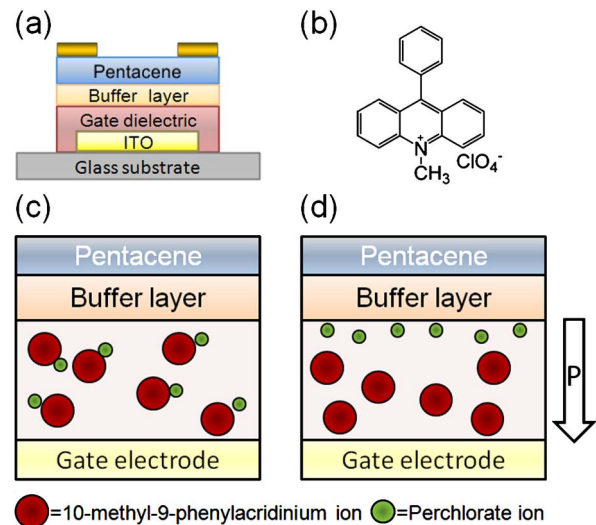


FIG. 1. (Color online) (a) Schematic representations of the OFETs with ion-dispersed gate dielectric. (b) Chemical structure of MPA<sup>+</sup>ClO<sub>4</sub><sup>-</sup>. [(c) and (d)] Schematic representations of the ion migration in the gate dielectric before and after applying an external electric field. An arrow shows the direction of the space charge polarization formed by an ion migration in the gate dielectric. The channel width and channel length of the OFETs are 24 500 and 75  $\mu\text{m}$ .

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dielectrics was 10-methyl-9-phenylacridinium perchlorate [MPA<sup>+</sup>ClO<sub>4</sub><sup>-</sup>, Fig. 1(b)]. PMMA and MPA<sup>+</sup>ClO<sub>4</sub><sup>-</sup> were dissolved in acetonitrile, where the concentration of PMMA was 5 wt % (the molar ratio of the constitutional repeating unit of PMMA to MPA<sup>+</sup>ClO<sub>4</sub><sup>-</sup> was 50 to 1). The gate dielectric layer was fabricated on an ITO/glass substrate with the spin-coating method. After annealing the ion-dispersed layer at 100 °C for 2 h in air, the PMMA buffer layer was fabricated by spin-coating of the PMMA xylene solution (10 wt %) on the ion-dispersed layer film. The role of PMMA buffer layer is to delay the migration of anion when an external electric field was applied for 10 min and prevents the chemical doping of MPA<sup>+</sup>ClO<sub>4</sub><sup>-</sup> into the active layer (*vide infra*). The total thickness of the ion-dispersed layer and the buffer layer was 690 nm. As an active layer of the OFETs, thin films of pentacene (Aldrich, purified by vacuum sublimation twice) were formed by vacuum deposition at a deposition rate of 0.02 nm s<sup>-1</sup> on the dielectrics, followed by the deposition of a gold top electrode at a deposition rate of 0.03 nm s<sup>-1</sup> through a shadow mask. The film thicknesses of pentacene and gold were 30 and 50 nm. The channel length ( $L$ ) and channel width ( $W$ ) were 75 and 24 500  $\mu\text{m}$ .

As shown in Fig. 1(c), MPA<sup>+</sup>ClO<sub>4</sub><sup>-</sup> ion pairs were uniformly dispersed in the as-formed gate dielectrics. When the external electric field is applied to the gate dielectrics, the MPA<sup>+</sup> and ClO<sub>4</sub><sup>-</sup> ions migrate in opposite directions and form a space charge polarization in the gate dielectric [Fig. 1(d)]. Comparing the size of MPA<sup>+</sup> cations (10 Å) and of ClO<sub>4</sub><sup>-</sup> anions (3.5 Å) (Ref. 11) with the diameter of the free volume hole of PMMA (5.4 Å),<sup>12</sup> the cations can hardly migrate in the dielectrics due to the molecular sieve effect of PMMA polymer chains. Also, MPA<sup>+</sup> cations would be stabilized by the interaction with oxygen in a carbonyl group of PMMA. Therefore, the polarization of our dielectrics would be mainly due to the migration of ClO<sub>4</sub><sup>-</sup> anions. The space charge polarization was formed by applying an external voltage ( $V_{\text{ex}}$ ) to the gate electrode with a Keithley 2400 SourceMeter for a certain bias time ( $T_{\text{bias}}$ ). Both source and drain electrodes on the gate dielectrics were grounded and used as counterelectrodes. Electric characteristics of the OFETs were measured by applying a gate voltage ( $V_G$ ) and a source-drain voltage ( $V_D$ ) with a Keithley 4200 semiconductor characterization system in dry nitrogen. Capacitances of the gate dielectrics were measured using a capacitor structure without pentacene layer [glass substrate/ITO electrode/gate dielectrics (690 nm)/Al electrode (100 nm)] with an Agilent 4284A LCR meter.

Figure 2 shows the output characteristics of the OFETs with the ion-dispersed gate dielectrics after ( $T_{\text{bias}}=0$  and 10 min).  $V_G$  was swept from 30 to -60 V with a step voltage of -5 V. The output characteristics clearly show that the drain current ( $I_D$ ) increases with increasing  $T_{\text{bias}}$ , where  $I_D$  value at  $V_G=-50$  V is enhanced more than 1.9 times for  $T_{\text{bias}}=10$  min [Fig. 2(b)] compared to  $T_{\text{bias}}=0$  min [Fig. 2(a)]. We observed a clear saturation of  $I_D$  at the region of larger  $V_D$ . The observed increase in  $I_D$  indicates that the number of the charge carriers was increased by applying  $V_{\text{ex}}$ .

Figure 3(a) shows the change in transfer characteristics of the OFETs at  $V_D=-60$  V, measured at different  $T_{\text{bias}}$  ( $V_{\text{ex}}=-60$  V) from 0 to 10 min with a 2 min period. At  $T_{\text{bias}}=0$  min, we measured the transfer characteristics twice and observed the identical transfer characteristics. This con-

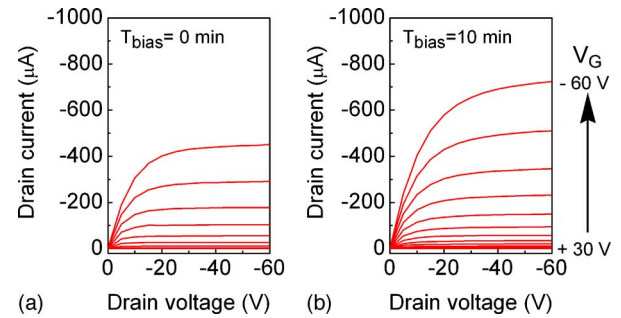


FIG. 2. (Color online) Output characteristics of the OFETs with an external electric field of  $V_{\text{ex}}=-60$  V at (a)  $T_{\text{bias}}=0$  min and (b)  $T_{\text{bias}}=10$  min. The gate voltages were changed from 30 to -60 V with a step of -5 V.

firms that the measurement does not affect the transfer characteristics and that the shift in the transfer characteristics in Fig. 3 is mainly caused by applying  $V_{\text{ex}}$ . We estimated  $V_{\text{th}}$  values through a linear fit and its intercept ( $I_D^{1/2}=0$ ) of the plot of  $I_D^{1/2}$  versus  $V_G$  [inset of Fig. 3(b)]. A large  $V_{\text{th}}$  shift of 22 V (from -35.1 to -13.1 V) was readily achieved as  $T_{\text{bias}}$  increases [Fig. 3(b)]. After the measurement of  $V_{\text{th}}$  with a negative external voltage ( $V_{\text{ex}}=-60$  V), a positive external voltage ( $V_{\text{ex}}=60$  V) was applied. The positive  $V_{\text{ex}}$  not only enabled to return to the initial  $V_{\text{th}}$  but also to increase  $V_{\text{th}}$  (data not shown). These results demonstrate that  $V_{\text{th}}$  of the OFETs is tunable by changing the direction of  $V_{\text{ex}}$  and  $T_{\text{bias}}$ . The slopes of the linear region in the inset of Fig. 3(b) were unchanged, suggesting that the dielectric permittivity of the gate dielectrics and the mobility of the active layer remain constant. Indeed, we confirmed that the dielectric permittivity of the ion-dispersed gate dielectrics (4.1 nF cm<sup>-2</sup> at 100 Hz) was unchanged when neither the negative nor the positive external voltage ( $V_{\text{ex}}=-60$  V, +60 V) was applied.

The carrier mobility was calculated by fitting the plot of the square root of  $I_D$  versus  $V_G$  with the following equation:<sup>13</sup>

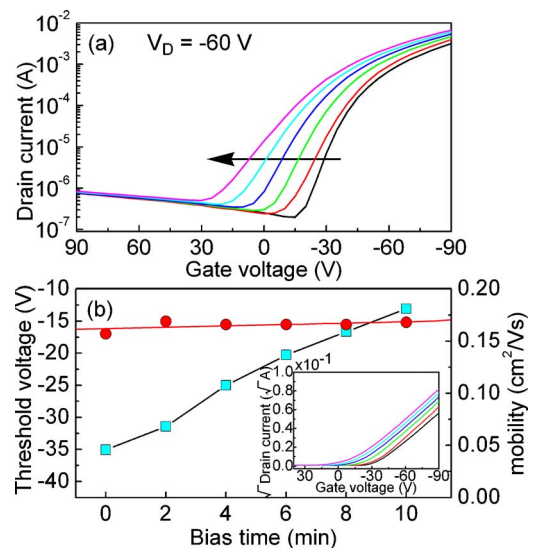


FIG. 3. (Color online) (a) Transfer characteristics of the OFETs at  $V_D=-60$  V with ion-dispersed gate dielectrics at various  $T_{\text{bias}}$  ( $V_{\text{ex}}=-60$  V).  $T_{\text{bias}}$  varies from 0 to 10 min in steps of 2 min. (b) Changes in  $V_{\text{th}}$  (square) and of the mobility (circle) as a function of  $T_{\text{bias}}$ . Inset: Plot of the square root of the drain current vs the gate voltage of the OFETs with ion-dispersed gate dielectrics at various  $T_{\text{bias}}$ .

$$I_D = \frac{WC\mu}{2L}(V_G - V_{th})^2, \quad (1)$$

where  $C$  is the capacitance per unit area of the gate dielectrics,  $\mu$  is the carrier mobility, and  $V_{th}$  is the threshold voltage. For the as-prepared OFETs ( $T_{bias}=0$  min),  $V_{th}$ ,  $\mu$ , and the on/off current ratio were  $-35.1$  V,  $0.16$  cm<sup>2</sup>/V s, and  $6.2 \times 10^4$ . The mobility of the OFET remained constant with increasing  $T_{bias}$  [Fig. 3(b)]. The relatively low  $\mu$  values observed in our study would be due to the contact resistance between the Au electrode and the pentacene, which can be improved by reducing the contact barrier.<sup>14</sup>

It is possible that the ions having migrated interact electrochemically with an active layer and enhance the  $I_D$ .<sup>15,16</sup> However, this is not the case in our system since the buffer layer effectively prevents the interaction (*vide infra*). If the electrochemical doping occurs between the ions having migrated and the active layer, the saturation of the drain current may not be clearly observed.<sup>17</sup> As shown in Fig. 2, the drain current saturation was observed, and this result suggests that the observed  $V_{th}$  shift is mainly due to the electrostatic charging mechanism.

To obtain more insights on the electrochemical interaction at the active layer of the OFETs, ultraviolet/visible (UV-visible) reflection absorption spectra of the OFETs were measured with a JASCO V-570 spectrometer (see Fig. S1 in supplemental information<sup>18</sup>). To separate the MPA<sup>+</sup>ClO<sub>4</sub><sup>-</sup> ion pairs in the dielectrics after applying  $V_{ex}$ , we applied the electric field ( $V_{ex}=-60$  V) to the ITO electrode. If ClO<sub>4</sub><sup>-</sup> anions migrate to the dielectrics/pentacene interface, the electrochemical reaction could occur between the ClO<sub>4</sub><sup>-</sup> anions and the active layer. In this case, the absorption spectra of the pentacene will be changed by the formation of the pentacene cation. In the OFETs without a buffer layer, the changes in the absorption caused by the formation of the pentacene cation changes were observed, whereas, in the OFET with the buffer layer, the changes in the absorption were not observed. These results clearly show that the electrochemical doping in the active layer was effectively prevented by the buffer layer.

In conclusion, we have demonstrated the control of the  $V_{th}$  in the OFETs using ion-dispersed gate dielectrics. The space charge polarization in the gate dielectrics largely affects to the electrical characteristics of the OFETs, where a large decrease in  $V_{th}$  was achieved. The shift direction of  $V_{th}$  was easily tuned by the polarity of the external voltage. The dielectric permittivity of the gate dielectrics and the mobility

of the active layer were unchanged after the polarization of the gate dielectrics. The results of the UV-visible differential absorption spectra indicate that there is no chemical doping in the active layer of the OFETs with the buffer layer. These results indicate that the shifts in the threshold voltages originate from the polarization of the gate dielectrics.

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- <sup>18</sup>See EPAPS Document No. E-APPLAB-94-027908 for UV-visible absorption spectra of the OFET. For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.