

Polymer Dielectrics and Orthogonal Solvent Effects for High-Performance Inkjet-Printed Top-Gated P-Channel Polymer Field-Effect Transistors

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We investigated the effects of a gate dielectric and its solvent on the characteristics of top-gated organic field-effect transistors (OFETs). Despite the rough top surface of the inkjet-printed active features, the charge transport in an OFET is still favorable, with no significant degradation in performance. Moreover, the characteristics of the OFETs showed a strong dependency on the gate dielectrics used and its orthogonal solvents. Poly(3-hexylthiophene) OFETs with a poly(methyl methacrylate) dielectric showed typical p-type OFET characteristics. The selection of gate dielectric and solvent is very important to achieve high-performance organic electronic circuits.

Keywords: Inkjet-printing, OFET, dielectric, solvent.

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I. Introduction

Solution-processed conjugated molecules enable the manufacturing of a variety of low-cost electronic devices by unconventional patterning methods such as inkjet, screen, or gravure printing with high throughput [1], [2]. Although organic field-effect transistors (OFETs) using conjugated molecules as an active layer are not suitable for electronics requiring high charge-carrier mobility due to an intrinsic limitation, their advantage in terms of manufacturing make them ideal for large-area, flexible, transparent, and disposable electronic devices, such as drivers for flexible or transparent displays [3]-[5], digital circuits for radio frequency identification (RFID) tags [6], sensors [7], and memory [8]-[10]. Moreover, the charge-carrier mobility of state-of-the-art organic semiconductors is comparable with amorphous silicon transistors, and thus many applications will be replaced by cost-effective OFETs in the near future. For the last decade, high-performance organic semiconductors have been actively developed to achieve comparable mobility with amorphous silicon [11]-[13]. Controlling the physical chemistry at a semiconductor/dielectric interface is also quite important to optimize the device performance since OFETs are operated through the modulation of a charge carrier flow at one and two monolayers of a semiconductor/dielectric interface [14]. One dramatic example is the generation of n-type transporting in conventional conjugated polymers via a junction with a hydroxyl-free dielectric interface [15], [16].

Top-gate/bottom-contact (TG/BC) OFETs have many advantages compared with other bottom-gate geometries such as

a relatively low contact resistance, better environmental stability of organic semiconductors due to the auto-encapsulation effect of the overlaid gate, and the gate dielectric layer [17], [18]. Nevertheless, top-gate OFETs have not been popularly used by many research groups due to difficulties in the deposition of two organic layers serially through a solution process without dissolution or swelling of the underlayer. In particular, conjugated polymers or solution-processed small molecules are dissolved in similar solvents for typical polymer insulators, for example, poly(methyl methacrylate) (PMMA) and polystyrene (PS). In addition, a wet process must be conducted on the relatively weak conjugated molecules enabling unwanted chemical deterioration of the active materials, for example, oxidation or reduction due to chemical doping. In a top-gate structure, a semiconductor/dielectric interface is formed by the reversed process in terms of bottom gate structure, that is, solution deposition of an insulating polymer on solid conjugated molecules. It is naturally expected that the characteristics of top-gated OFETs depend not only on gate dielectrics and interface chemistry but also on the solvents and processing conditions of gate dielectrics because the surface of a semiconducting layer can be slightly changed into a more reactive quasi-liquid state by contact with the solvent of the gate dielectrics if the solvent does not show perfect orthogonality to the semiconductor. Moreover, when semiconductor films are patterned by printing methods, such as inkjet or gravure printing rather than spin-coating, this typically induces a rough top surface. This rough interface can be a problem in that it deteriorates the efficient charge transport in the semiconductor/dielectric interfacial layer.

Herein, we report effects of gate dielectrics and solvents on the characteristics of top-gated p-channel polymer FETs. Typical p-type conjugated polymers are inkjet-printed, and various gate dielectric polymers and orthogonal solvents are used here to investigate the interfacial phenomena (see Fig. 1). Orthogonal solvent means that solvents dissolve a gate insulating polymer but does not dissolve an underlaid semiconducting polymer; thus, it enables the deposition of several polymer films through a solution processes without damage to the underlaid film. Inkjet-printed p-channel polymer FETs show a strong dependency of transistor characteristics on the chemical properties of gate dielectrics and the solubility of the gate dielectric solvent to overlaid conjugated polymers, but a relatively weak dependency on the rough top surface of the inkjet-printed polymer semiconductor in top-gated polymer OFETs.

II. Experiment

1. Fabrication of Organic Field-Effect Transistors

Corning Eagle 2000 glass slides were used as substrates after

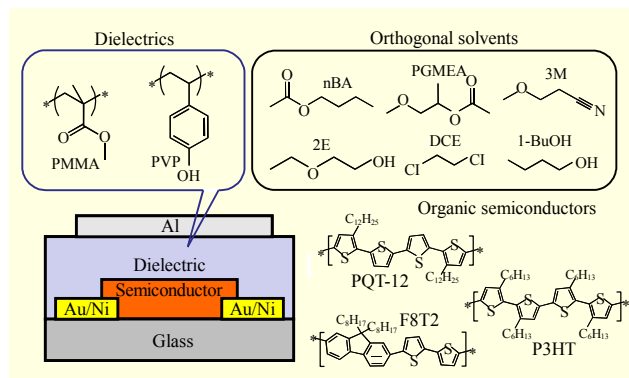


Fig. 1. Schematic device configuration of a top-gate/bottom-contact polymer FET and chemical structure of polymer gate dielectrics (PMMA and PVP) used as solvents for gate dielectric coating (nBA, PGMEA, 3M, 2E, DCE, and 1-BuOH) and semiconducting polymers (PQT-12, P3HT, F8T2).

cleaning sequentially in an ultrasonic bath with deionized water, acetone, and isopropanol for 10 min each. Gold (Au) patterns for the source and drain electrodes were fabricated using a conventional photolithography technique. The semiconducting polymers, poly(3-hexylthiophene) (P3HT, Rieke Metal Inc.), poly(3,3'-dialkyl-quaterthiophene)s (PQT-12, American Dye Source, Inc.), and poly(9,9-dioctylfluorene-alt-bithiophene) (F8T2, American Dye Source Inc.) were dissolved in anhydrous chlorobenzene (CB) or p-xylene for ca. 5 mg/ml, respectively, and the solution was then filtered via a 0.2 μm PTFE syringe filter before inkjet-printing. Inkjet-printing was carried out using a custom-built research inkjet printer (UJ 200MF, Unijet Inc.) in the air of a clean room laboratory facility. A piezoelectric drop-on-demand dispensing head (Microfab Tech. Inc.) with a 50 μm orifice diameter was used at an operation frequency of 1 kHz.

For the case of P3HT and F8T2, the films were annealed at 110°C for 30 min to remove the solvent in a nitrogen filled glove box with low oxygen and moisture level (<5 ppm). PQT-12 films were annealed at 135°C for 20 min and slowly cooled down to room temperature. For the polymer dielectric layer, PMMA (Aldrich, MW=120,000) or poly(4-vinyl phenol) (PVP, Aldrich, MW=20,000) was used without further purification. PMMA (80 mg/ml) and PVP (80 mg/ml) were dissolved in anhydrous n-butyl acetate (nBA), propylene glycol methyl ether acetate (PGMEA), 3-methoxypropionitrile (3M), 2-ethoxyethanol (2E), 1,2-dichloroethane (DCE), and 1-butanol (1-BuOH), and spin-coated at 2,000 rpm for 1 min. The films were annealed at 80°C for 1 h in the same glove box. Top-gated transistors were completed by the formation of a gate electrode on the active region of the transistors via evaporation of thin aluminum (Al) films with a shadow mask. The completed OFET device structure and molecular structures of

the polymer semiconductors, gate dielectrics, and orthogonal solvents are represented in Fig. 1.

2. Characterization

The electrical characteristics were measured with a Keithley 4200-SCS in a nitrogen-filled glove box. The transistor parameters, such as charge carrier mobility (μ_{FET}) and threshold voltage (V_{Th}), were calculated in the saturation regime using the standard formalism for FETs [19]. The surface morphology of films was investigated by atomic force microscope (AFM, Nanoscope III, Veeco Instrument Inc.) via tapping-mode. UV-Vis-near IR absorption spectra were measured using a Shimadzu UV-3600 spectrometer. The surface topology of the inkjet-printed features was measured using an XP-1 surface profiler system (Ambios Technology). Cross-section transmission electron microscope (TEM) images of the inkjet and spin-coated P3HT FETs were processed by a dual beam focused ion beam (DB-FIB) (Helios NanoLabTM, FEI) after completing the fabrication of the FET devices, and the images were captured using a 200 kV field-emission transmission electron microscope (FE-TEM) (JEM-2100F, JEOL Ltd.).

III. Results and Discussions

1. Inkjet-Printed Polymer Semiconductors

The formation of stable and uniform droplets can be considered a key step in an inkjet printing process. The diameter, volume, and velocity of the P3HT inkjet droplets were measured as ca. 33 μm , 16.1 pl, and 3.5 m/s, respectively. After the formation of inkjet droplets, the P3HT solution was directly printed onto a glass substrate with a substrate temperature (T_s) of 25°C without any surface treatment. An optical microscope image of the inkjet-printed P3HT features is shown in Fig. 2(a). The printed active features could be modified by changing the printing parameters (pixel number, pixel pitch, drop number, and drop pitch) and jetting parameters (drop volume, drop velocity, and operation frequency of the piezoelectric nozzle).

The thickness profiles of the inkjet-printed P3HT lines had very rough surface topology with thickness deviation of ~ 30 nm. The thickness profiles of the inkjet-printed P3HT lines were measured using a surface profiler, as represented in Fig. 2(b). Rough surface topology resulted from the “coffee-ring” effect during the inkjet printing process. The coffee-ring effect is a frequently observed remarkable phenomenon of inkjet-printed features on a non-absorbing substrate, such as glass and Si-wafers. Deegan and others first explained that the ring is produced because the contact line is pinned, and thus solvent

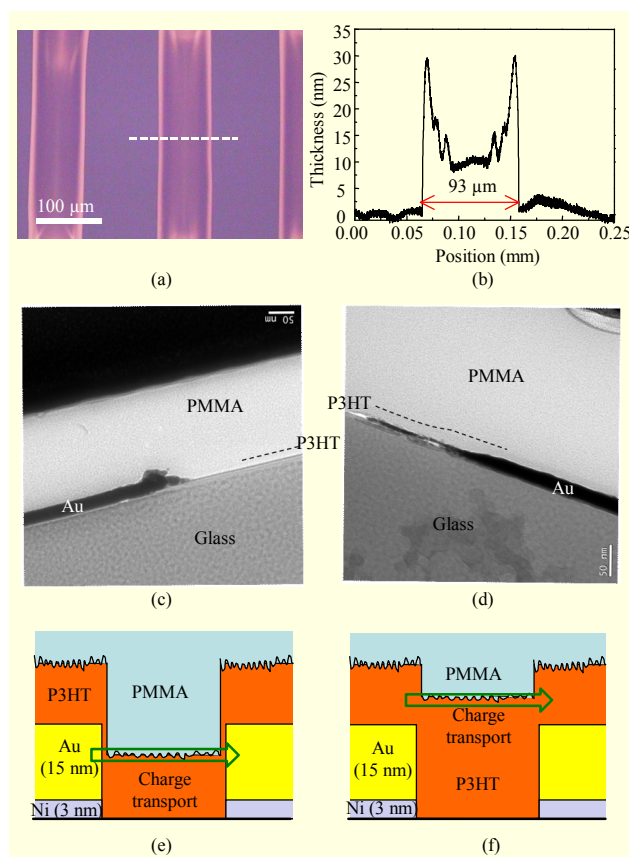


Fig. 2. (a) Inkjet-printed P3HT active feature, (b) surface profile, (c) TEM image of inkjet-printed P3HT, (d) TEM image of spin-coated P3HT devices, (e) schematic illustration of charge transport in inkjet-printed, and (f) schematic illustration of spin-coated P3HT devices.

lost by evaporation at the droplet’s edge must be replaced by solvent drawn from the center of the droplet [20]. The flow bringing fluid from the center to the edge of the droplet also carries solute, which is deposited in a ring at the edge as the solvent evaporates there [20]. Hu and others reported that the coffee-ring phenomenon requires not only a pinned contact line and high evaporation rate near the droplet’s edge, but also the suppression of the Marangoni effect resulting from the latent heat of evaporation [21]. For clean interfaces, free of surfactants, the Marangoni flow reverses the coffee-ring phenomenon and produces deposition at the droplet center rather than at the edge [21].

The propensity was for the P3HT molecules to be deposited at the boundaries of a printed feature, which was caused by the higher evaporation rate of the CB solvent at a droplet’s pinned contact line compared to its center. In addition, the CB solvent normally induced more pronounced coffee-ring features than those of toluene and o-xylene solvents. This may have been caused from the contact angle differences formed by the printed drop on the substrate and the clustering of polymer

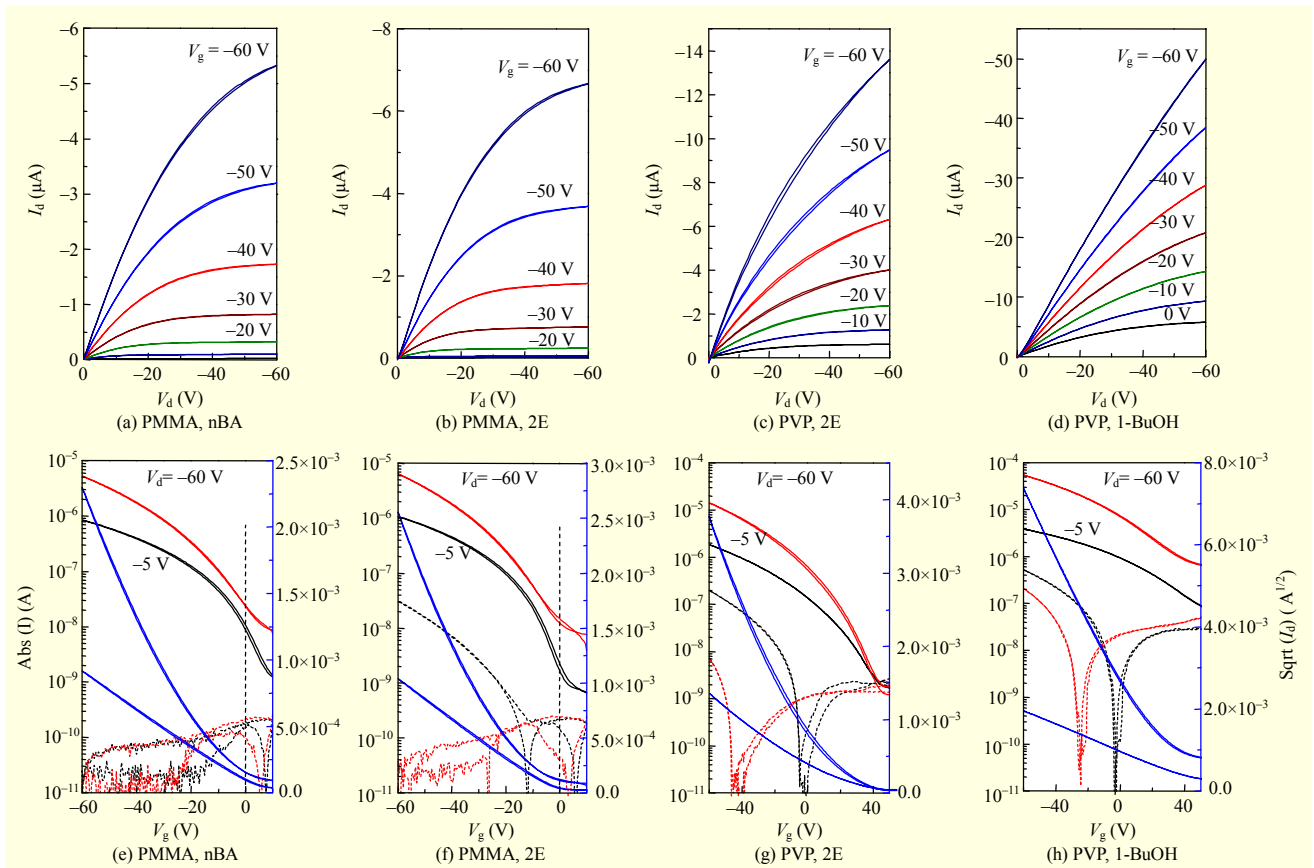


Fig. 3. Output and transfer characteristics of top-gated P3HT transistors with PMMA [solvent: (a), (e) nBA or (b), (f) 2E] or PVP [solvent: (c), (g) 2E or (d), (h) 1-BuOH] gate dielectrics.

chains due to physical cross-links by different interaction energies between the polymer molecules and organic solvents [22]. The coffee-ring effect could be reduced by printing onto a heated substrate, which causes a reduction in the material transfer to the contact line since there is an increase in the evaporation rate at every point of the deposited feature, or by increasing the amount of solute. As another promising idea for solving this problem, Lim and others used additional solvent with low surface tension energy and a high boiling point. The addition to the solution resulted in a recirculation flow in single droplets induced by a Marangoni flow (surface-tension-driven flow), which arises during the drying processes in the direction opposite to the convective flow [23]. However, because of the limited solubility (gelling) to other organic solvents for P3HT or typical conjugated polymers, it was difficult to find other good organic solvents rather than chlorinated solvents reducing the coffee-ring effect.

2. Charge Transport in Inkjet-Printed Polymer Field-Effect Transistors

As can be seen in Figs. 3(a) and 3(e) and Table 1, in spite of the very rough top-surface topology of the inkjet-printed P3HT

Table 1. Device characteristics of top gate p-channel or n-channel polymer transistors ($L=20\text{ }\mu\text{m}/W=1\text{ mm}$) with PMMA or PVP dielectric formed from various solvents.

Active	Dielectric (Solvents)	μ_{FET} (cm^2/Vs)	V_{Th} (V)	$I_{\text{on}}/I_{\text{off}}$
P3HT	PMMA ^{a)} (nBA)	0.02 to 0.04	-17 to -20	$\sim 5 \times 10^3$
	PMMA ^{b)} (2E)	0.03 to 0.04	-22 to -23	$\sim 5 \times 10^3$
	PVP ^{c)} (2E)	0.02 to 0.03	-1 to -5	$\sim 10^4$
	PVP ^{d)} (1-BuOH)	0.03 to 0.04	27 to 28	$\sim 10^2$
PQT-12	PMMA ^{a)} (nBA)	0.06 to 0.08	-17 to -19	$\sim 5 \times 10^3$
	PVP ^{d)} (1-BuOH)	0.05 to 0.06	-1 to -2	$\sim 10^3$

a) $t = 520 \sim 550\text{ nm}$, $C_i = 6.0\text{ nF}/\text{cm}^2$; b) $t = 470 \sim 480\text{ nm}$, $C_i = 6.2\text{ nF}/\text{cm}^2$; c) $t = 490 \sim 500\text{ nm}$, $C_i = 8.2\text{ nF}/\text{cm}^2$; d) $t = 480 \sim 500\text{ nm}$, and $C_i = 8.3\text{ nF}/\text{cm}^2$.

features, the OFET performances of the inkjet-printed devices did not degrade significantly (there were slight reductions in

the field-effect mobilities (μ_{FET}) of about 10% to 20%), compared to those of spin-coated OFET devices, which had smooth and flat top surfaces [24]. This can be presumably explained based on two main reasons: (i) the directions of the inkjet-printed lines were preferable for mobile charge transport, and (ii) there was efficient charge injection from the near edge of the Au S/D electrode.

In this study, the overlapped inkjet-printed lines had an orientation parallel to the charge transport direction of the interdigitated S/D electrode. Therefore, as expected, the surface morphology was very smooth in the parallel direction, especially in the region between the Au S/D electrodes, while the very rough top surfaces in the direction perpendicular to the inkjet-printed features might be much more problematic for the charge transport. It can also be considered that smooth areas in these rough microscopic areas show no significant degradation in the molecular ordering of inkjet-printed polymer semiconductors, although roughness at the macroscopic scale is quite significant.

To investigate the different charge injection and transport features of inkjet-printed and spin-coated OFET devices, cross-section images of these devices were obtained using focused ion beam milling and a transmission electron microscope (FIB-TEM) (Figs. 2(c) and 2(d)). In the case of an inkjet-printed device, a thin active layer (ca. 10 nm thick) in the central active area caused the direct injection of mobile charges from the edge of the Au source electrode and transport between the S/D electrodes. On the other hand, the spin-coated OFET devices showed that an active channel region was formed above the S/D electrode (ca. 30 nm thick film, with an overall covering of the Au electrode). Thus, charge injection occurred at both the edge and top-surface of the source electrode. These two different charge injection and transport models, between spin-coated and inkjet-printed OFET devices, could be applied to each of the devices. Schematic illustrations of these presumed models are shown in Figs. 2(e) and 2(f). However, these are only provisional models for the charge injection and transport behaviors. Thus, more sophisticated studies are required.

3. Organic Field-Effect Transistor Characteristics

The TG/BC P3HT FETs with PMMA gate dielectric showed good p-channel transistor characteristics, with a hole mobility $\sim 0.025 \text{ cm}^2/\text{Vs}$ and V_{Th} of ca. -23 V . The fundamental device parameters such as μ_{FET} , V_{Th} , and on/off ratio ($I_{\text{on}}/I_{\text{off}}$) are listed in Table 1. The properties of inkjet-printed P3HT FETs are comparable to those of spin-coated P3HT FETs [24]. Therefore, this can be attributed to a well-defined active area in combination with the TG/BC staggered device geometry, which is preferable for mobile charge injection and transport.

It is commonly known that photo-oxidation causes P3HT molecules to have an unstable property in ambient air because of their relatively low highest occupied molecular orbital (HOMO) energy level [25]. However, the inkjet-printed P3HT FETs with a top-gated structure in this study only showed a small performance degradation after exposure to air for a relatively long time, even when the inkjet printing process was carried out in air. This improved air-stability was due to a reduction process during thermal annealing in the N_2 -purged glove box ($\text{O}_2 < 5 \text{ ppm}$) before PMMA gate dielectric coating, along with the self-encapsulation effects of the top-gate dielectrics (low oxygen permeability of the PMMA film of ca. $29.1 \times 10^{-15} \text{ cm}^2/\text{Pa}\cdot\text{s}$) [26], and the blocking of illumination by external light by the upper-deposited gate electrode (Al), which plays a role in preventing the photo-oxidation reaction of P3HT molecules.

The small gate bias hysteresis behavior can be attributed to the low density of shallow trap sites in the semiconductor's active layer and/or interfaces between the semiconductor and gate dielectrics, which could be generated during the inkjet printing of the active channel layer or spin-coating of a top-gate dielectric layer. This phenomenon again verified that no significant performance degradation from the inkjet-printed OFET fabrication process was found, and the rapid recovery during the thermal annealing process in the N_2 inert condition presumably played a specific role in the low shallow trap density. In addition, the efficient injection of the mobile charge carriers (holes) into the active channel region from the bottom S/D electrode in the TG/BC device geometry was attributed to the low contact resistance, no super-linear output characteristics at the low drain voltage region, as shown in Figs. 3(a) through 3(d). In the staggered TG/BC configuration, mobile charges are not only injected from the edge of the electrode but also from those parts of the electrode that overlap with the gate electrode, contributing to a dependency of the current on the distance from the edge [27].

4. Effects of Polymer Gate Dielectrics and Orthogonal Solvents

To fabricate high-performance top-gated polymer transistors, the selection of benign gate dielectric solvent is quite important to avoid performance degradation via dissolution or swelling of semiconducting polymer providing interface roughness and/or molecular disorder. However, the processes used to find an orthogonal solvent require significant trial and error or know-how, and there is currently no general theory and methodology for selection. Some gate dielectric polymers, that is, fluorinated polymers (that is, Cytop) or PVP, can find a benign solvent relatively easily since common conjugated polymers

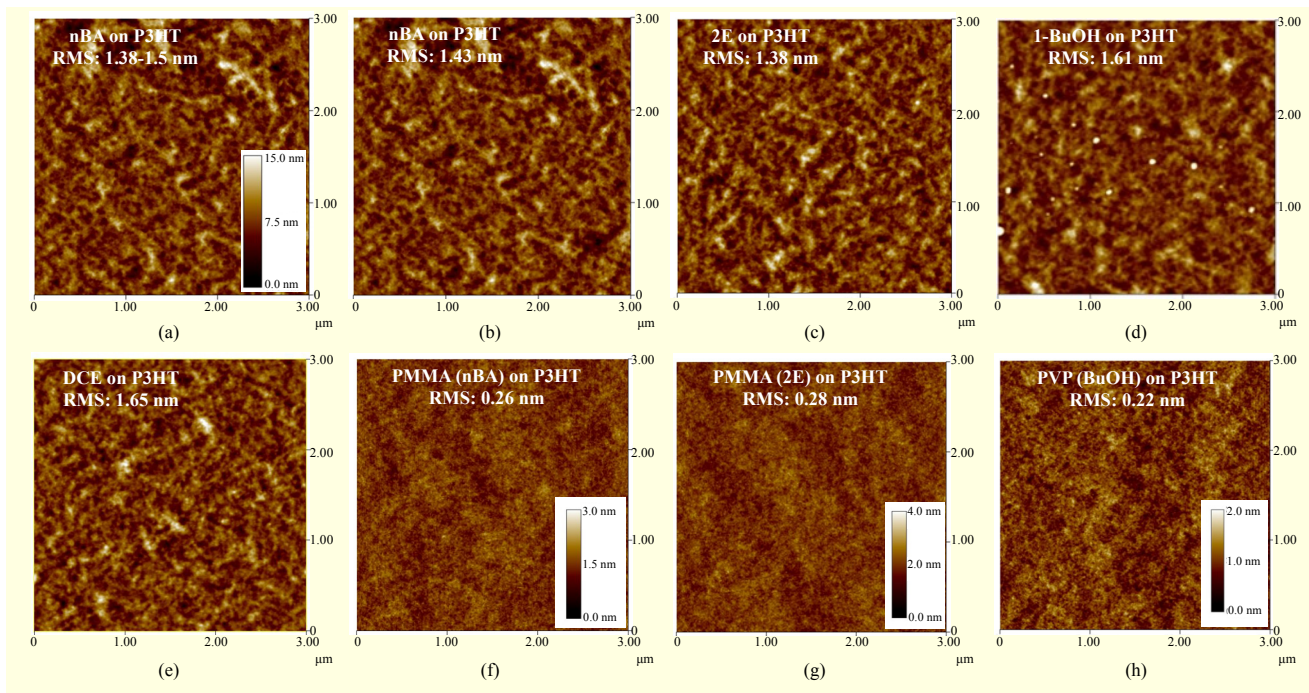


Fig. 4. AFM images of (a) bare P3HT film or solvent spin-coated P3HT film surfaces. (b), (c), (d), and (e) were taken after spin-coating (2,000 rpm, 1 min) of nBA, 2E, 1-BuOH, and DCE, and drying at hot plate (100°C, 30 min), respectively. AFM images of gate dielectric coated P3HT films with (f) PMMA (nBA), (g) PMMA (2E), and (h) PVP (1-BuOH).

do not dissolve their fluorinated or alcoholic solvent. For the case of PMMA and PS, however, it is more difficult to find suitable orthogonal solvents since they are typically dissolved in similar solvents with conjugated polymers. One simple way is by forcibly dissolving insulating polymers into the solvent, which requires heating and a long agitation time. The nBA for PMMA is a typical example for this case. Additionally, 2E can dissolve completely adequate concentrations of both PMMA and PVP after overnight agitation with slight heating. To this end, we chose nBA and 2E or 2E and 1-BuOH as orthogonal solvent for PMMA or PVP, respectively. The conjugated polymers used did not dissolve in these orthogonal solvents, and the roughness of the semiconducting polymer films is almost similar after 1-minute spin-coating of the solvents. As can be seen in Figs. 4(a) through 4(d), the root-mean-square (RMS) roughness of these P3HT films showed almost similar values with pristine P3HT film.

We fabricated top-gated P3HT FETs with four different conditions. Gate dielectric films were formed from PMMA in (i) nBA or (ii) 2E solvent, or from PVP in (iii) 2E or (iv) 1-BuOH solvent. The deposited films after spin-coating of PMMA or PVP showed a very smooth surface microscopically with less than 0.3-nm RMS roughness (3 $\mu\text{m} \times 3 \mu\text{m}$ in Fig. 4). Figure 3 exhibits typical output and transfer characteristics of these four P3HT FETs. All transistor parameters such as μ_{FET} and V_{Th} were calculated in the saturation regime using the

standard formalism for FETs [19] and are summarized in Table 1. Top-gated P3HT FETs with PMMA dielectric showed typical p-channel transistor characteristics operating in accumulation mode with almost zero onset voltage (V_{on}) regardless of the solvent used. The calculated μ_{FET} is as high as 0.02 - 0.04 cm^2/Vs and consistent with previous reports [28]. In addition, the performance is comparable with bottom-gate P3HT transistors with a SiO_2 insulator [29]. Note that the anhydrous and highly purified solvent must be used for the gate dielectric to avoid chemical contamination of active organic semiconductors by a small amount of water in the solvent. On the other hand, P3HT FETs with PVP dielectric showed a significant shift in V_{Th} and V_{on} in the positive direction, as shown in Figs. 3(g) and 3(h). We found that the large transfer curve shift is mainly induced not by the orthogonal solvent but by the gate dielectric PVP itself since a P3HT device with PMMA or PVP dielectric dissolved in same solvent (2E) showed quite different properties, as can be seen in Figs. 3(f) and 3(g). The significant shift of V_{Th} and V_{on} is due to accumulated holes in the P3HT/PVP interface, presumably due to negative charge transfer across the interface between P3HT and PVP and immobilization of transferred charge by trapping in the hydroxyl group of the PVP dielectric [15], [16] or immobile ions in the relatively polar PVP dielectric. The hydroxyl groups of PVP have a key role in the charge transfer and trapping since several groups have reported a stable

bottom-gated OFET (no transfer curve shift) with hydroxyl-free PVP by cross-linking with poly(melamine-co-formaldehyde) [30]–[32]. A significant shift of transfer curve by the charge transfer and trapping was also observed via a fluorinated self-assembled monolayer treatment at the semiconductor-gate dielectric interface [33] or through light irradiation at the transistors [34], [35].

Even though the solvent of the gate dielectric does not have as strong an effect as the gate dielectric itself on the characteristics of top-gated polymer transistors, it should be noted that careful selection of the orthogonal solvent can relieve the degree of V_{Th} and V_{on} shift in PVP devices to some extent. As shown in Figs. 3(g) and 3(h), P3HT transistors with PVP in 2E solvent showed smaller V_{Th} and V_{on} shifts than devices with PVP in 1-BuOH solvent. This result indicates that the preliminary doping effect of hydroxyl moiety in the solvent of the gate dielectric on P3HT is ignorable since both 2E and 1-BuOH solvents have similar amounts of hydroxyl moiety. The reason for this difference in the characteristics of PVP devices based on solvent has yet to be completely clarified. It might be a result from the difference in polarity [36] or solubility of the two solvents, that is, 2E and 1-BuOH to P3HT. The polarity of the solvents can modulate the semiconductor/dielectric interface state, and thus it has a strong correlation with the magnitude of V_{Th} shifts. 1-BuOH (solvent dielectric constant $\epsilon_r = 17.5$) was a more polar and thus more electronegative solvent than 2E ($\epsilon_r = 13.4$); therefore, a greater concentration of holes might be accumulated at the interface of P3HT/PVP dielectrics in a 1-BuOH solvent system.

The energy levels for semiconducting polymer have a key role in a transfer curve shift. Therefore, further evidence for the transfer curve shift in our top-gated polymer FETs with PVP dielectric could be verified through a comparison with a more ambient-stable conjugated polymer such as PQT-12 or F8T2. PQT-12, developed by the Xerox group, has shown better air and environmental stability than P3HT due to its lower energetic levels (oxidation potential), as shown in Figs. 5(a) and 5(c) [11]. Top-gated PQT-12 FETs with PVP in 1-BuOH showed a much lower shift of V_{Th} and V_{on} than those of P3HT FETs, shown in Fig. 5(a). Moreover, F8T2 FETs did not show a positive transfer curve shift, but a high V_{Th} due to a large charge injection barrier from Au electrode to the semiconductor, shown in Fig. 5(b). These are definitely due to the low-lying energetic levels of PQT-12 and F8T2, and thus the less-effective charge doping between the semiconductor and hydroxyl groups and/or ions in the PVP than P3HT FETs. In the UV/VIS/NIR absorption spectra, shown in Fig. (6), broad subband gap absorption at the infrared region in only the PVP-coated P3HT film indicates that spontaneous charge doping took place due to the hydroxyl moieties in PVP (mainly

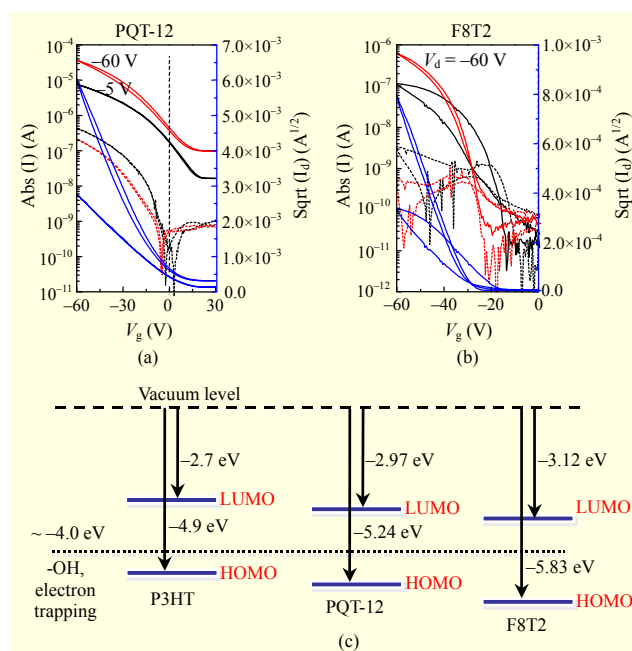


Fig. 5. Transfer curves of top-gated (a) PQT-12 and (b) F8T2 transistors with PVP gate dielectric (solvent: 1-BuOH), and (c) schematic diagram of energetic levels for PQT-12, P3HT, and F8T2, and electron trapping in a hydroxyl-group.

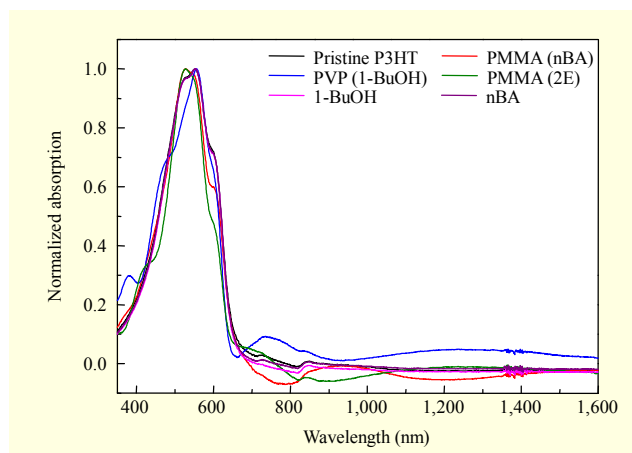


Fig. 6. UV/VIS/NIR absorption spectra of pristine P3HT, pure solvent spin-coating with nBA or 1-BuOH, PMMA (nBA and 2E), and PVP (1-BuOH) on P3HT.

electrons) via the junction of the PVP and P3HT films without any transistor operation. The subbandgap absorption was not seen in either the P3HT or PVP films. These observations indicate the presence of a ground-state charge transfer from P3HT into a hydroxyl group in PVP through the spontaneous removal of electrons (oxidation) at the interface [37]. Therefore, it can be concluded that the systematical shifts in transfer curves of top-gated polymer FETs originated from the charge doping by the polymer dielectric itself (here, mainly a hydroxyl

group) not by its orthogonal solvent.

The top-gated OFET device performance showed a strong correlation with solubility between the orthogonal solvent and semiconductors. The typical marginal solvent, that is, DCE, slightly dissolves the underlaid semiconductor film and induces molecular disorder, and thus the device performance is also dramatically degraded. The P3HT FETs with PMMA gate dielectric and DCE solvent exhibited a low μ_{FET} of $\sim 0.004 \text{ cm}^2/\text{Vs}$ and large V_{Th} of $\sim -13 \text{ V}$.

5. Complementary Inverter and Ring Oscillators

For demonstration of high-speed organic integrated circuits based on top-gated polymer FETs, a hydroxyl-free polymer dielectric and a perfectly orthogonal solvent are needed to prevent electron trapping, charge doping, and semiconductor surface roughness via swelling/dissolution of the underlying conjugated polymer. Based on this background, we used the PMMA dielectric solution in a 2E solvent to fabricate high-performance complementary inverters and ring oscillators using inkjet-printed p-type (P3HT, P2100 (Polyera Inc.)) and n-type (N2200, Polyera Inc.) polymer semiconductors [24]. Thus, the inverters showed high voltage gains of more than ~ 30 , and the operation frequency of the ring oscillators was measured as high as ca. 50 kHz [24].

IV. Conclusion

Inkjet-printing is a promising micro-patterning method to fabricate printed electronic devices. Although the active features of inkjet-printing showed a slightly rough interface, no significant degradation of the transistor performance was exhibited in the top-gated OFETs. This suggests that the overlapped inkjet-printed lines have an orientation parallel to the charge transport direction of the interdigitated S/D electrode, and an efficient charge injection from the near edge of the Au S/D electrode. In addition, we investigated the effect of gate dielectric and its solvent on the characteristics of top-gated p-channel polymer field-effect transistors. The characteristics of printed OFETs showed a strong dependency on the gate dielectrics and solvents used. Top-gated P3HT transistors with PMMA showed typical p-type OFET characteristics with reasonably high μ_{FET} (up to $\sim 0.05 \text{ cm}^2/\text{Vs}$) using completely orthogonal solvents, whereas they showed degraded mobility when using a marginal solvent, DCE. On the other hand, P3HT transistors with PVP exhibited large V_{Th} and V_{on} shift toward the positive direction due to ground state charge transfer (oxidation) from P3HT and trapping in hydroxyl moiety and/or ions in the PVP. The selection of a proper gate dielectric and its solvent is very important in demonstrating individual high-

performance OFET devices and their complementary inverter and ring oscillator circuits.

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