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The influence of gate dielectrics on a high-mobility n-type conjugated polymer in organic thin-film transistors

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Organic thin-film transistors based on a high mobility n-type semiconductor poly{[n,n9-bis (2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,59-(2,29-bithiophene)} P(NDI2OD-T2) and different polymer gate dielectrics are fabricated. The average electron mobility decreases from 0.76 to 0.08 cm^2/Vs with the increase of the gate dielectric constant from 2.6 to 7.8. The P(NDI2OD-T2) film shows unconventional face-on molecular packing, which results in short distances and pronounced interactions between electrons and gate dielectric. Therefore, the decrease of the electron mobility with the increasing dielectric constant is attributed to the Fröhlich polaron effect for the interaction between electrons in the channel and ionic polarization cloud in the gate dielectric. © *2012 American Institute of Physics*. [doi:10.1063/1.3678196]

Solution processable organic thin-film transistors (OTFTs) based on conjugated polymers have been extensively studied for various applications, including flexible displays, radio frequency identification tags, sensors, and memories, etc.[1–4] Recently, the n-type conjugated polymer poly{[n,n9-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,59-(2,29-bithiophene)} (P(NDI2OD-T2)) has attracted much attention for its high electron mobility (up to 0.85 cm^2/Vs), high stability in ambient conditions, and large solubility in comment solvents.[5] One interesting property of P(NDI2OD-T2) is the carrier mobility that is not sensitive to the dielectric constant of the gate insulator, which is different from many p-type organic semiconductors that exhibit lower mobility for higher gate dielectric constant.[6,7] However, the gate dielectrics employed in the P(NDI2OD-T2) OTFTs have low relative dielectric constants that are between 2.0 and 3.6 while high-k gate dielectrics have not been used to test the effect.[5] Therefore, we fabricated and studied OTFTs with different gate dielectrics with the relative dielectric constants ranging from 2.6 to 7.8.

P(NDI2OD-T2) (ActivInk™ N2200) was ordered from Polyera Co. and used without further purification. Polystyrene (PS, *M*w = 3.5 kDa), poly(methyl methacrylate) (PMMA, *M*w = 996 kDa), poly(4-vinylphenol) (P4VP, *M*w = 1.1 kDa), poly(4-vinylphenol-*co*-methyl methacrylate) (P4VP-*co*-PMMA, *M*w = 10 kDa), and poly(vinyl alcohol) (PVA, *M*w = 146-186 kDa) were purchased from Sigma-Aldrich. Figure 1(a) shows the schematic diagram of a top-gate OTFT. Cr/Au films were evaporated on the surfaces of glass substrates as source and drain electrodes through a shadow mask. The channel length (L) and width (W) were 100 μm and 2 mm, respectively. P(NDI2OD-T2) was dissolved in toluene at the concentration of 5 mg/ml and spin-coated on the substrates, followed by thermal annealing at the temperature of 120 °C for 1 h in a N_2-filled glovebox. Figure 1(b) shows the atomic force microscopy (AFM) image of a P(NDI2OD-T2) polymer film that has the surface roughness (rms) of about 0.82 nm. The film consists of fibrils that are about 20–30 nm wide and up to micrometer long, which is similar to the films reported before.[5]

Subsequently, PS, PMMA, P4VP, and P4VP-*co*-PMMA polymers dissolved in methyl ethyl ketone (MEK) and PVA polymer dissolved in deionized water were spin-coated on top of the P(NDI2OD-T2) films to form the gate insulator layers. The thicknesses of the PS, PMMA, P4VP, P4VP-*co*-PMMA, and PVA polymer layers were 660 nm, 630 nm, 530 nm, 420 nm, and 810 nm, respectively. Then the samples were annealed at 60 °C for 3 h in the glovebox. Finally, Al gate electrodes were evaporated on top of the devices through a shadow mask. The OTFTs were characterized with a semiconductor parameter analyzer (Agilent 4156C) in the glovebox.

Figures 2(a) and 2(b) show the transfer and output characteristics of an OTFT based on P(NDI2OD-T2) and PS as the active layer and gate dielectric, respectively. The device shows linear carrier mobility of 0.62 cm^2/Vs and on/off ratio of 10^6. Figure 2(c) show the performance of an OTFT based on P4VP gate dielectric. The carrier mobility and on/off ratio are 0.15 cm^2/Vs and 10^4, respectively. Figure 2(d) shows the average saturation and linear mobilities of P(NDI2OD-T2) with different gate dielectrics. For each dielectric, more than ten devices were fabricated and the average mobility was calculated. The maximum saturation mobility is 0.96 cm^2/Vs for the device with PS gate dielectric, which is higher than the value obtained by Yan *et al.*[5] It is interesting to find that the carrier mobility decreases with the increase of dielectric constant, being different from the conclusions reported before.[5] For the device with PVA gate dielectric, the carrier mobility is only about 0.1 cm^2/Vs. All of the parameters of the OTFTs are also shown in Table I.

To better understand the effect of the dielectric constant on the carrier mobility of P(NDI2OD-T2), we measured the devices at different temperatures. As shown in Figure 3(a),

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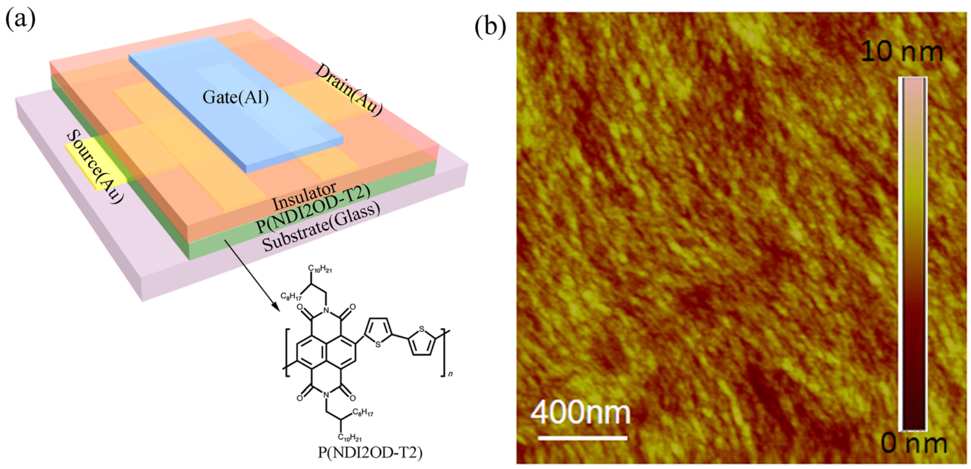

FIG. 1. (Color online) (a) Schematic diagram of a top-gate OTFT based on P(NDI2OD-T2) and (b) AFM image of a P(NDI2OD-T2) film spin-coated on a glass substrate.

the carrier mobility increases with the increase of temperature. The relationship between the carrier mobility μ and the temperature T can be fitted with the equation $\mu = \mu_0 \exp(-\Delta/k_B T)$, where μ_0 is the mobility prefactor, k_B is the Boltzman constant, and Δ is the thermal activation energy.[8] The activation energy increases with the increase of dielectric constant as shown in Table I.

The gate dielectric of an OTFT may influence the carrier transport in the organic semiconductor due to the following two possible effects. Veres *et al*. reported that a high-k gate dielectric can induce a broader distribution of density of states in the organic semiconductor of an OTFT due to the electrostatic dipole disorder in the gate dielectric and thus the carrier mobility is decreased.[6] The second effect is the formation of Fröhlich polarons (quasiparticle) in the organic semiconductor due to the interaction between the carriers and the ionic polarization cloud in the gate dielectric.[7] For the above two effects, the interactions between gate dielectric and carriers in the channel are very sensitive to the distance.[6,7] It is noteworthy that P(NDI2OD-T2) has long side chains, which can separate the backbone of the polymer chain from the gate dielectric.[5] Therefore, the separation between the backbone of P(NDI2OD-T2) chain and the gate dielectric is related to the orientation of the molecular packing (π-staking) of P(NDI2OD-T2). Figure 3(b) shows the grazing incidence x-ray diffraction (GIXD, Regaku 9 KW SmartLAB) pattern of a P(NDI2OD-T2) film coated on a glass substrate. We can find a high (010) peak in the out-of-plane diffraction pattern while none in the in-plane pattern, indicating that the polymer film is dominated by face-on molecular packing,[9] which is different from some high-mobility conjugated polymers, such as poly(3-hexylthiophe).[1] The face-on molecular packing implies a short distance between the backbone of P(NDI2OD-T2) and the gate dielectric as shown in the inset of Figure 3(b) although it is difficult to decide the distance accurately.

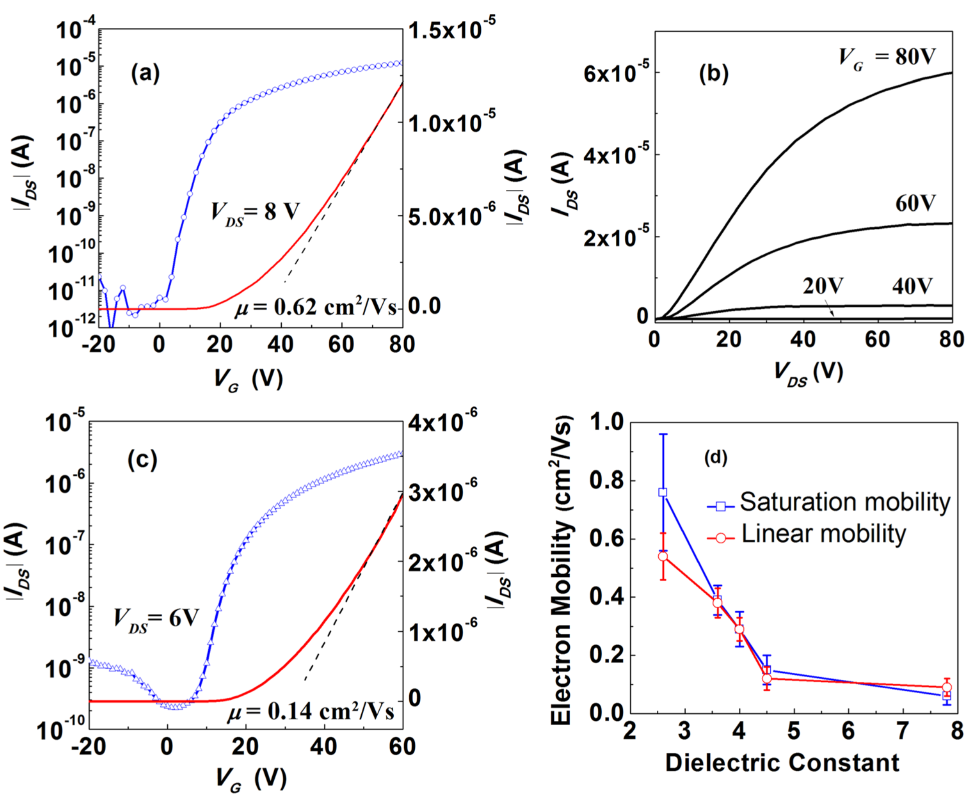

FIG. 2. (Color online)(a) Transfer characteristics ($I_{DS} \sim V_G$, $V_{DS} = 8$ V) and (b) output characteristics ($I_{DS} \sim V_D$) of an OTFT based on P(NDI2OD-T2) and PS gate dielectric. (c) Transfer characteristics of an OTFT with P4VP gate dielectric. (d) Carrier mobilities as functions of the relative dielectric constants of gate insulators.

TABLE I. The parameters of P(NDI2OD-T2) OTFTs with different gate dielectrics.

Dielectric	PS	PMMA	P4VP-*co*-PMMA	P4VP	PVA
ε_s	2.6	3.6	4.1	5.3	7.8
ε_∞	2.5	2.2	—	2.4	2.4
β	0.003	0.041	—	0.065	0.092
μ_{sat} (cm^2/Vs)	0.76 ± 0.15	0.4 ± 0.05	0.30 ± 0.06	0.15 ± 0.05	0.08 ± 0.03
μ_{lin} (cm^2/Vs)	0.54 ± 0.08	0.38 ± 0.05	0.29 ± 0.04	0.12 ± 0.04	0.09 ± 0.03
E_b (meV)	38.1	40.1	34.9	39.2	36.7
Δ (meV)	79	92	—	126	—

Next, we will discuss the effect of gate dielectrics on OTFTs based on P(NDI2OD-T2). Assuming the density of states $N(E)$ in an organic semiconductor is given by $N(E) = (N_t/E_b)e^{-E/E_b}$, where N_t represents the total concentration of trap states and E_b is the distribution width of the exponential traps, the channel current of a transistor I_{DS} (when $V_{DS} \ll V_G$) is given by[8,10,11]

$$I_{DS} = A(V_G - V_{FB})^{(2E_b/kT)-1}, \quad (1)$$

where A is a parameter, V_{FB} is the flatband voltage, and T is the temperature. The transfer curves of all OTFTs can be fitted very well with Eq. (1) and the distribution width E_b can be extracted as shown in Table I. It is interesting to find that E_b is very similar in the P(NDI2OD-T2) OTFTs with different gate dielectrics. Therefore, the electrostatic dipole disorder in the gate dielectric is not the main reason for the different carrier mobilities in the OTFTs. Richards *et al.*[12] reported that the influence of the electrostatic dipole disorder in the gate dielectric on the distribution of states in an organic semiconductor only exists in a short distance and the effect will be very weak when the distance is more than 3 Å. Therefore, this effect is negligible in the OTFTs.

For the effect of Fröhlich polaron, the polaron binding energy E_p decreases with the reciprocal of the distance to the gate dielectric,[7] whereas the dipole interaction between the gate dielectric and the active layer falls off with the inverse square of the distance.[12] So the Fröhlich polaron effect may be more pronounced in OTFTs based on conjugated polymers with side chains. According to the variable temperature measurements, the activation energy increases with the increase of dielectric constant. Mobility edge (ME) model is normally used for describing the carrier transport in OTFTs based on high-mobility organic semiconductors.[11,13,14] The thermal activation energy of the carrier mobility Δ is given by $\Delta = E_p/2 + E_{FM}$, where E_{FM} is the energy difference between the Fermi level and the mobility edge.[8] E_p is the polaron binding energy of the small polarons formed in the organic semiconductor due to the carrier-lattice[15] and carrier-dielectric[7] interactions. So the Fröhlich polaron binding energy E_p in P(NDI2OD-T2) is given by[7]

$$E_p = 2\Delta - E_{FM} = \frac{a_B}{z}\beta(\mathrm{Ryd}), \quad (2)$$

where $a_B = 0.53$Å is the Bohr radius, z is the interaction distance, Ryd = 13.6 eV is the Rydberg constant and β is a parameter for the ionic polarizability of the interface, which is related to the dielectric constants of the gate dielectric[16] (ε_s, ε_∞) and P(NDI2OD-T2) ($k = 3$) and given by $\beta = (\varepsilon_S - \varepsilon_\infty)/((k + \varepsilon_S)(k + \varepsilon_\infty))$. $\varepsilon_\infty = n_d^2$, n_d is the refractive index of the gate dielectric. Assuming the increase of Δ is due to the Fröhlich polaron effect, we estimate the interaction distance z to be 5.3 Å by fitting the relationship between Δ and β with Eq. (2) as shown in the inset of Figure 3(a). So the interaction distance is a reasonable value for P(NDI2OD-T2) chains with face-on molecular packing.

In conclusion, high performance n-typed OTFTs based on P(NDI2OD-T2) and different gate dielectrics are fabricated. We observe the influence of the gate dielectric constant on the carrier mobility in the OTFTs. P(NDI2OD-T2) shows

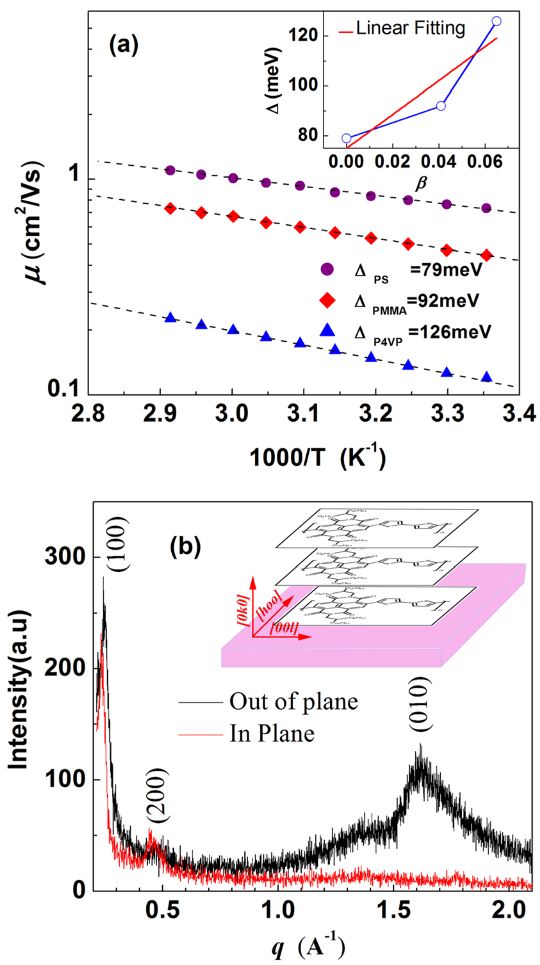

FIG. 3. (Color online) (a) Saturation mobilities in OTFTs with different gate dielectrics (PS, PMMA, P4VP) measured at variable temperatures. The dashed lines show the fitting of the results with the equation $\mu = \mu_0 \exp(-\Delta/k_B T)$. Inset: The activation energy Δ as a function of β. (b) GIXD pattern of a P(NDI2OD-T2) film under in-plane and out-of-plane x-ray scattering.

unconventional face-on molecular packing, which induces a relatively short distance and a pronounced interaction between a carrier and gate dielectric. By fitting the device performance, we find that the Fröhlich polaron effect is the main reason for the decreased electron mobility with the increase of the gate dielectric constant in the n-type OTFTs.

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