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Description	

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

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Abstract

We demonstrate organic field effect transistors (OFETs) with an ion-dispersed polymer for the gate dielectrics. By applying external electric field (V_{ex}), the dispersed ions can migrate by electrophoresis and separated ion pairs form space charge polarization in the gate dielectrics. After V_{ex} was applied, the drain current is increased over 7 times and threshold voltage is decreased from -12.9 V to -2.9 V. The shift direction of V_{th} is controllable by the polarity of the V_{ex}. Results of ultraviolet/visible differential absorption study reveal that the active layer of OFETs is charged not only electrostatically but electrochemically with increasing the time after V_{ex} was applied.

Keywords: Organic field-effect transistors (OFETs), Threshold voltage shift, Polarization, Gate dielectric

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Main text

1. Introduction

In recent years, organic field-effect transistors (OFETs) using organic semiconductors attracted much research interests due to their unique advantages, which include a variety of molecular designs, light weight, low cost fabrication and mechanical flexibility. In particular, research interest into the gate dielectrics are recently increasing. Since the choice of the gate dielectrics directly affects the electric properties of OFETs [1]. For example, it has been reported that high-k gate dielectrics or very thin gate dielectrics can reduce the operation voltage of OFETs [2, 3]. Kobayashi et al. reported threshold voltage (V_{th}) of the OFETs can be tuned by using polar self-assembled-monolayers (SAMs) inserted at the interface [4]. The shift of V_{th} was also reported OFETs using ferroelectric gate dielectrics (FeFET), where the origin of the shift is due to remnant polarization in gate dielectrics [5, 6]. These results indicate that V_{th} is susceptibly affected by the surface or bulk polarization of gate dielectrics. In other words, the shift of V_{th} can be achieved by controlling the polarization of gate dielectrics.

Recently we have reported the effect of gate dielectrics polarization on the electric characteristics of OFETs, where the polarization was achieved by the alignment of permanent dipoles in polymer chains [7]. The polarization of gate dielectrics induced the mobile charge carrier in the semiconductor layer at the semiconductor-dielectric interface and as a result, V_{th} shifted toward a lower voltage. By using polarized gate dielectrics, V_{th} of OFETs were decreased by 6 V compared to that of OFETs using non-polarized gate dielectrics. However, the decrease of V_{th} was limited by the small amount of polarization, a limitation which was caused by the difficulty of aligning of permanent dipoles in the solid dielectric film. Indeed, the ratio of alignment of permanent dipoles was estimated to be c.a.

0.25% of total amount of permanent dipoles. For a further decrease of V_{th}, novel approaches will be necessary to realize a higher magnitude of the polarization in the gate dielectrics.

Ion migration in polymer gate dielectric is one of the candidates to realize a higher magnitude of polarization of gate dielectric, because ions in a matrix polymer can easily migrate by an external electric field and form a space charge polarization. This polarization is easily tunable by the amount of dispersed ions and the ion migration length. The ion migration length can be controlled by the time an external electric field was applied. Furthermore, negative ions can be doped in organic semiconductor to increase carrier density. In this study, we report that the reduction of V_{th} can be achieved by using the ion-dispersed gate dielectric. Result of ultraviolet/visible (UV-VIS) absorption study reveals that the active layer of OFETs is charged not only electrostatically but electrochemically with increasing the time after V_{ex} was applied.

2. Experimental

Figure 1a shows schematic structures of OFETs used in this study, where indium tin oxide (ITO) on glass was used as the gate electrode. Figure 1b shows the chemical structure of 10-methyl-9-phenylacridinium perchlorate ($MPA^+ClO_4^-$), which was dispersed in Polymethylmethacryrate (PMMA). Schematic representations of ion migration in the gate dielectrics before and after applying an external electric field (V_{ex}) are shown in Figs. 1c and 1d. When we applied V_{ex} to the gate electrode with a Keithley 2400 SourceMeter for a certain bias time (T_{bias}), both source and drain electrodes on the gate dielectrics were grounded and used as counter electrodes. While V_{ex} is applied to the gate dielectrics, the ions of MPA^+ and ClO_4^- migrate in opposite directions and form a space charge polarization in the gate dielectric. Comparing the sizes of MPA^+ cations (10

Å) and ClO_4^- anions (3.5 Å) [8] with the diameter of the free volume hole of PMMA (5.4 Å) [9], the cations can hardly migrate in the dielectric due to the molecular sieve effect of PMMA polymer chains. Also, MPA^+ 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_4^- anions.

PMMA and $MPA^+ClO_4^-$ were dissolved in acetonitrile, where the mol ratio of constitutional repeating unit of PMMA to ionic compound was 50 to 1. The dielectric film was fabricated by spin-coat on ITO/glass substrate and the film thickness was 400 nm. As an active layer of OFETs, thin films of pentacene (Aldrich, purified by vacuum sublimation) were formed by vacuum deposition at the rate of 0.03 nm s^{-1} on the dielectrics, followed by the deposition of a gold comb-shape electrode at the a deposition rate of 0.03 nm s^{-1} through a shadow mask. The film thicknesses of pentacene and gold were 30 nm and 50 nm. The channel length (W) and channel width (L) were 75 μm and 24500 μm. Electric characteristics of OFETs were measured with a Keithley 4200 semiconductor characterization system in dry nitrogen atmosphere. Capacitances of the dielectrics were measured with a capacitor structure of glass substrate /ITO electrode/ion-dispersed dielectrics (400 nm)/pentacene (30 nm)/Al electrode (100 nm) using an Agilent 4284A LCR meter.

UV-VIS differential absorption spectra of the OFETs were measured with a JASCO V-570 spectrometer. We used the capacitor structure for the absorption spectra. The film thicknesses of ion-dispersed dielectrics and pentacene were exactly the same used for OFETs. The Al film act as a top electrode and a mirror for reflection absorption spectra measurement. To separate the $MPA^+ClO_4^-$ ion pairs in the dielectrics, we applied V_{ex} of -30 V to ITO electrode for T_{bias}. The differential absorption spectra were measured by

subtracting the absorption spectra without the electric field from those after applying the electric filed for a certain bias time.

3. Results and Discussion

3.1 Characteristics of OFETs with ion-dispersed gate dielectrics

Figures 2a-2c show the output characteristics of the OFETs with the ion-dispersed gate dielectrics at the T_{bias} of 1 min, 9 min and 19 min. The gate voltages were changed from 6 V to -30 V with the step of -3 V. The output characteristics clearly show that drain current (I_D) was increased with increasing T_{bias}, where I_D value at the V_G = -30 V with T_{bias} = 19 min (Fig. 2c) is increased over 7 times compared to that with T_{bias} = 1 min (Fig. 2a). This result indicates that the amount of the charge carriers was increased after applying V_{ex}. Increasing I_D as increasing T_{bias} indicates that the magnitude of polarization of the gate dielectrics was enhanced by the electrophoresis of $MPA^+ClO_4^-$ ion pairs and the active layer was charged by the space charge polarization.

The ion migration would cause the two possible charging mechanisms, one is the electrostatic (field-effect) charging and the other is the electrochemical (doping) charging [10]. The critical difference between these two mechanisms is whether the ions in the gate dielectrics reach to the semiconductor layer [11]. In the electrostatic mechanism, an electric double layer is formed inside the gate dielectrics. The drain current saturation in the output characteristics caused by channel pinch-off is an indicator of this mechanism. In the case of electrochemical mechanism, the migrated ions penetrate into the active layer and the doping of the active layer occurs. In this case, the saturation of drain current may not be clearly observed [12]. As shown in Figs. 2a and 2b, the drain current saturation was observed at the T_{bias} = 1 min and 9 min, whereas the drain current saturation was not

clearly observed at the T_{bias} = 19 min (Fig. 2c). These results suggest that the initial charging mechanism is electrostatic and it gradually switches to electrochemical with increasing T_{bias} since the migrated ClO_4^- anions in the gate dielectrics slowly reached to the active layer/gate dielectrics interface and penetrated into the active layer.

Figure 2d shows the change of the transfer characteristics of the OFETs at V_D = -30 V, measured at different T_{bias}. A prominent feature in the transfer characteristics is that the "off current" of the characteristics was increased at T_{bias} = 19 min. This is a clear evidence for the ClO_4^- anions penetrated into the semiconductor layer and doped the pentacene. As a result, doped pentacene layer showed high conductivity[13] and off current of OFET was increased. This result consisted with the changes of UV-VIS reflection absorption spectra *(vide infra)*. Interestingly, the off current was decreased after applying the positive gate bias (V_{ex} =30 V), since the positive gate bias move away the ClO_4^- ions from the pentacene and reduce the doped pentacene.

The carrier mobility was estimated by fitting the plot of the square root of I_D versus V_G with the following equation:[14]

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

Where C is the capacitance per unit area of the gate dielectrics and measured value of 6.6 nFcm^{-2} at 100 Hz, μ is the carrier mobility and V_{th} is the threshold voltage. For an OFET (T_{bias} = 1 min), V_{th} and the on/off current ratio was -12.9 V and 1.2×10^2. The mobility was calculated to be 0.13 cm^2 V^{-1} s^{-1}.

Figure 3a shows the plot of the square root of I_D versus V_G (V_D = -30 V) for the OFETs with ion-dispersed gate dielectrics at different T_{bias} (V_{ex} = -30 V). The V_{th} clearly decreased with increasing T_{bias} and over 10 V reduction of V_{th} was easily achieved after 19 min. The amount of the V_{th} reduction was much larger than that we obtained using

polarized gate dielectrics with the alignment of permanent dipoles [7]. The capacitance measurement of the ion-dispersed gate dielectrics revealed that the dielectric permittivity of the gate dielectrics did not changed after T_{bias} was applied. These results are consistent with our proposed mechanism such that the shift of the V_{th} is mainly due to the polarization formed by the separated ion pairs in the gate dielectrics [15].

Figure 3b shows the changes of V_{th} as a function of T_{bias} and the bias direction. Through a linear fit and its intercept ($I_D^{1/2} = 0$) of the plot of the square root of I_D versus V_G, V_{th} was estimated. After the measurement of the V_{th} with negative bias (V_{ex} = -30 V), applying the V_{th} with the positive bias (V_{ex} = 30 V) enable to return to the initial V_{th}. As shown in Fig 3b, the V_{th} was decreased from -12.9 V to -2.9 V with the negative bias and increased from -2.9 V to -17.0 V with the positive bias. These results clearly demonstrate that the direction and magnitude of the polarization of gate dielectrics were controlled by changing the bias direction and T_{bias}.

3.2 UV-VIS differential absorption spectra

Figure 4a shows the reflection absorption spectra of the device at V_{ex} = 0 V. The peak at around 450 nm is attributed to $MPA^+ClO_4^-$ ion, the two peaks at 600-700 nm are the absorption of pentacene[13] and the broad absorption 800 nm is attributed to the interference of PMMA dielectrics. As discussed before, the dominant charging mechanism may switch from the electrostatic to electrochemical with increasing T_{bias}. Figure 4b shows the UV-VIS differential absorption spectra, which were obtained by subtracting the spectra at V_{ex} = 0 V from those applied at V_{ex} = -30 V for T_{bias} = 5 min, 10 min and 30 min. Several features in the spectral shape were observed with increasing T_{bias}. At T_{bias} = 5 min, a small peak appears at 680 nm and the intensity of peak at 670 nm was slightly decreased. The

origins of the new peak at 680 nm and the bleaching at 670 nm would be explained by two scenarios. The one was the Franz-Keldysh effect caused by electrostatically polarized gate dielectrics and the other was the electrochemical doping effect caused by migrated ClO_4^- anions. In the former, the edge of an absorption peak shifts towards lower energy with increasing an external static electric field[16]. In the later, the shape of the absorption spectra does not change but the intensity of the absorption peak decreases with increasing the electrochemical doping levels [10]. In the absorption spectra at T_{bias} = 5 min, the new peak at 680 nm can be attributable to the shift of absorption edge due to Franz-Keldysh effect and the decrease in the intensity at 670 nm can be ascribed to electrochemical doping effect. Judging from the results of that no increase in I_D was observed up to T_{bias} = 9 min in Fig. 2d, the charging mechanisms of the OFETs at T_{bias} = 5 min would be electrostatic. On the other hand, the decrease in the intensities at 580 nm and 670 nm was clearly observed with increasing T_{bias}. These results suggest that the pristine pentacene was doped when T_{bias}=10 min and 30 min. Since output characteristics at T_{bias} = 19 min shows the increase of the I_D as a function of gate voltage and saturation of I_D is no longer clearly observed (Fig. 2c), the active layer of OFETs is mainly charged by electrochemically with increasing T_{bias}.

In conclusion, we have demonstrated the threshold voltage shift of OFETs using ion-dispersed gate dielectrics. The ion migration was largely effect on the electrical characteristics of OFETs, where over 10 V decrease of V_{th} were easily achieved. The shift direction of was controlled by the direction of the polarization. In addition, further application of the T_{bias} caused the electrochemical reaction between the dispersed ions and the active layer. The active layer was charged not only electrostatically but also electrochemically as increasing T_{bias}.

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Figure captions

FIG. 1. (a) Schematic representations of OFETs with an ion-dispersed polymer for the gate dielectrics. (b) Chemical structure of 10-methyl-9-phenylacridinium Perchlorate. ($MPA^+ClO_4^-$) (c) Schematic representations of ion dispersion in the gate dielectrics. (d) Schematic representations of space charge polarization after ion migration in the gate dielectrics.

FIG. 2. Output characteristics of the OFET by external electric field of V_{ex} = -60 V at (a) T_{bias} = 1 min, (b) T_{bias} = 9 min and (c) T_{bias} = 19 min. The gate voltages were changed from 6 V to -30 V with the step of -3 V. (d) Transfer characteristics (V_D = -30 V) for the OFETs with ion-dispersed gate dielectrics depending at various T_{bias} (T_{bias} =1 min, T_{bias} =9 min and T_{bias} =19 min).

FIG. 3. (a) The plot of the square root of I_D versus V_G (V_D = -30 V) for OFETs with ion-dispersed gate dielectrics depending at various T_{bias} (T_{bias} =1 min, T_{bias} =9 min and T_{bias} =19 min). (b) Changes of V_{th} depending on the T_{bias}. Negative bias was applied for T_{bias} = 0 min to 19 min and positive bias was applied for T_{bias} = 19 min to 38 min.

FIG. 4. (a) Absorption spectra of the capacitor conformation device. The inset shows that the absorbance spectra of pentacene thin-film, MPA^+ClO4^- in acetonitrile and PMMA film. (b) The UV-VIS difference absorption spectra under different T_{bias}. Baseline correction was done by a 2-point baseline using straight line between 400 nm and 830 nm.

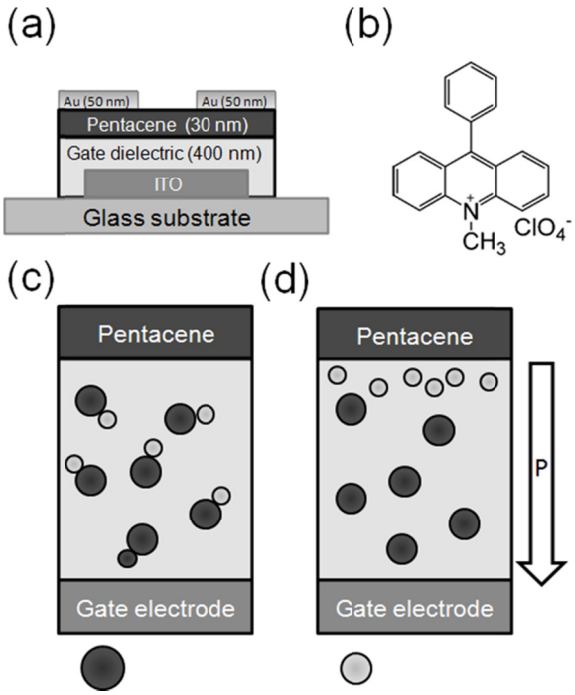

Figure 1

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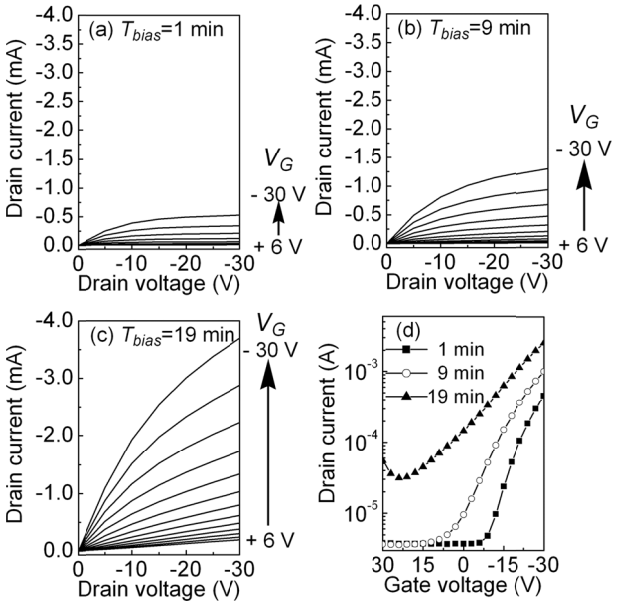

Figure 2

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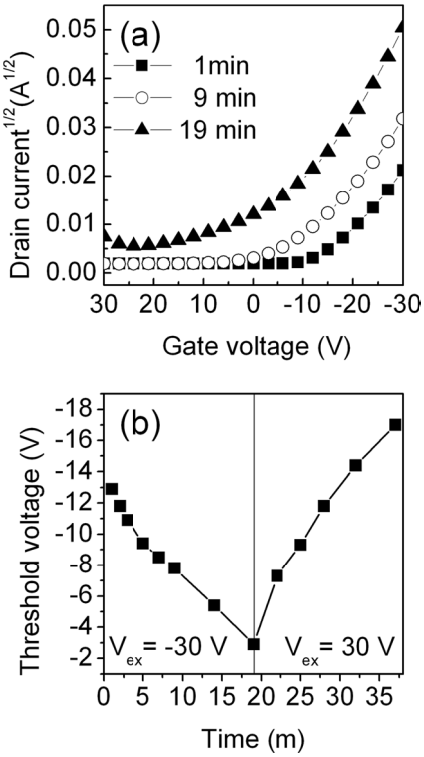

Figure 3

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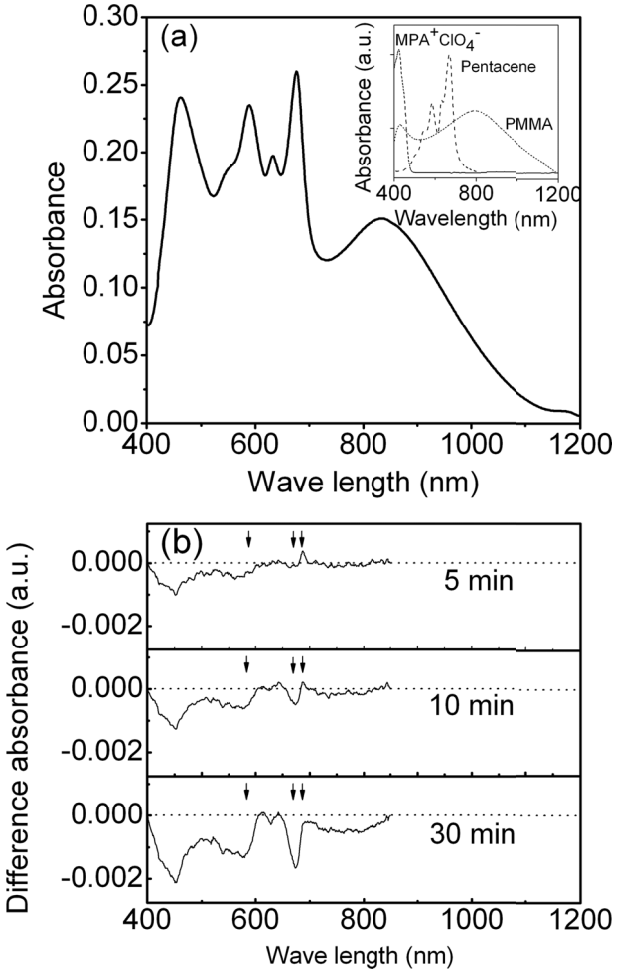

Figure 4

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