

Significant dependence of morphology and charge carrier mobility on substrate surface chemistry in high performance polythiophene semiconductor films

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The authors report a significant dependence of the morphology and charge carrier mobility of poly(2,5-bis(3-dodecylthiophene-2-yl)thieno[3,2-b]thiophene) (pBTTT) films on the substrate surface chemistry upon heating into its liquid crystal phase. In contrast with films on bare silicon oxide surfaces, pBTTT films on oxide functionalized with octyltrichlorosilane exhibit substantial increases in the lateral dimensions of molecular terraces from nanometers to micrometers, increased orientational order, and higher charge carrier mobility. The large-scale crystallinity of this polymer plays an important role in the high carrier mobility observed in devices, but renders it more sensitive to substrate surface chemistry than other conjugated polymers. © 2007 American Institute of Physics. [DOI: 10.1063/1.2472533]

Semiconducting polymers are being developed for use as the active layer in thin-film transistors (TFTs) for flat panel displays and radio frequency identification tags.^{1,2} The charge carrier mobility of the semiconductor is the critical materials parameter that determines TFT performance.³ Understanding the relationship between the processing of the polymer, its morphology, and the resulting thin-film transistor performance is critical to the improvement of the devices. Numerous studies have correlated the morphology of semiconducting polymer films to their charge carrier mobility.⁴⁻⁶ It is widely believed that the substrate chemistry plays a key role in the development of the polymer semiconductor morphology because of observations that substrate surface treatment strongly influences charge carrier mobility.

Silicon oxide is the most widely used model dielectric in polymer semiconductor TFTs. Treating the oxide with hydrophobic agents can increase the measured charge carrier mobility by up to three orders of magnitude.⁷⁻⁹ Morphology improvement is the most common explanation, but chemical groups on bare silicon oxide could act as traps for charge carriers.¹⁰ For poly(3-hexylthiophene) (P3HT), x-ray diffraction (XRD) rocking curves show a greater concentration of highly oriented crystals upon hydrophobic surface treatment.⁷ In poly[5,5'-bis(3-alkyl-2-thienyl)-2,2'-bithiophene] (PQT), it has been shown that films cast and heated on a hydrophobic surface can be delaminated and transferred to an oxide surface and maintain high mobility.¹¹ The mobility only drops after the transferred film is heated on the oxide. These results suggest morphological changes, but the small domain size (≈ 10 nm) of typical semiconducting polymers makes confirmation by direct imaging difficult.

In this letter, we find that the morphology, molecular orientation, and charge carrier mobility can depend significantly on substrate chemistry, with much larger morphological effects than previously observed for polymer semiconductors. We employ a combination of structure analysis methods to study the morphology of poly(2,5-bis(3-dodecylthiophene-2-yl)thieno[3,2-b]thiophene) (pBTTT), a polymer semiconductor that exhibits large crystalline terraces that can extend laterally for several hundreds of nanometers. Because pBTTT thin film domains are larger and more oriented than those of typical polymer semiconductors, they exhibit an unambiguous and directly measurable substrate effect. We find that pBTTT films cast on hydrophobic surfaces are more ordered than identical films cast on oxide surfaces after heating the film into the liquid crystal (LC) regime.

Substrates were cleaned with an ultraviolet-ozone cleaner immediately before film deposition. Octyltrichlorosilane (OTS) was deposited by immersing freshly cleaned silicon substrates in a 0.002 mol/L solution of OTS in anhydrous hexadecane for 12 h. Samples were then sonicated in baths of chloroform, isopropanol, and de-ionized water. Bottom contact TFTs were fabricated by depositing gold/titanium (45 nm/5 nm) electrodes on oxidized, highly doped, $\langle 100 \rangle$ silicon wafers (200 nm oxide). The pBTTT films were deposited on the substrates by spin coating from a 5 mg/ml solution in 85 °C 1,2 dichlorobenzene.¹² Films were cast at 1500($\cdot 2\pi$) rad/min using a 100($\cdot 2\pi$) rad/min s ramp rate. Films were divided into as-cast (OX-AC and OTS-AC) and those that received a heat treatment to the LC regime (OX-LC and OTS-LC). The heat treatment involved placing the films on a hot plate (180 °C) for 5 min, followed by a slow cool (≈ 10 °C/min). All polymer processing and measurements were performed in nitrogen.

The saturation mobility of TFTs made with pBTTT exhibited a dependence on substrate chemistry similar to that

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TABLE I. Average saturation mobilities of ≈ 50 TFTs for oxide and OTS-treated oxide substrates before (AC) and after heating to the LC regime (LC). Data are reported with the standard uncertainty.

Substrate	μ_{AC} (cm ² /V s)	μ_{LC} (cm ² /V s)
Oxide	0.10 \pm 0.02	0.03 \pm 0.01
OTS	0.12 \pm 0.02	0.27 \pm 0.05

observed for PQT (Table I).¹³ OTS-AC and OX-AC exhibited similar saturation mobilities. The charge carrier mobility for OTS-LC increased by about three times while OX-LC decreased by about four times. Figure 1 shows transfer curves for all four films.

Atomic force microscopy (AFM) images of thin pBTTT films (≈ 20 nm) heated to the LC regime have a terraced microstructure, as shown in Fig. 2. OTS-LC has much larger terraces than OX-LC, with the topmost terraces on OTS-LC microns in size and the lower terraces even larger. For OX-LC, the terraces are only about 100 nm in size. All as-cast films show no terracing and appear similar independent of substrate. It should be noted that AFM images of OX-LC appear more crystalline than as-cast films on either substrate despite having a lower charge carrier mobility. The order gained by heating atop oxide, however, could be offset by the apparent grain boundaries created during terrace formation. Grain boundaries in low molar mass P3HT have been shown to be detrimental to charge carrier mobility.¹⁴

The Bragg scattering intensity of XRD increases upon heating for OTS-LC and OX-LC, as shown in Fig. 3(a). The increases in scattering intensity of the Bragg peaks are consistent with terrace formation. Terrace formation requires both an increased extent of crystal orientation and an increased overall crystallinity. The width of the diffraction peaks decreases upon heating, indicating crystal growth normal to the substrate. From the peak width obtained from both OTS-LC and OX-LC, we obtain a crystal thickness that is the same as the film thickness, which shows that the domains extend from the substrate to the film surface. XRD also shows that the lamellar spacing decreases upon heating for LC films (19.6 Å for OTS-AC and 19.0 Å for OTS-LC) with a slight difference between OTS-LC and OX-LC (19.3 Å on oxide versus 19.0 Å on OTS).

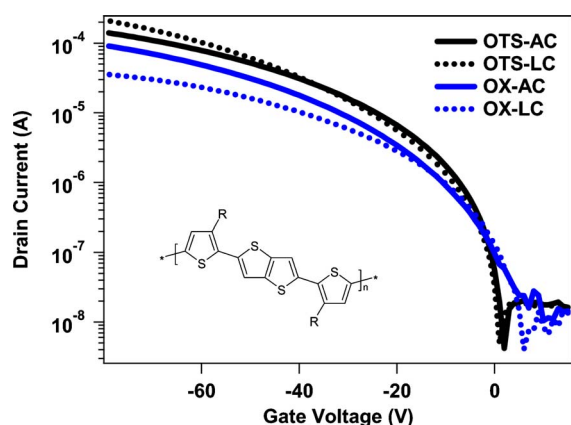


FIG. 1. (Color online) Transfer curves of pBTTT transistors with oxide and OTS surface chemistries before (AC) and after heating to the LC regime (LC). Channel width=1 mm and length=20 μ m. The difference in onset voltage between OTS and oxide films is comparable to the run to run variation. The standard uncertainty for current and voltage is 1%.

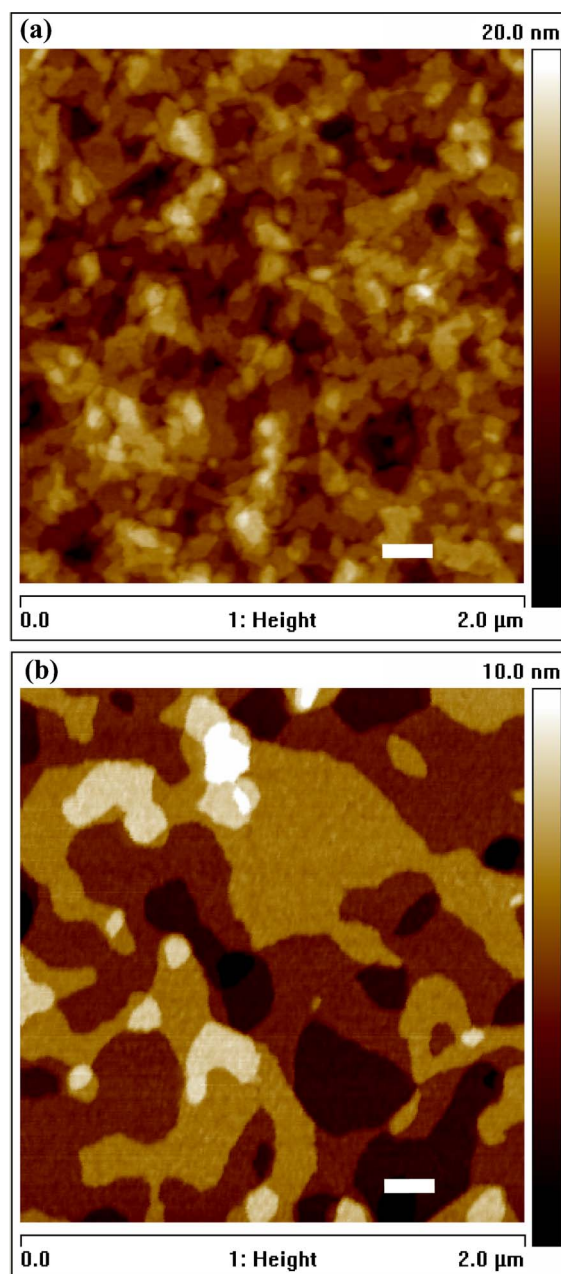


FIG. 2. (Color online) AFM images comparing (a) OX-LC and (b) OTS-LC. Scale bar denotes 200 nm.

On the other hand, near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, a nondestructive surface-sensitive method for determining molecular orientation, shows that π -plane orientation improves upon heating for OTS-LC but does not improve for OX-LC [Fig. 3(b)]. The higher dichroic ratios of OTS-LC are consistent with the increased crystallinity in AFM and the greater diffraction intensity in XRD. NEXAFS measures the average orientational order of the conjugated plane at the top or bottom interface, while XRD measures the quality and regularity of the lamellar terracing throughout the entire film. Evidently this orientational order is degraded somewhat in the smaller terraces of OX-LC, most likely because disorder is contributed from the greater number of grain boundaries.

The difference in terrace size between OTS-LC and OTS-AC suggests different nucleation densities, with the smaller islands on oxide films resulting from a greater nucle-

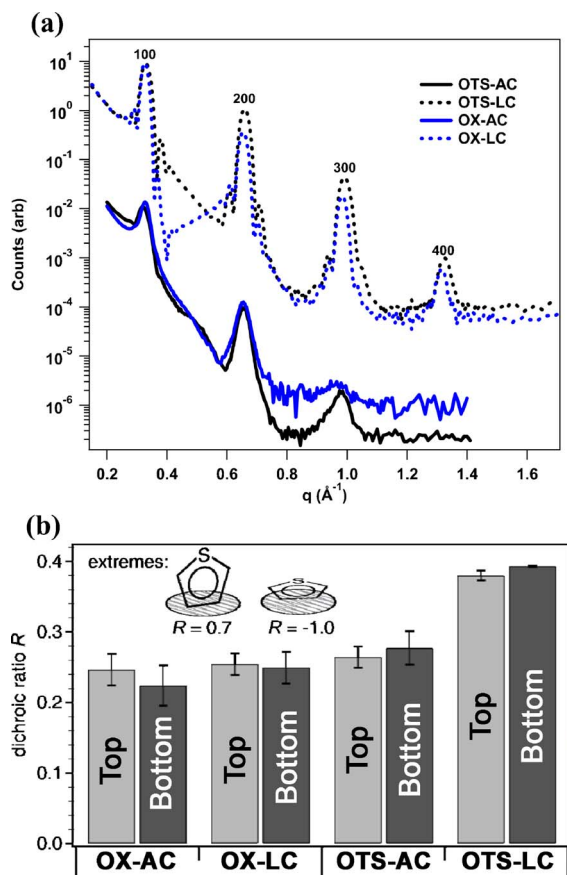


FIG. 3. (Color online) (a) Specular XRD data and (b) NEXAFS bar graph of conjugated plane dichroic ratio as a function of surface chemistry, thermal history, and interface (top or bottom). The XRD data for the heat treated films are offset for clarity. The standard uncertainties for q and intensity are 1% and 5%, respectively.

ation density. Since the oxide surfaces are smoother than OTS treated surfaces (measured by AFM), it seems likely that the nucleation sites have a chemical rather than topographical origin, and the addition of OTS blocks these sites. We speculate that reactive groups on the oxide chemically pin molecules to the surface, which serve as heterogeneous nucleation sites. The most likely pinning process would involve an interaction between the surface reactive groups and the thiophene ring. Since the plane-on orientation is unfavorable (no plane-on orientation is detected by NEXAFS at the bottom interface, limiting the possible molecules affected to less than $\approx 10\%$ of a monolayer), the pinning would occur sporadically and not in a comprehensive monolayer. Our speculation of the bonding between the film and the substrate is supported by the far greater adhesion of OX-LC films to the substrate noted during preparation of NEXAFS bottom interface samples (OTS-LC films can be easily delaminated with PDMS (Ref. 11) while OX-LC films will only delaminate after immersion in water). It remains unclear whether heating on oxide directly reduces the charge carrier mobility by disrupting morphology or indirectly reduces mobility by increasing trap states. A direct disruption of morphology would involve the formation of additional grain boundaries, voids, or amorphous regions. An indirect effect would involve trap exposure or creation. Relaxation upon heating, for example, could reposition the molecules closer to existing

traps on the oxide surface. The increased adhesion could also be explained by the removal of water molecules that formerly passivated the oxide; both this possibility and chemical pinning of the molecule to the substrate could create new charge carrier traps.

The large and oriented crystals of pBTTT films help to manifest the substrate effect. The domain size in as-cast films is independent of substrate treatment because the nucleation is dominated by the casting process. We hypothesize that no clear and measurable effect of substrate chemistry on film morphology is observed in P3HT and PQT because their characteristic domain size is smaller than the mean spacing between surface nucleation sites.

In summary, we have shown that the increased crystallinity of pBTTT reveals an unusually strong morphological dependence on the substrate surface chemistry. OTS treatment reduces the surface nucleation density of bare oxide, resulting in micron-scale terraced pBTTT films with improved charge transport. The strong adhesion of films to bare oxide surfaces after heat treatment indicates the presence of chemical interactions between the substrate and film that could lead to electrical trap creation. Although the influence of substrate chemistry on charge transport will originate from an interrelated combination of morphological and electrical effects at the substrate interface, the strong dependence of morphology on the surface chemistry plays an important role in the large hole mobility of this polymer semiconductor.

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- ¹G. Horowitz, *J. Mater. Res.* **19**, 1946 (2004).
- ²H. Katz and Z. Bao, *J. Phys. Chem. B* **104**, 671 (2000).
- ³M. L. Chabinyk and A. Salleo, *Chem. Mater.* **16**, 4509 (2004).
- ⁴H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, and D. M. de Leeuw, *Nature (London)* **401**, 685 (1999).
- ⁵R. J. Kline, M. D. McGehee, E. N. Kadnikova, J. Liu, J. M. J. Frechet, and M. F. Toney, *Macromolecules* **38**, 3312 (2005).
- ⁶D. M. DeLongchamp, B. M. Vogel, Y. Jung, M. C. Gurau, C. A. Richter, O. A. Kirillov, J. Obrzut, D. A. Fischer, S. Sambasivan, L. J. Richter, and E. K. Lin, *Chem. Mater.* **17**, 5610 (2005).
- ⁷R. J. Kline, M. D. McGehee, and M. F. Toney, *Nat. Mater.* **5**, 222 (2006).
- ⁸Y. Wu, P. Liu, B. S. Ong, T. Srikumar, N. Zhao, G. Botton, and S. Zhu, *Appl. Phys. Lett.* **86**, 1 (2005).
- ⁹J. Veres, S. Ogier, G. Lloyd, and D. de Leeuw, *Chem. Mater.* **16**, 4543 (2004).
- ¹⁰L. 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).
- ¹¹M. L. Chabinyk, A. Salleo, Y. L. Wu, P. Liu, B. S. Ong, M. Heeney, and I. McCulloch, *J. Am. Chem. Soc.* **126**, 13928 (2004).
- ¹²I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyk, R. J. Kline, M. D. McGehee, and M. F. Toney, *Nat. Mater.* **5**, 328 (2006).
- ¹³A. Salleo, T. W. Chen, A. R. Volkel, Y. Wu, P. Liu, B. S. Ong, and R. A. Street, *Phys. Rev. B* **70**, 115311 (2004).
- ¹⁴R. J. Kline, M. D. McGehee, E. N. Kadnikova, J. Liu, and J. M. J. Frechet, *Adv. Mater. (Weinheim, Ger.)* **15**, 1519 (2003).