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Air-Processable Silane-Coupled Polymers to Modify a Dielectric for Solution-Processed Organic Semiconductors

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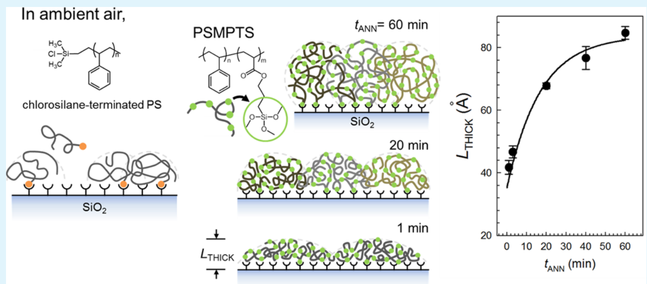
Supporting Information

ABSTRACT: Poly(styrene-*r*-3-methacryloxypropyltrimethoxysilane) (PSMPTS) copolymers were synthesized by the free radical polymerization of styrene and 3-methacryloxypropyltrimethoxysilane (MPTS) for use as surface modifiers. PSMPTS copolymers were spun-cast onto a hydrophilic SiO_2 layer and were then annealed at 150 °C in ambient air. The polystyrene (PS)-based copolymer, with a molecular weight of 32 700 g mol^{-1} and approximately 30 MPTS coupling sites, was easily grafted onto the SiO_2 surface after annealing periods longer than 1 min, yielding a physicochemically stable layer. On the untreated and polymer-treated dielectrics, spin-casting of an ultrasonicated poly(3-hexyl thiophene) (P3HT) solution yielded highly interconnected crystal nanofibrils of P3HT. The resulting organic field-effect transistors (OFETs) showed similar mobility values of 0.01−0.012 cm^2 V^{-1} s^{-1} for all surfaces. However, the threshold voltage (V_{th}) drastically decreased from +13 (for bare SiO_2) to 0 V by grafting the PSMPTS copolymers to the SiO_2 surface. In particular, the interfacial charge traps that affect V_{th} were minimized by grafting the 11 mol % MPTS-loaded copolymer to the polar dielectric surface. We believe that this ambient-air-processable silane-coupled copolymer can be used as a solution-based surface modifier for continuous, large-scale OFET fabrication.



KEYWORDS: *silane polymer, polymer grafting, solution-processable semiconductor, poly(3-hexyl thiophene), organic field-effect transistor*

1. INTRODUCTION

Organic field-effect transistors (OFETs) have received considerable attention over the past decade owing to their potential applications in integrated circuits, including radio frequency identification tags, smart cards, sensors, and organic active matrix displays.[1−7] The field-effect mobility (μ_{FET}) of OFETs is clearly comparable to that of amorphous silicon-based devices.[8−12] During the last two decades, μ_{FET} values of polymer field-effect transistors (FETs) have increased significantly from less than 10^{-3} cm^2 V^{-1} s^{-1} to more than 10 cm^2 V^{-1} s^{-1}, which exceeds those of amorphous silicon FETs.[10,13] These improvements are mainly related to the drastic enhancement in both intra- and intermolecular conjugation lengths of organic semiconductors via novel synthetic approaches or optimization of the interface engineering between organic semiconductors and dielectrics.[10,13] It is well-known that the charge-carrier transport in OFETs is vertically confined to ultrathin semiconducting layers (<5 nm) near the gate dielectrics.[8,14] Also, the surface properties of dielectrics are major factors that determine the number of interfacial trap sites originating from polar surface moieties, less-conjugated crystallites of semiconducting polymers, and grain boundaries (GB).[11,12,15] Therefore, organo-compatible dielectrics with fewer trap sites are necessary to achieve high-performance solution-processed OFETs.

Nonpolar self-assembled monolayers (SAMs) or common polymer thin films can induce organo-compatible dielectric surfaces with fewer charge-trapping sites.[11,12,16,17] End-functionalized polymers have been extensively used as surface-grafting modifiers in surface- and interface-related nanoscience and nanotechnology.[11,12,18−20] Yang and co-workers have reported that the organo-compatibility of hydroxyl-rich oxide or polymer dielectrics could be improved through grafting of chlorosilane-end coupled polystyrene (PS) to these surfaces.[11,12,18] In this case, the grafted polymer-layers maintained excellent solvent resistance without any dewetting or delaminating, even under direct solvent contact. Generally, end-functionalized polymers in dried films tend to be slowly grafted even at high temperatures because there is only one coupling site present on each polymeric molecule. In particular, ambient-air conditions, such as oxygen and humidity levels, should be carefully controlled to avoid the deactivation of limited coupling sites, particularly for air-sensitive chlorosilane-terminated polymers.[21]

Unlike these one-point coupling polymers, binary vinyl copolymers containing multiple coupling sites can be quickly

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grafted to various oxide surfaces.[22−25] One of the most important coupling agents is 3-methacryloxypropyltrimethoxysilane (MPTS). Copolymers containing MPTS have been easily copolymerized with various vinyl monomers and used for the practical adhesion of polymers to minerals.[22−25]

To develop an ambient-air grafting method of silane-coupled polymer chains to hydroxyl-group containing oxide or polymer surfaces, we synthesized poly(styrene-*r*-3-methacryloxypropyl trimethoxysilane) (PSMPTS) copolymers containing 5−11 mol % MPTS by free radical polymerization. PSMPTS copolymers were dissolved in toluene and the solutions were spun-cast onto 300 nm-thick SiO_2 dielectrics. The polymer films were then annealed at 150 °C to thermally graft the polymer chains to the SiO_2 surface. Finally, the annealed films were subsequently rinsed with excess toluene. On the untreated and polymer-grafted SiO_2 dielectrics, well-dispersed nanofibrillar networks of poly(3-hexyl thiophene) (P3HT) were formed via spin-casting a previously ultrasonicated P3HT solution. The resulting P3HT-based OFETs showed not only similar μ_{FET} values of 0.01−0.012 $cm^2\ V^{-1}\ s^{-1}$ but also significant changes in threshold voltage (V_{th}) ranging from +13 V (untreated) to 0 V (polymer-treated). In particular, the 11 mol % MPTS-loaded copolymer with approximately 30 coupling sites was uniformly grafted to the SiO_2 dielectric surface, even under ambient air. The grafted polymer layer allowed reliable fabrication of a P3HT OFET with V_{th} equaling approximately 0 V and negligible hysteresis. We believe that the ambient-air processable silane-coupled PSMPTS copolymers can be used as a dielectric modifier for SiO_2 dielectrics for continuous, solution-processed OFET applications.

2. EXPERIMENTAL SECTION

2.1. Materials and Device Preparation. Styrene (St, Aldrich, ≥ 99%) was passed through neutral alumina, dried over calcium hydride, distilled under reduced pressure, and degassed using three freeze−pump−thaw cycles. This purification process was also performed for anisole (Junsei, 98.0%), MPTS (TCI, 98.0%), and 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Wakko, 96%). P3HT was synthesized via the Grignard metathesis method with a $Ni(dppp)Cl_2$ catalyst;[26] the other reagents were used without purification. PSMPTS copolymers with different compositions were synthesized by using various monomer feed ratios ($[St]_o/[MPTS]_o$= 99/1−97/3, see Figure 1). As a typical example, St (1 mL, 8.7 mmol), MPTS

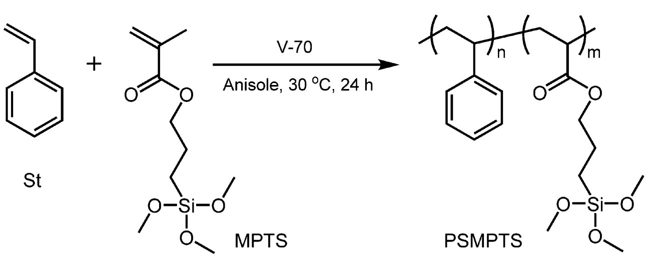

Figure 1. Synthesis of poly(styrene-*r*-3-methacryloxypropyltrimethoxysilane) (PSMPTS) copolymer.

(0.0219 g, 0.088 mmol), and V-70 (0.0093 g, 1 wt % of total monomer) were dissolved in 1 mL of anisole under a nitrogen atmosphere. The mixture was purged with nitrogen for 10 min and polymerized at 30 °C for 24 h. The resulting product was diluted with tetrahydrofuran (Duksan, >99.5%) and precipitated in a large amount of methanol. The precipitated polymer was collected by filtration and was dried under vacuum for 24 h.

A 300 nm-thick SiO_2 layer thermally grown onto a highly *n*-doped Si substrate was used as a gate dielectric. The SiO_2/Si substrates were first cleaned in boiling acetone, and then UV-ozone (UVO_3)-treated for 30 min. In ambient air, the solutions of PSMPTS copolymers in toluene were spun-cast onto the hydroxyl-groups presenting SiO_2 surfaces. Dimethylchlorosilane-terminated PS ($PS\text{-}Si(CH_3)_2Cl$, number-average molecular weight, M_n = 26 000 g mol^{-1}, i.e., 26 kDa), was also used as a reference polymer. The 20−30 nm thick films were annealed at 150 °C for different annealing times (t_{ANN}) ranging from 0 to 60 min. Then, the annealed films were solvent-rinsed with an excess of toluene to remove any unreacted polymer residue.

A 0.2 wt % solution of P3HT in toluene was ultrasonicated at 18 °C for 10 min to develop highly crystalline nanofibrils, and then P3HT films were spun-cast on untreated and polymer-treated SiO_2 substrates from the ultrasonicated solution. Finally, top contact electrodes were fabricated by thermally evaporating Au through a shadow mask (channel length, L = 100 μm; channel width, W = 1500 μm) onto the P3HT layers.

2.2. Characterization. The molecular weights and distribution of the polymers produced were determined with gel permeation chromatography (GPC, JASCO PU-2080 plus SEC) calibrated with a PS standard series. The level of monomer conversion was determined using a gravimetric method and the polymer composition was determined using ^{1}H nuclear magnetic resonance (NMR, Bruker Ascend 400, 400 MHz) analysis. Thermal behavior of the PSMPTS series was measured using differential scanning calorimetry (DSC, Q20, TA Instruments). The morphology, thickness, and surface hydrophobicity of the PSMPTS-treated SiO_2 dielectrics were characterized using atomic force microscopy (AFM, Multimode 8, Bruker), X-ray reflectivity (XRR, beamline X9, Brookhaven National Laboratory, USA), and water contact angle measurements, respectively. The crystalline structures of P3HT on the gate dielectrics were investigated using AFM and synchrotron-based grazing-incidence X-ray diffraction (GIXD, beamline 9A, Pohang Acceleration Laboratory, Korea). Electrical characteristics of all the P3HT OFETs were measured in a N_2-purged glovebox (H_2O < 0.1 ppm; O_2 < 0.1 ppm) at room temperature using a Keithley 4200 SCS. Values of μ_{FET} and V_{th} were calculated in the saturation regime (drain voltage, V_D = −40 V) using the equation $I_D = \mu_{FET} C_i W (2L)^{-1} (V_G - V_{th})^2$, where C_i is the capacitance of the dielectric sandwiched between the Au dots and highly doped *n*-type (100) Si substrate, was measured using an Agilent 4284 precision LCR meter.

3. RESULTS AND DISCUSSION

Most inorganic oxides (e.g., SiO_2, Al_2O_3) or high-κ polymer dielectrics having hydrophilic surface characteristics, i.e., high surface energy (γ), inhibit the preferential edge-on crystal growth of π-conjugated polymers. It has been reported that slight differences in molecular interactions at the semiconductor-dielectric interface drastically changed the crystalline structures of both vacuum- and solution-processed organic semiconductors in terms of crystallinity, GBs, and crystal orientation.[11,12,15−17] To minimize the interfacial mismatches, high-γ surfaces have usually been treated with SAMs or polymers.[11,12,15−17] For solution-processable organic semiconductors, it is necessary for the polymer-modified surfaces to maintain a consistent wettability against the hydrophilic oxides. This is achieved by grafting polymers to active moieties on the surfaces or cross-linking the polymer.[11,12,18−20,27−29]

As mentioned earlier, MPTS has a trimethoxysilane (TS) moiety, which is one of the most important grafting sites for coupling polymers to oxide surfaces. In the present study, MPTS was copolymerized with St to create PSMPTS copolymers. Table 1 shows characteristics of the synthesized PSMPTS copolymers. M_n of the PSMPTS copolymers ranged from 13 400 to 34 000 g mol^{-1}, as determined by GPC analysis (see Figure S1 in the Supporting Information). The mol % of each monomer in the PSMPTS copolymers was determined by ^{1}H NMR spectra showing different integration ratios of

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Table 1. Typical Characteristics of a PSMPTS Copolymer Series Synthesized in This Study

notation	feed ratio $[St]_o/[MPTS]_o$	mol % St	mol % MPTS	M_n (g mol^{-1})	M_w/M_n	T_g (°C)
PSMPTS-5	99/1	95	5	13400	2.03	86.1
PSMPTS-8	98/2	92	8	15900	2.18	84.8
PSMPTS-11[a]	97/3	89	11	32700	2.71	78.3

[a]AIBN (1 wt %), 60 °C, 24 h.

aromatic proton peaks at 6.5 and 7.1 ppm (for the St units) and a methyl peak at 3.6 ppm (for the MPTS units) (see Figure S2 in the Supporting Information). The molar compositions of MPTS units in the copolymers were 5, 8, and 11%, respectively. Based on the GPC and ^{1}H NMR results, it was estimated that all of the copolymers contained at least 6 (for PSMPTS-5) and up to 30 (for PSMPTS-11) TS moieties per chain. This would presumably allow much more rapid grafting of the copolymers to a SiO_2 surface than silane-coupled polymers with a single chlorosilane moiety. As the MPTS mol % increased, the glass transition temperature (T_g) of PSMPTS as determined by DSC monotonically decreased (see Figure S3 in the Supporting Information).

To investigate the grafting efficiency of the copolymers to hydroxyl-group on the surface, PSMPTS solutions were spun-cast onto a UVO_3-treated 300 nm-thick SiO_2 layer on a heavily *n*-doped Si substrate. The resulting 20–30 nm thick PSMPTS films were then annealed at 150 °C for t_{ANN} = 60 min. The annealed films were subsequently rinsed with an excess of toluene to remove any uncoupled PSMPTS residue from the SiO_2 surfaces (see the Experimental Section for more details).

Figure 2 shows AFM topographies of the untreated and PSMPTS-treated SiO_2 substrates. With the benefit of multiple

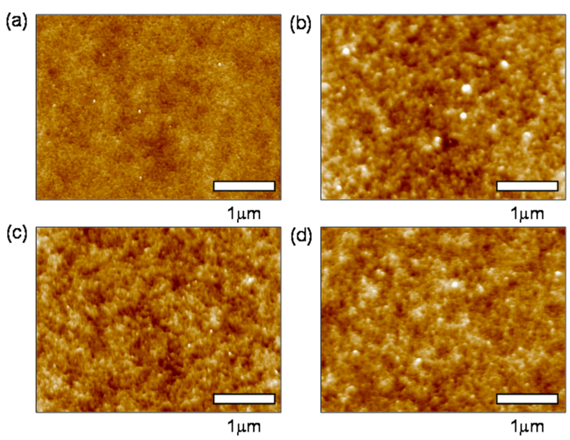

Figure 2. AFM topographies of (a) bare SiO_2 (R_q = 0.27 nm) and (b–d) PSMPTS-treated SiO_2 bilayer dielectrics with different PSMPTS copolymer layers: (b) PSMPTS-5 (R_q = 0.36 nm), (c) PSMPTS-8 (R_q = 0.33 nm), and (d) PSMPTS-11 (R_q = 0.30 nm).

TS coupling sites distributed throughout the PSMPTS chains, the copolymers were grafted to the SiO_2 surfaces in ambient air and formed relatively smooth polymer-coated layers with root-mean-square surface roughness (R_q) values of 0.30–0.36 nm. However, the AFM topography of the end-grafted PS-$Si(CH_3)_2Cl$ layer on the SiO_2 surface showed locally uncovered regions due to the air-sensitive chlorosilane moiety, resulting in a relatively high R_q value of 0.37 nm (see Figure S4a in the Supporting Information). As the MPTS composition in PSMPTS increased from 5 to 11 mol %, it was found that the R_q values of the copolymer coated-SiO_2 surfaces decreased from 0.36 to 0.30 nm. PSMPTS-5, which had six coupling sites, yielded a low-grafting efficiency, showing irregularly polymer-coated regions (see Figure 2b). In contrast, PSMPTS-11, which had the highest number of coupling sites, seemed to be uniformly grafted to the SiO_2 surface and had a similar roughness level (R_q = 0.30 nm) to that (0.27 nm) of the untreated SiO_2 surface.

Surface-grafted polymer layers, acting as organic interlayers between semiconducting films and inorganic oxide (or high-κ polymer) dielectrics, chemically deactivate or physically bury the number of polar moieties on the dielectric surfaces. It is known that end-functionalized polymers with a single coupling site form either brush or pancake type molecular layers on surfaces, and their thickness depends on the areal grafting density and chain length.[30,31] For the PSMPTS copolymers with multiple coupling sites, it was found that the thermal grafting time (t_{ANN}) at 150 °C drastically changed the thicknesses of the grafted PSMPTS layers. Figure 3a shows

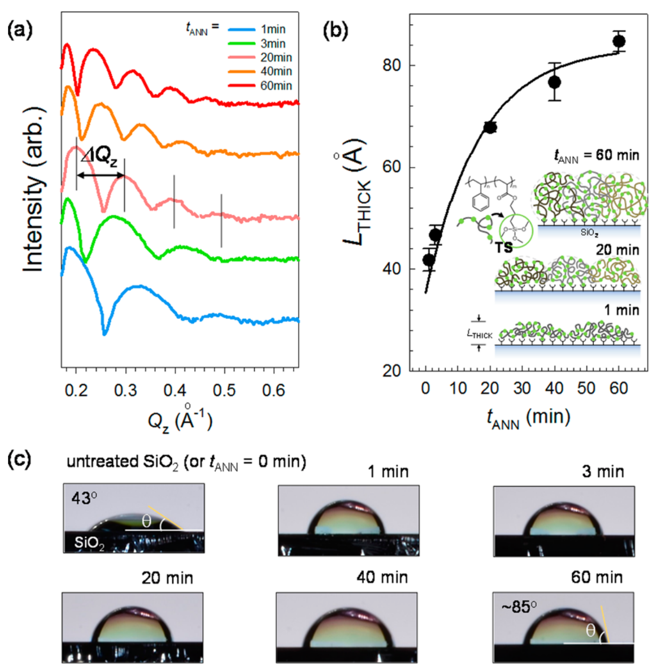

Figure 3. (a) X-ray reflectivity profiles of the PSMPTS-11 layers on SiO_2 surfaces and (b) the calculated values of L_{THICK}. The inset represents the schemes of the conformation of grafted chains on the SiO_2 surfaces with an increase in t_{ANN}. (c) Variation in water contact angle on the PSMPTS-11-treated SiO_2 bilayer as a function of t_{ANN}.

XRR profiles of PSMPTS-11-treated SiO_2 bilayer dielectrics fabricated with t_{ANN} ranging from 0 to 60 min in ambient air. All the XRR profiles for the grafted PSMPTS-11 layers showed discernible peak intervals, ΔQ_z, ranging from 0.075 to 0.153 Å^{-1}, which were used to calculate the layer thickness ($L_{THICK} = 2\pi/\Delta Q_z$). L_{THICK} tended to increase with increasing t_{ANN}, with a maximum thicknesses of 84 Å observed for t_{ANN} = 60 min, as shown in Figure 3b. After short-term annealing at 150 °C, e.g., 1 or 3 min, PSMPTS-11 was grafted to the SiO_2 surface layers with a thickness of more than 40 Å. Based on the L_{THICK} variations of PSMPTS-11, which has a radius of gyration of

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Table 2. Electrical Characteristics of P3HT OFETs Fabricated with Different Dielectrics

dielectric	surface modifier	dielectric roughness (R_q, nm)	μ_{FET} ($cm^2\ V^{-1}\ s^{-1}$)	V_{th} (V)	I_{on}/I_{off}
untreated SiO_2		0.27	0.010 ± 0.003	13	$>10^5$
PS-Si(CH_3)$_2$Cl	26 kDa PS-Si(CH_3)$_2$Cl	0.37	0.011 ± 0.002	10	$>10^5$
PSMPTS-treated SiO_2	PSMPTS-5	0.36	0.011 ± 0.003	6	$>10^5$
	PSMPTS-8	0.33	0.011 ± 0.002	4	$>10^5$
	PSMPTS-11	0.30	0.012 ± 0.002	0	$>10^5$

approximately 10 nm, it was found that the grafting densities of PSMPTS-11 chains increased monotonically with an increase in t_{ANN} due to the randomly distributed TS coupling sites in the copolymer, as shown in the inset in Figure 3b. Figure 3c shows digital images of water droplets on these copolymer-grafted SiO_2 surfaces. The untreated SiO_2 and the polymer-treated surface that was not thermally annealed (t_{ANN} = 0 min) still maintained a hydrophilic character, as determined by the low water contact angles (θ_{water}) of approximately 43°. In contrast, all the thermally grafted polymer-SiO_2 surfaces showed similar surface hydrophobicity, with θ_{water} values of 83−86°. Based on these results, it is apparent that PSMPTS copolymers containing multiple coupling sites can undergo rapid multisite grafting to SiO_2 surfaces, resulting in an increase in L_{THICK} as a function of t_{ANN}.

To develop a uniformly grafted layer of the PSMPTS copolymers to hydroxyl groups on the SiO_2 dielectric, spun-cast PSMPTS films were treated at 150 °C for 60 min and subsequently rinsed with an excess of toluene. All the PSMPTS-SiO_2 bilayer dielectrics had C_i values between 10.4 and 10.8 nF cm^{-2}, similar to that (10.9 nF cm^{-2}) of the untreated 300 nm-thick SiO_2 layer due to ultrathin polymeric layer, i.e., 50−84 Å (see Table 2).

As semiconducting channel layers, solution-processed P3HT films can contain various complex microstructures depending on the solvent solubility, solvent evaporation rate, and processing temperature. Recently, it has been reported that a fast crystallization of strongly π-conjugated P3HT can be induced by ultrasonicating a dilute P3HT solution.[32−34] To fabricate well-interconnected nanofibril crystallites of π-conjugated P3HT (M_n = 21 000 g mol^{-1}, M_w/M_n = 1.17) on the gate dielectrics, a solution of 0.2 wt % P3HT in toluene was first ultrasonicated in a double jacketed beaker maintained at 18 °C for 10 min. This ultrasonicated solution was then spun-cast onto all the SiO_2 gate dielectrics. Figure 4 shows AFM topographies of the ultrasound-assisted P3HT crystallites spun-cast on the untreated and PSMPTS-treated SiO_2 dielectrics. On the untreated and PSMPTS-treated SiO_2 surfaces showing different surface roughnesses and energies, P3HT nanofibrils were highly extended and percolated, with a lateral width of 24−30 nm. The similar crystal morphologies of P3HT on these gate dielectrics were mainly related to the directed self-assembly of P3HT in the previously ultrasonicated solution.[32,33]

Synchrotron-based GIXD analysis was also performed to evaluate the π-conjugated orientations of P3HT in these films (see Figure 5). 2D GIXD patterns of the ultrasound-assisted P3HT films spun-cast on the dielectrics showed intense out-of-plane and in-plane X-ray reflections along the Q_z and Q_{xy} axes, respectively. It should be noted that the beam center and (100) peak position of the patterns were blocked with an Al beam stopper to avoid any detector saturation due to the strong X-ray reflections. The (h00) and (010) reflections along the Q_z and Q_{xy} axes, respectively, corresponded to a multistacked crystal structure, where "edge-on" P3HT chains were preferentially oriented with a (100) layer spacing of about 16.6 Å and an intermolecular $\pi-\pi$ distance of ~3.80 Å.[35] As expected from the AFM morphologies in Figure 4, all the 2D GIXD patterns of the ultrasound-assisted P3HT films were similar to each other in intensity and orientation. The similarities between P3HT crystallites formed in the ultrasound-assisted films, including crystallinity, π-conjugated orientation, and crystal interconnection, may provide density of states in the conducting channel similar to those previously observed,[36,37] suggesting that these P3HT films on the different gate dielectrics might have similar structural charge traps.

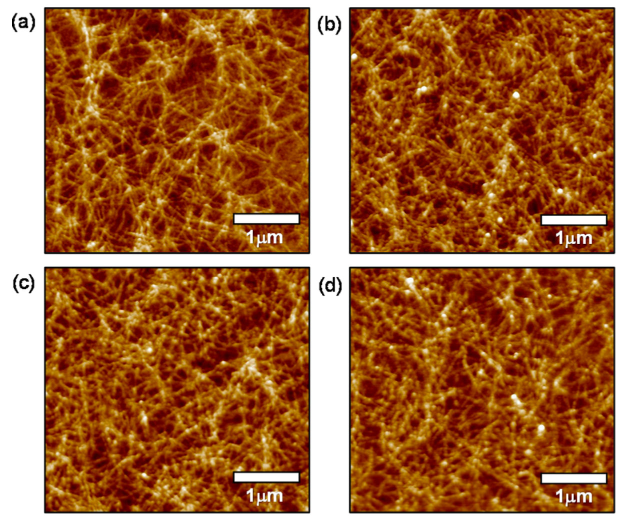

Figure 4. AFM topographies of ultrasound-assisted P3HT films spun-cast on (a) untreated and (b−d) PSMPTS-treated SiO_2 bilayer dielectrics: (b) PSMPTS-5, (c) PSMPTS-8, and (d) PSMPTS-11.

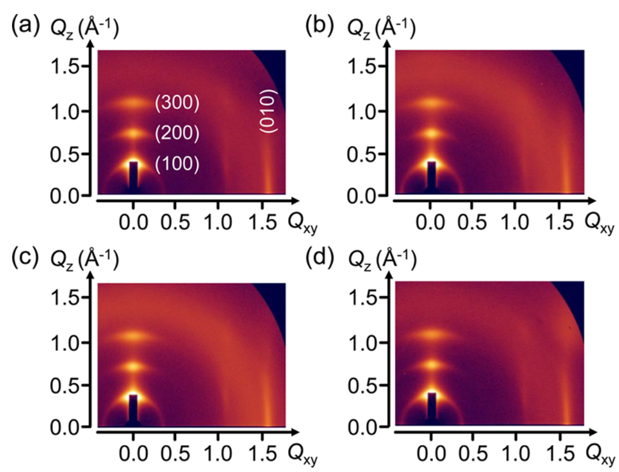

Figure 5. 2D GIXD patterns of the ultrasound-assisted P3HT films spun-cast on different gate dielectrics: (a) untreated SiO_2, (b) PSMPTS-5 SiO_2, (c) PSMPTS-8 SiO_2, and (d) PSMPTS-11 SiO_2.

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Top-contacted electrode OFETs were fabricated by the thermal evaporation of Au through a shadow mask (L = 100 μm; W = 1500 μm) onto the P3HT films. Figure 6 shows the electrical characteristics of the P3HT OFETs for all the gate dielectrics. First, the drain current-gate voltage (I_D-V_G) transfer curves of the P3HT OFETs based on untreated, 26 kDa PS-Si$(CH_3)_2$Cl- and PSMPTS-treated SiO_2 dielectrics were measured in the saturation regime (drain voltage, V_D = −40 V) (see Figure 6a). Based on the resulting $|I_D|^{0.5}-V_G$ plots (see Figure 6b), the electrical properties of the OFETs, including μ_{FET}, V_{th}, and I_{ON}/I_{OFF}, were determined and are summarized in Table 2. OFETs with typical p-type transistor characteristics (see Figure 6c) yielded similar μ_{FET} values of 0.010−0.012 cm^2 V^{-1} s^{-1}, as well as negligible V_G-sweep hysteresis. However, V_{th} values were drastically shifted to the negative direction from +13 V (for untreated SiO_2) and +10 V (for 26 kDa PS-Si$(CH_3)_2$Cl-treated SiO_2) to 0 V (for the PSMPTS-11-treated SiO_2). The PSMPTS-11-treated SiO_2 system with an 84 Å-thick PS-based interlayer showed the best electrical performance (μ_{FET} = 0.012 cm^2 V^{-1} s^{-1}, V_{th} = 0 V, and $I_{on}/I_{off} > 10^5$).

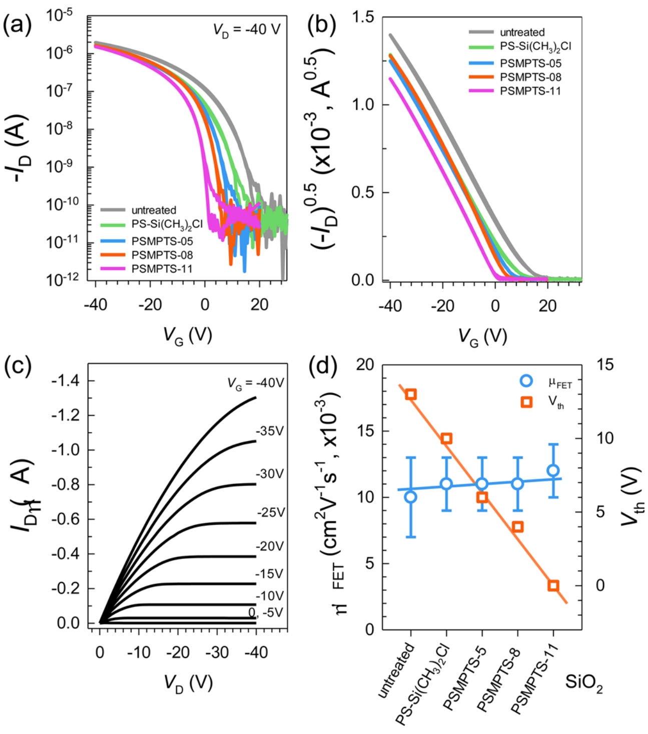

Figure 6. (a−c) Electrical performances of P3HT OFETs: (a) I_D-V_G transfer curves and (b) the resulting $|I_D|^{0.5}-V_G$ plots, (c) I_D-V_D output curves of the PSMPTS-11-treated SiO_2 system, and (d) variations of μ_{FET} and V_{th} of the P3HT OFETs fabricated on untreated, PS-Si$(CH_3)_2$Cl-, and PSMPTS-treated SiO_2 dielectrics.

Because the crystalline morphologies and π-conjugated orientations of the P3HT layers were very similar among all the dielectrics, the V_{th} shift of the P3HT OFETs was mainly related to the variations in trap density at the semiconductor−dielectric interface. The interfacial traps are usually due to surface imperfections of the dielectrics, such as polar moieties. As interfacial trap sites, hydroxyl groups on an untreated SiO_2 layer could be passivated by the PSMPTS copolymer chains chemically coupled with the hydroxyl groups. As the coupling densities of the PSMPTS chains increased on the SiO_2 surfaces, the decrease of the hydroxyl groups at the P3HT-dielectric interface induced a negative shift in V_{th}.[38] Similarly, the 26 kDa PS-Si$(CH_3)_2$Cl chains under an inert condition (H_2O < 0.1 ppm; O_2 < 0.1 ppm) could efficiently passivate the polar moieties on the SiO_2 surface due to the improved coupling activity of the air-sensitive chlorosilane site. The corresponding P3HT OFET showed the V_{th} value of −1 V, in comparison to +10 V of the air-processed PS-Si$(CH_3)_2$Cl-treated system (see Figure S5 in the Supporting Information).

In summary, the introduction of ultrathin polymer interlayers between solution-processed semiconductors and a polar dielectric surface was successfully demonstrated to optimize the electrical properties of solution-processed polymer FETs. Ambient-air grafting of solution-processable PS-based random copolymers with multiple coupling sites allowed for physicochemically stable polymer layers on hydroxyl group containing SiO_2 surfaces. The optimization of thermally grafted PSMPTS layers drastically reduced the interfacial charge traps in OFETs.

4. CONCLUSIONS

As dielectric modifiers, various PSMPTS copolymers with MPTS units of 5−11 mol % were synthesized by a free radical polymerization of styrene and MPTS. The PSMPTS copolymers were spun-cast onto hydroxyl-groups presenting SiO_2 dielectrics, annealed at 150 °C, and subsequently rinsed with an excess of toluene. Interestingly, PSMPTS-11 was thermally grafted when exposed to high temperature for more than 1 min and formed a much denser hydrophobic layer on the SiO_2 surface with an increase in annealing time. A preultrasonicated P3HT solution was spun-cast on all the dielectrics, and the ultrasound-assisted P3HT films showed a highly interconnected networks of P3HT nanofibrils, where most of the semiconducting polymer chains were preferentially oriented with an "edge-on" conformation. The resulting P3HT OFETs showed similar μ_{FET} values of 0.01−0.012 cm^2 V^{-1} s^{-1}. However, values of V_{th}, related to the interface polar charge traps, were drastically changed from +13 (for untreated SiO_2) to 0 V (for the PSMPTS-treated SiO_2). These results strongly suggest that the facile and rapid grafting of PS-based copolymers onto SiO_2 dielectrics in ambient air can be used as a continuous solution-based dielectric treatment for large-scale OFET fabrication.

■ ASSOCIATED CONTENT

Supporting Information

GPC, ^{1}H NMR and DSC analyses, AFM topographies, and typical I_D-V_G transfer curves of P3HT OFET. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

AFM, atomic force microscopy
GB, grain boundary
GIXD, grazing-incidence X-ray diffraction
M_n, Number-average molecular weight
OFET, organic field-effect transistor
P3HT, poly(3-hexyl thiophene)
PS, polystyrene
PSMPTS, polystyrene-*random*-poly(3-methacryloxypropyltrimethoxysilane)
SiO_2, silicon dioxide
TS, trimethoxysilane

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