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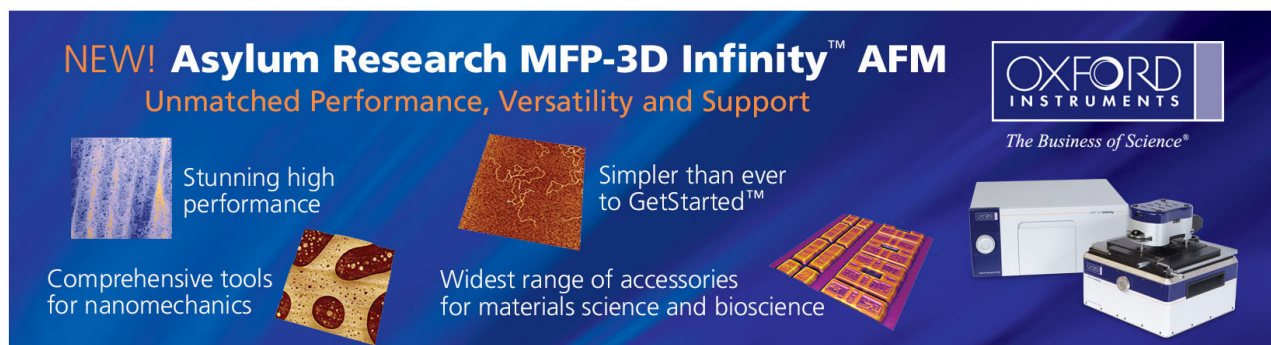
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## Improved air stability of *n*-channel organic thin-film transistors with surface modification on gate dielectrics

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The air stability of *n*-channel organic thin film transistors based on *N,N'*-dioctyl-3,4,9,10-perylene tetracarboxylic diimide is improved when modifying the dielectric surfaces with polymer insulators. The hydrophobic nature of the polymer surface inhibits protonation of the siloxyl groups on the SiO<sub>2</sub> surface, leading to fewer SiO<sup>-</sup> groups that can behave as electron traps. Among the polymer insulators tested, the devices modified with hydroxyl-free polymers exhibited the best air stabilities. © 2008 American Institute of Physics. [DOI: 10.1063/1.2980421]

Organic thin film transistors (OTFTs) are currently the subject of intensive research owing to their potential applications in low-cost, flexible electronic products, such as flat-panel displays, smart cards, and radio frequency identification tags.<sup>1</sup> *p*-channel OTFTs have been prepared that perform in a manner comparable with that of amorphous Si;<sup>2-4</sup> for example, hole mobilities higher than 1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> have been demonstrated for devices based on pentacene.<sup>3,4</sup> Although high-performance *n*-channel devices have also been reported, they function only under inert atmospheres because atmospheric O<sub>2</sub> and H<sub>2</sub>O behave as oxidants and/or electron traps responsible for *n*-channel degradation under ambient conditions.<sup>1,5-10</sup> One approach toward ambient-stable *n*-channel OTFTs is the use of organic compounds possessing strong electron-withdrawing units (e.g., CN groups or F atoms) as the semiconducting materials.<sup>11-15</sup> The presence of electron-withdrawing side chains increases the electron affinity, stabilizes the charge carriers, and improves the packing of the molecules, thereby preventing the diffusion of O<sub>2</sub> and H<sub>2</sub>O into the conducting channel.<sup>1</sup> Although this approach is very promising, complicated chemical syntheses are often necessary. In this study, we substantially improved the air stability of *n*-channel OTFTs based on *N,N'*-dioctyl-3,4,9,10-perylene tetracarboxylic diimide (PTCDI-C8), which was previously considered<sup>16</sup> to be an unstable *n*-channel organic semiconductor in air, by modifying the device dielectric surface with insulating polymers (Fig. 1). We found that the devices modified with hydroxyl-free polymers had the best air stability, presumably because of passivation of the siloxyl groups (electron trapping sites) on the SiO<sub>2</sub> surface.

Figure 1 illustrates the device structure employed in this study. Heavily *n*-doped silicon wafers covered with a 200 nm thermally grown SiO<sub>2</sub> layer were prepared as substrates. Polymer solutions were spin coated onto the SiO<sub>2</sub> surfaces pretreated with UV ozone under an ambient atmosphere. The polymer dielectric materials studied (Fig. 1) were poly(methyl methacrylate) (PMMA), poly- $\alpha$ -methylstyrene (P $\alpha$ MS), poly(vinyl alcohol) (PVA), and poly(4-vinylphenol) (PVP). PMMA and PS were dissolved in toluene (1.0 wt %), PVA was dissolved in de-ionized water (2.0 wt %), and PVP (3.0 wt %) and

poly(melamine-*co*-formaldehyde) methylated (1.5 wt %), a cross-linking agent, were dissolved in propylene glycol monomethyl ether acetate. The cross-linked PVP films were first baked at 120 °C for 5 min and then at 200 °C for 20 min. The other three kinds of polymer films were thermally annealed at 100 °C for 1 h. The thicknesses of the polymer layers were controlled at ~70 nm. A semiconducting layer of 50 nm PTCDI-C8 was subsequently deposited at room temperature onto each of the polymer insulators at a base pressure of 3 × 10<sup>-6</sup> torr. To complete the devices, gold was deposited under vacuum through a shadow mask to serve as source and drain electrodes. The channel length (*L*) and width (*W*) were 90 and 2000  $\mu$ m, respectively. The transfer properties of the devices were measured by using Keithley 4200 semiconducting parameter analyzer under ambient conditions or in a N<sub>2</sub>-filled glove box. The surface morphology of the PTCDI-C8 films was measured using a Digital Instruments Dimension 3100 atomic force microscope (AFM).

Figure 2 displays the transfer characteristics of the devices modified with different polymer insulators under ambient conditions. Each device exhibits typical *n*-channel behavior. Table I lists the electron mobilities, calculated from the slopes of the plots of the square root of the drain current versus gate voltage in the saturation region. The devices modified with PMMA and P $\alpha$ MS exhibited higher mobilities and on-off ratios than did the devices modified with the polymers containing hydroxyl groups (PVP and PVA). Further-

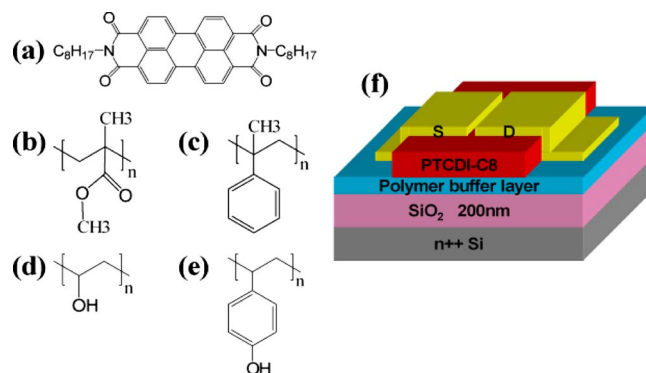


FIG. 1. (Color online) Chemical structures of (a) PTCDI-C8, (b) PMMA, (c) P $\alpha$ MS, (d) PVA, and (e) PVP. (f) Device structure fabricated in this study.

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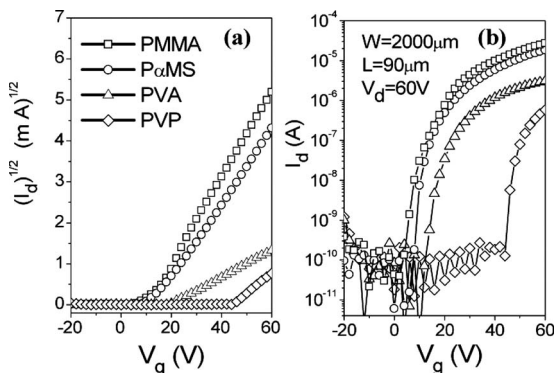


FIG. 2. (a) Plots of the square root of the drain current vs the gate voltage. (b) Transfer characteristics of the devices modified with the various polymer dielectric materials. The curves were all recorded under ambient conditions.

more, the threshold voltages ( $V_{th}$ ) of the devices modified with PMMA (10.72 V) and P $\alpha$ MS (15.01 V) were considerably lower than those of the devices modified with PVP (46.31 V) and PVA (20.22 V). Because a higher density of electron traps on a dielectric surface usually leads to an increased threshold voltage, our results indicate that the hydroxyl groups of the buffer polymers must somehow induce the formation of electron traps. On the other hand, the complete absence of hydroxyl groups (electron traps) on the P $\alpha$ MS and PMMA surfaces led to enhanced  $n$ -channel conduction.

Figure 3 reveals the stability of the devices under ambient conditions. The relative humidity during the period of measurement was controlled at 50%–55%. The devices modified with PMMA and P $\alpha$ MS exhibited better air stability than did the bare-SiO<sub>2</sub> device and those modified with PVP and PVA. For example, the electron mobility and on/off ratio of the device incorporating PMMA as the modifying layer remained almost unchanged for the first 15 days. The mobility did drop, however, to 0.05 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> after 29 days, and eventually to 0.03 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> after 60 days. In contrast, when the dielectric buffer layer was PVP or PVA, the electronic mobility and on/off ratio both dropped rapidly. The PVA and PVP devices exhibited poorer  $n$ -channel air stability than did the PMMA and P $\alpha$ MS devices. Indeed, after 20 days, we could not observe any apparent field effect.

The morphology of the PTCDI-C8 films deposited on different polymer dielectric layers was examined by AFM (Fig. 4). All the surfaces showed typical rodlike grains.<sup>17</sup> Although the grain size of PTCDI-C8 on PVP was slightly different from those of the other three cases, very little dif-

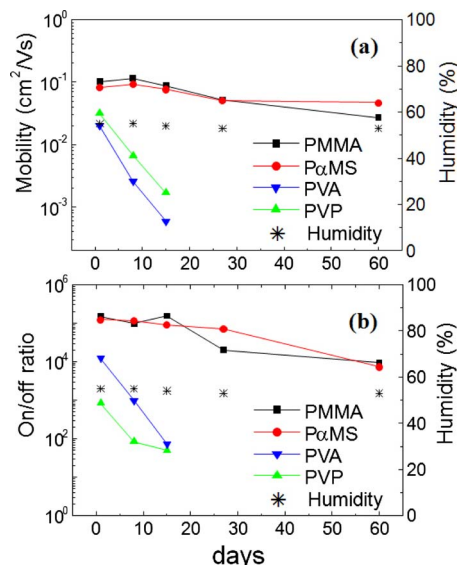


FIG. 3. (Color online) Air-stability measurements of PTCDI-C8 OTFTs. (a) Electron mobilities and relative humidity as a function of time. (b) On/off ratios plotted as a function of time. Between each measurement, the devices were stored in a cabinet, in which the relative humidity was also controlled at 50%–55%.

ference were observed between the PTCDI-C8 films on PMMA, P $\alpha$ MS, and PVA surfaces. Thus, there is no apparent correlation between the morphology and the device performance measured under ambient conditions.

Previous studies have indicated that charge transport occurs only in the first few monolayers of molecules on a dielectric surface.<sup>18</sup> Therefore, we deposited only 7-nm-thick layers of PTCDI-C8 on the various dielectric surfaces. The insets of Fig. 4 display the corresponding morphologies. The grain size of PTCDI-C8 deposited on PVA was smaller than those of the other systems; indeed, the other PTCDI-C8 films, including the one deposited on bare SiO<sub>2</sub> [inset to Fig. 4(e)], had similar morphologies. These observations are consistent with the performances of the device measured in a N<sub>2</sub>-filled glove box (Table I), where the PVA-based device exhibited the lowest mobility. Because smaller grains result in a higher density of grain boundaries, the electron transport was disrupted by the traps located between the grains. Further, contact angle measurements (Table I) revealed that the PVA film possessed a very high surface energy, which inhibited the growth of ordered PTCDI-C8 crystals. In contrast, the low surface energy of the P $\alpha$ MS film presumably led to preferential crystal orientation of PTCDI-C8 for effective

TABLE I. Characteristics of PTCDI-C8 OTFTs modified with various polymer dielectrics, measured both in a N<sub>2</sub>-filled glove box and under ambient conditions, in comparison with the results of contact angle measurements.

Dielectric	Surface energy (mN/m)	Water contact angle (deg)	Ambient atmosphere		N <sub>2</sub> -filled glove box	
			Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	On/off ratio	Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	On/off ratio
SiO <sub>2</sub>	45.3	50.3	...	...	0.13	1.7 × 10 <sup>5</sup>
P $\alpha$ MS	24.7	98.0	0.090	3.0 × 10 <sup>5</sup>	0.33	2.4 × 10 <sup>5</sup>
PVP	42.0	72.5	0.022	4.4 × 10 <sup>3</sup>	0.17	4.0 × 10 <sup>4</sup>
PMMA	37.7	76.1	0.11	3.3 × 10 <sup>5</sup>	0.14	4.8 × 10 <sup>5</sup>
PVA	55.5	21.0	0.015	3.1 × 10 <sup>4</sup>	0.056	4.3 × 10 <sup>4</sup>

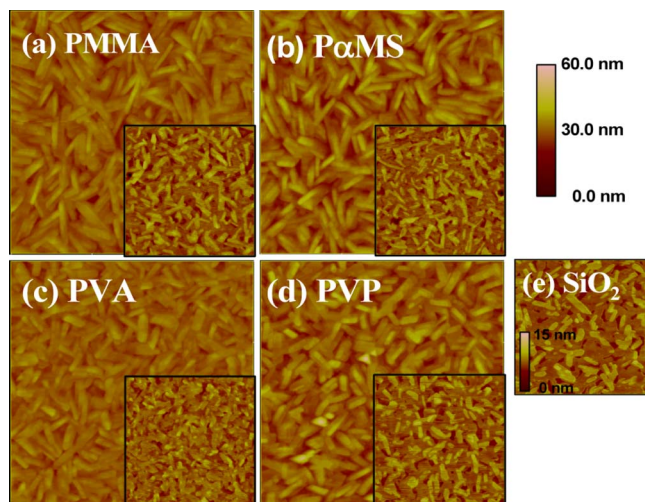


FIG. 4. (Color online) The morphological images ( $3 \times 3 \mu\text{m}^2$ ) of 50 nm PTCDI-C8 thin films on various polymer dielectrics surfaces: (a) PMMA, (b) P $\alpha$ MS, (c) PVA, and (d) cross-linked PVP. Insets:  $1.5 \times 1.5 \mu\text{m}^2$  AFM images of 7 nm PTCDI-C8 thin films deposited on the corresponding polymer dielectric surfaces. (e) AFM image of the 7 nm PTCDI-C8 thin film deposited on the native SiO<sub>2</sub> surface. The color scale on the top-right represents the  $3 \times 3 \mu\text{m}^2$  AFM images; that in (e) represents the  $1.5 \times 1.5 \mu\text{m}^2$  images.

electron transportation, thereby leading to higher electron mobility under the inert environment.

Whereas the device performances under inert conditions were related to the surface morphology PTCDI-C8 films and the surface energy of the dielectric layer, the electrical properties under ambient conditions were more sensitive to the water and moisture affinities. Table I lists the water contact angles of various dielectric surfaces. The P $\alpha$ MS and PMMA surfaces were rather hydrophobic, suggesting that their improved air stability was probably associated with their moisture affinities (Fig. 3). From a recent study of the influence of H<sub>2</sub>O and O<sub>2</sub> on the performance of OTFTs, Kumaki *et al.* concluded that the adsorption of H<sub>2</sub>O resulted in deprotonation of siloxyl groups (SiOH) to form electron trapping groups (SiO<sup>-</sup>), in contrast, the deprotonation of SiOH with O<sub>2</sub> must involve an electron transfer reaction.<sup>19</sup> For our systems, we observed clear *n*-channel field-effect behavior when using SiO<sub>2</sub> as the dielectric surface and measuring the device performance under inert conditions (Table I). This result differs from the disappearance of the *n*-channel behavior of an untreated SiO<sub>2</sub> surface, as observed by Chua *et al.*,<sup>6</sup> which probably arose due to the rather low sensitivity to the charging of silanol groups of PTCDI derivatives. In contrast, we observed no field effect when the device was measured in air. Therefore, we infer that the polymers probably inhibited the approach of H<sub>2</sub>O molecules to the conducting channel. The hydrophobicity of the polymers, relative to that of the SiO<sub>2</sub> surface, limits the absorption of humidity, thereby retarding the degradation of the *n*-channel behavior under ambient conditions. For the devices incorporating PVP and PVA, the polymers were not only more hydrophobic than

SiO<sub>2</sub>, but their hydroxyl groups were probably less acidic, leading to less of a tendency to undergo deprotonation with H<sub>2</sub>O.<sup>20</sup> Therefore, the PVP- and PVA-based devices exhibited higher air-stability than did the device fabricated on the bare SiO<sub>2</sub> surface.

In conclusion, we have found that the modification of SiO<sub>2</sub> surfaces using hydroxyl-free polymer insulators, such as PMMA and P $\alpha$ MS, can improve the air stability of *n*-channel OTFTs. We attribute this behavior to passivation of the siloxyl groups (electron trapping sites) on the SiO<sub>2</sub> surface. The results presented here are significant because no complicated chemical synthesis of *n*-channel organic materials with strong electron withdrawing groups is required to prepare these OTFT devices. Finally, our preliminary result indicates that this method could be used for other *n*-channel semiconductors, such as C<sub>60</sub>, suggesting that the phenomena reported here are quite general for *n*-channel OTFTs.

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- <sup>1</sup>J. Zaumseil and H. Sirringhaus, *Chem. Rev. (Washington, D.C.)* **107**, 1296 (2007).
- <sup>2</sup>A. Facchetti, M. H. Yoon, and T. J. Marks, *Adv. Mater. (Weinheim, Ger.)* **17**, 1705 (2005).
- <sup>3</sup>H. Klauk, M. Halik, U. Zschieschang, G. Schmid, W. Radlik, and W. Weber, *J. Appl. Phys.* **92**, 5259 (2002).
- <sup>4</sup>Y. Y. Lin, D. J. Gundlach, S. F. Nelson, and T. N. Jackson, *IEEE Electron Device Lett.* **18**, 606 (1997).
- <sup>5</sup>Z. Bao, *Adv. Mater. (Weinheim, Ger.)* **12**, 227 (2000).
- <sup>6</sup>L. L. Chua, J. Zaumseil, J. F. Chang, E. C. W. Ou, P. K. H. Ho, H. Sirringhaus, and R. H. Friend, *Nature (London)* **434**, 194 (2005).
- <sup>7</sup>S. Tatemichi, M. Ichikawa, T. Koyama, and Y. Taniguchi, *Appl. Phys. Lett.* **89**, 112108 (2006).
- <sup>8</sup>Y. Hosoi and Y. Furukawa, *Mol. Cryst. Liq. Cryst.* **462**, 37 (2007).
- <sup>9</sup>D. Kumaki, S. Ando, S. Shimono, Y. Yamashita, T. Umeda, and S. Tokito, *Appl. Phys. Lett.* **90**, 053506 (2007).
- <sup>10</sup>T. D. Anthopoulos, B. Singh, N. Marjanovic, N. S. Sariciftci, A. M. Ramiel, H. Sitter, M. Cölle, and D. M. de Leeuw, *Appl. Phys. Lett.* **89**, 213504 (2006).
- <sup>11</sup>Z. Bao, A. J. Lovinger, and J. Brown, *J. Am. Chem. Soc.* **120**, 207 (1998).
- <sup>12</sup>H. E. Katz, A. J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y. Y. Lin, and A. Dodabalapur, *Nature (London)* **404**, 478 (2000).
- <sup>13</sup>C. R. Newman, C. D. Frisbie, D. A. da S. Filho, J. Brédas, P. C. Ewbank, and K. R. Mann, *Chem. Mater.* **16**, 4436 (2004).
- <sup>14</sup>B. Yoo, T. Jung, D. Basu, A. Dodabalapur, B. A. Jones, A. Facchetti, M. R. Wasielewski, and T. J. Marks, *Appl. Phys. Lett.* **88**, 082104 (2006).
- <sup>15</sup>R. Schmidt, M. M. Ling, J. H. Oh, M. Winkler, M. Könnemann, Z. Bao, and F. Würthner, *Adv. Mater. (Weinheim, Ger.)* **19**, 3692 (2007).
- <sup>16</sup>Y. Hosoi, D. Tsunami, H. Ishii, and Y. Furukawa, *Chem. Phys. Lett.* **436**, 139 (2007).
- <sup>17</sup>B. A. Jones, A. Facchetti, M. R. Wasielewski, and T. J. Marks, *J. Am. Chem. Soc.* **129**, 15259 (2007).
- <sup>18</sup>G. Horowitz, *J. Mater. Res.* **19**, 1946 (2004).
- <sup>19</sup>D. Kumaki, T. Umeda, and S. Tokito, *Appl. Phys. Lett.* **92**, 093309 (2008).
- <sup>20</sup>M. H. Yoon, C. Kim, A. Facchetti, and T. J. Marks, *J. Am. Chem. Soc.* **128**, 12851 (2006).