The Role of OTS Density on Pentacene and C₆₀ Nucleation, Thin Film Growth, and Transistor Performance

By Ajay Virkar, Stefan Mannsfeld, Joon Hak Oh, Michael F. Toney, Yih Horng Tan, Gang-yu Liu, J. Campbell Scott, Robert Miller, and Zhenan Bao*

In organic thin film transistors (OTFTs), charge transport occurs in the first few monolayers of the semiconductor near the semiconductor/dielectric interface. Previous work has investigated the roles of dielectric surface energy, roughness, and chemical functionality on performance. However, large discrepancies in performance, even with apparently identical surface treatments, indicate that additional surface parameters must be identified and controlled in order to optimize OTFTs. Here, a crystalline, dense octadecylsilane (OTS) surface modification layer is found that promotes two-dimensional semiconductor growth. Higher mobility is consistently achieved for films deposited on crystalline OTS compared to on disordered OTS, with mobilities as high as 5.3 and 2.3 cm² V⁻¹ s⁻¹ for C₆₀ and pentacene, respectively. This is a significant step toward morphological control of organic semiconductors which is directly linked to their thin film charge carrier transport.

1. Introduction

Conjugated small molecular and polymeric semiconductors are being investigated as candidates for next generation large-area flexible electronic devices. The central research focus has been improvement of charge transport in organic thin film transistors (OTFTs). Charge transport takes place primarily within the first few monolayers at the dielectric/semiconductor interface; therefore, device performance is dominated by the properties of these interfacial layers. Grain boundaries between crystalline domains affect device performance, acting as barriers to charge transport. Consequently, highly crystalline films deposited via a layer-by-layer growth mode are desirable due to fewer in-plane boundaries.

Octadecylsilanes (OTS), specifically octadecyltrimethoxysilane (OTMS) and octadecyltrichlorosilane (OTCS), have been widely used to modify the SiO₂ dielectric surface and have resulted in dramatic improvement of the field-effect mobility for a variety of semiconductors. The hydrophobic nature of OTS is thought to passivate the SiO₂ surface, increase semiconductor crystal quality, reduce interfacial trap states, and in some cases planarize the surface. Previous reports have attributed the improvement of mobility on OTS-treated surfaces to a drastic reduction in surface energy by hydrophobic surface modification. However, a wide range of charge-carrier mobilities has been reported by a number of research groups for the same organic semiconductor on OTS, suggesting the need to understand the nature of the underlying OTS layer. For example, the reported mobilities of pentacene OTFTs with OTS-modified SiO₂ ranges from 0.03 to greater than 2 cm² V⁻¹ s⁻¹. Previous work has shown that both inorganic and organic materials growth is highly sensitive to the chemical nature, packing, and defects of the underlying self-assembled monolayer (SAM). Recently, Cho and coworkers studied the dependence of pentacene TFTs on OTS order. They found improved performance when the OTS layer was prepared at lower temperatures so that the monolayer was ordered. However, conclusive and quantitative reasons for the differences in growth mode, and number of transistors tested were not discussed. They suggested that a lower nucleation density is observed on ordered OTS due to a greater pentacene diffusivity. In an earlier report Cho and coworkers studied the chain length dependence of alkyl-silane treated SiO₂ on pentacene TFTs. In this report they found that pentacene diffusivity was the largest and nucleation density was the lowest on the most disordered shorter chained alkyl-silanes. However, in both of these reports the role of the surface on heterogeneous nucleation was not considered, which we show in this work is a major factor governing OTFT performance. The incongruence in these results stems from the fact that both growth mode and nucleation density are highly sensitive to the surface. Furthermore, models which
have been developed for inorganic nucleation and thin film growth often fail to accurately represent organic thin film growth due to the differences in molecular symmetry and bonding.

In addition, some semiconductors only show marginally improved performance on an any OTS-treated surface compared to SiO₂ despite the large difference in surface energy.⁵ This suggests, as Markov and others have theorized, that each combination of molecule and substrate must be considered unique.¹⁷⁻¹⁹ The most relevant factor affecting growth, and consequently charge-carrier mobility, is the specific energetic interaction between the semiconductor and the surface.¹⁷⁻¹⁹ We show that this interaction is influenced considerably by the phase of the underlying OTS monolayer, even though all the OTS phases have identical chemical compositions, and similar surface energies and roughness.

2. OTS Film Preparation and Characterization

In this study, we investigated the effect of density and degree of ordering of OTS monolayers on the performance of two of the most widely studied and highest mobility organic semiconductors: pentacene (p-channel) and C₆₀ (n-channel).²,²²⁻²⁵ The Langmuir–Blodgett (LB) technique was employed to systematically vary the organization and density of the OTS monolayers. In this well-known ultrathin-film deposition technique, amphiphilic OTS molecules are compressed by applying a lateral pressure to the monolayer film at the air–water interface.²⁶ Under increase in applied lateral pressure, the film undergoes a transition from a 2D gas to a 2D liquid and finally to an ordered 2D solid.²⁶ From the Langmuir isotherms obtained in our study, the OTS film collapses at a surface pressure of ~55 mN m⁻¹ and there appears to be a phase transition leading to the most ordered phase at a surface pressure of ~40 mN m⁻¹ (Fig. 1). This phase change from one condensed (2D solid) phase to another condensed phase was also observed by Duran and coworkers.²⁷ Accordingly, surface pressures of 20, 35, and 50 mN m⁻¹ were chosen to study OTS films of different degrees of order (designated as LB-20, LB-35, and LB-50). Moreover, by studying LB-35 and LB-50 we were able to probe two distinct solid phases. During fabrication of the Langmuir films, OTMS molecules were hydrolyzed and partially polymerized on the trough at pH of 3.²⁷ The polymerized monolayer was Blodgett transferred to the thermally grown silicon oxide (300 nm) surface on a heavily doped silicon wafer, which is used as the gate electrode. For comparison, the commonly used OTMS-V and OTCS-V films were also prepared using procedures described in the literature.⁵,²⁸⁻³¹ Transistors were completed in top contact geometry with gold source and drain electrodes. The channel length was 50 µm and the width was 1000 µm.

The OTS monolayers were characterized using grazing angle attenuated total reflectance–Fourier transform infrared spectroscopy (GATR–FTIR) by examination of the C–H stretches of the CH₂ and CH₃ groups. Higher compression pressure produced films with increased total absorption area, indicating an increased film density (Fig. 2a). This was accompanied by a characteristic shift of aliphatic vibrational stretching modes to lower wave-numbers (from 2924 to 2918 cm⁻¹ for the asymmetric C–H stretch and from 2855 to 2851 cm⁻¹ for the symmetric C–H stretch), indicating a transition from a liquid-like (disordered) to crystalline layer.¹² The magnitude of the observed peak shifts is similar to those reported in the literature. The results are summarized in Table 1.

The OTS monolayers were further characterized using grazing incidence X-ray diffraction (GIXD). GIXD can probe in-plane order, it is the ideal technique to study the crystalline order of a monolayer. Only the highly dense LB-50 monolayer gave rise to a Bragg rod in the GIXD spectrum (Fig. 3 and 6d). This peak was not observed in the other OTS films studied showing that these are less ordered and noncrystalline. This indicates that indeed only the LB-50 monolayer has crystalline order. The calculated
confirming that lower mobilities observed for OTS-V-treated OTFTs are not due to surface roughness effects. The key film characteristics (C–H stretching mode frequencies, contact angle, and surface roughness) for all the OTS films remained unchanged after heating to 200 °C under argon, indicating the films are stable and do not undergo thermal phase changes in the temperature ranges used for semiconductor deposition.

3. Effects of OTS Density on Pentacene and C₆₀ Transistor Performance

The pentacene charge-carrier mobility (μ) extracted from saturation transfer characteristics is plotted as a function of the density (inverse mean molecular area (MMA)) of the OTS monolayer in Figure 2c. The MMA is calculated based on the total number molecules deposited on the Langmuir trough, and the total area occupied by the Langmuir film at the corresponding surface pressure. The average pentacene hole mobility measured for 50 devices on each type of OTS increases with increasing OTS density from 0.4 cm² V⁻¹ s⁻¹ for the least compressed LB film (LB-20) to 2.1 cm² V⁻¹ s⁻¹ on the most compressed (highest order) LB film (LB-50) despite only small differences in surface energy and roughness. This suggests that the density of OTS is a critical factor effecting performance. The mobility on the less dense OTS-V (MMA = 28.7 Å² molecule⁻¹) is comparable to the lowest compressed LB film (20 ms m⁻¹, MMA = 24.8 Å² molecule⁻¹) substrate despite lower film density. See Table 3 for summary of average electrical characteristics. C₆₀ OTFTs showed an electron mobility as high as 5.2 cm² V⁻¹ s⁻¹ (measured in nitrogen glovebox) on the LB-50 film and followed the same trend as pentacene with mobility decrease in the with decreasing OTS order. This C₆₀ mobility on the dense OTS is amongst the highest in the literature (see Table 4). The pentacene TFTs were fabricated on four different days during four different depositions, and the C₆₀ TFTs were deposited on

4.2 Å hexagonal lattice constant for the LB-50 OTS is consistent with previous reports for crystalline OTS. The LB–OTS peak does show some mild arching (Fig. 3a). It is likely that this tilt is due to the defects in the OTS film which arise from some ordered domains being noncoplanar with the majority of the film (Fig. 3c). Such defects can arise in LB films since the films are prepared by applying lateral compression.

The density and order of the LB films as a function of surface pressure were further characterized by ellipsometry, static water contact angle, and high resolution AFM (Table 2). As the monolayers were compressed, the film thickness and water contact angle increased, again indicating a denser monolayer. Using high resolution atomic force microscopy, it was determined that the LB films also showed larger overall domain size, roughly 30% larger than the vapor phase deposited films (see Supporting Information). The root mean square (RMS) roughness was similar for the LB films and the vapor deposited OTS-V film.

Table 1. Peak positions corresponding to absorption maxima for the various CH2 and CH3 stretch modes probed by GATR–FTIR.

<table>
<thead>
<tr>
<th>Peak Position [cm⁻¹]</th>
<th>Crystalline[a]</th>
<th>Liquid[a]</th>
<th>LB-50</th>
<th>LB-35</th>
<th>LB-20</th>
<th>OTS-V</th>
</tr>
</thead>
<tbody>
<tr>
<td>2851</td>
<td>2955</td>
<td>2851</td>
<td>2851</td>
<td>2852</td>
<td>2852</td>
<td>2852</td>
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<tr>
<td>2918</td>
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</tbody>
</table>

[a] Literature values for the crystalline or liquid the stretch modes of aliphatic chains (Ref. [32]).
length TFTs the contact resistance is typically negligible compared to channel resistances; the device performance is dominated by the channel.\cite{30,31} From the output characteristics the linear region of the IV curves show no non-linearity indicating that absence of contact issues. In order to test for the contribution of contact and channel resistances, several pentacene OTFTS with different channel lengths were tested and contact resistance was extracted. The contact resistances were nearly identical (within 3.0%) for TFTs fabricated on different OTS monolayers and were much smaller than the channel resistances indicating that indeed the channel effects dictate performance (Fig. 5).

Table 2. Properties of OTS monolayers studied

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molecular area [Å²molecule⁻¹]</th>
<th>Height [nm]</th>
<th>Contact angle [deg]</th>
<th>RMS roughness [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB-20</td>
<td>24.8</td>
<td>2.0</td>
<td>101.7</td>
<td>0.2</td>
</tr>
<tr>
<td>LB-35</td>
<td>22.5</td>
<td>2.1</td>
<td>102.6</td>
<td>0.3</td>
</tr>
<tr>
<td>LB-50</td>
<td>20.1</td>
<td>2.1</td>
<td>104.1</td>
<td>0.3</td>
</tr>
<tr>
<td>OTMS-V</td>
<td>32.6[a]</td>
<td>1.8</td>
<td>90.5</td>
<td>0.3</td>
</tr>
<tr>
<td>OTCS-V</td>
<td>28.7[a]</td>
<td>1.9</td>
<td>98.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

[a] These MMA values were estimated by calculating the area under the absorption peaks from the GATR–FTIR spectra for the two OTS-V surfaces, and comparing them to the area under the absorption peaks for LB films with known MMA values.

Table 3. Summary of pentacene TFT data measured in ambient conditions.
The values shown are averages over ~50 devices for each OTS substrate treatment

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th>Average μ [cm²V⁻¹s⁻¹] (SD)</th>
<th>Max μ [cm²V⁻¹s⁻¹]</th>
<th>I_on/I_off</th>
<th>V₉ [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB-20</td>
<td>0.4 (0.05)</td>
<td>0.6</td>
<td>10⁶</td>
<td>-18</td>
</tr>
<tr>
<td>LB-35</td>
<td>1.2 (0.08)</td>
<td>1.4</td>
<td>2 × 10⁶</td>
<td>-24</td>
</tr>
<tr>
<td>LB-50</td>
<td>2.1 (0.12)</td>
<td>2.3</td>
<td>2.5 × 10⁹</td>
<td>-20</td>
</tr>
<tr>
<td>OTMS-V</td>
<td>0.6 (0.1)</td>
<td>0.9</td>
<td>10⁶</td>
<td>-19</td>
</tr>
<tr>
<td>OTCS-V</td>
<td>0.2 (0.1)</td>
<td>0.27</td>
<td>2 × 10⁹</td>
<td>40</td>
</tr>
</tbody>
</table>

In order to determine the effect of OTS monolayer density on organic semiconductor nucleation and growth at the semiconductor/dielectric interface, pentacene thin films (nominally 3 nm thick, with known MMA values) were deposited on the OTS films under identical conditions as those used for OTFT fabrication. The transistor’s ‘on’ state, the majority of charge carriers are induced and transported in the first ~5 nm of semiconductor near the dielectric interface; the packing and morphology of the initially deposited interfacial layer are therefore critical.\cite{13-5} These were examined using AFM and GIXD, giving information about the morphology and crystalline order of the pentacene monolayer film directly involved in charge transport. AFM was performed immediately after deposition to ensure the film did not undergo reorganization. AFM was also performed before and after GIXD experiments to also ensure that films did not change during exposure to X-rays (typically for 30 min).

To determine if the packing of pentacene in the first monolayer is affected by the difference in OTS density, we carried out GIXD of the pentacene monolayers. The characteristic pentacene (11), (02), and (12) in-plane Bragg rods are seen in the GIXD spectra (Fig. 6). On the LB-50 film (Fig. 6d), an additional broad peak to the crystalline nature of the underlying OTS. The lattice constants of pentacene (a = 5.93 Å, b = 7.58 Å, γ ≈ 90°) extracted from the diffraction peaks were nearly identical regardless of the...
OTS preparation method and are similar to those reported for pentacene grown on hexamethyldisilazane (HMDS) or OTS.\cite{36,37} The pentacene GIXD spectra (position of peaks in \( Q_{xy} \) and \( Q_{z} \)) are also similar on all the OTS surfaces. This indicates that the difference in mobility on different OTS surfaces is not due to different pentacene packing motifs. It is also interesting to note that there is an additional diffraction peak at \( Q_{xy} = 1.6 \) on OTS-V (Fig. 6a) which corresponds to a portion of the film exhibiting the bulk pentacene phase. This 3D growth on OTS-V is further asserted by the AFM results discussed below. The full-width at half maximum (FWHM) of the diffraction peaks can be used to gauge the crystalline quality of the pentacene on various OTS surfaces. However, for all the films studied, the FWHM was resolution limited (domain size >10 nm) (see Section 5).

AFM of the nominally 3 nm pentacene films (Fig. 7) did, however, show a clear trend between thin film morphology and charge-carrier mobility. The growth mode on the highly ordered LB films showed the more desirable 2D layer-by-layer (Frank-van der Merwe type) growth (Fig. 7) as compared to the less favorable 3D (Volmer–Weber type) growth on OTS-V (Fig. 7a) which leads to many island boundaries after coalescence.\cite{2–4,17} The growth mode on OTS-V is purely 3D island-type; no complete monolayer forms within the first 3 nm of nominal film thickness before additional layer growth, though the individual crystalline islands are large and terraced. The island size is considerably larger on OTC-V than on the LB films, which are composed of smaller connected islands.

5. Discussion

The 3D versus 2D growth mode for the initial few layers on substrate is the result of competition between molecule–molecule interaction and molecule–substrate interaction.\cite{17,19} Three-dimensional growth is favored when molecule–molecule interaction dominates.\cite{17} The chemical potential difference (\( \Delta \mu \)) between the vapor phase (\( \mu_v \)) and the crystalline phase (\( \mu_c \)) is the driving force for crystallization and can be expressed as\cite{17}

\[
\Delta \mu = \int_{\mu_v}^{\mu_c} \frac{\partial \mu_v}{\partial P} dP - \int_{\mu_v}^{\mu_c} \frac{\partial \mu_c}{\partial P} dP \\
= \int (\mu_v - \mu_c) dP 
\]  \( (1) \)
where $P$ is pressure, $P_v$ the vapor pressure during deposition and is related to the flux of molecules from the source, and $P_c$ is equilibrium vapor pressure of the crystal at the substrate temperature.

Two-dimensional growth is possible when 

$$D_m = \frac{C_m}{C_2} \frac{C_1}{C_0} \frac{C_0}{C_1} \frac{C_0}{C_1}$$

where $C_m$ is the interlayer interaction energy between the semiconductor molecule and the first partial layer of semiconductor deposited on the surface, and $C_{mol-substrate}$ is the interaction energy between the semiconductor molecule and the substrate (OTS). In Equation (1) the second equality, the partial derivative of chemical potential in phase $i$ with respect to pressure is equal to the molar volume ($V_i$) of phase $i$:

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} = V_i$$

$V_i$ is the molar volume of the vapor and $V_c$ the molar volume of the crystal. Since $V_c \gg V_v$ and because the pressure used during vapor deposition is low enough to assume ideal gas behavior ($P \sim 10^{-6}$ torr) where $V_v = \frac{RT}{P}$, Equation (2) can be rewritten

$$\Delta \mu \approx RT \ln \frac{P_v}{P_c}$$

The equivalent vapor pressure ($P_v$) can be calculated as a function of the deposition rate ($\theta$) and temperature using

$$\theta \left(\frac{molecules}{cm^2 \text{ sec}}\right) = 3.513 \times 10^{32} \frac{P_v}{RT}$$

The equilibrium vapor pressure of a crystal ($P_c$) at substrate temperature $T_{sub}$ is given by

$$P_c = \exp \left( A - \frac{\Delta H_{sub}}{RT_{sub}} \right)$$

where $\Delta H_{sub}$ is the enthalpy of sublimation and $A$ is a constant related to entropy and have been calculated elsewhere ($\Delta H_{sub} = 37.8 \text{ kcal mol}^{-1}$). Combining Equations (4–6), the chemical potential driving force can be estimated from the known heat of sublimation, and input experimental parameters:

$$\Delta \mu \approx \Delta H_{sub} + RT_{sub} \ln \left( \sqrt{2\pi MRT_{sub}} \theta \right) - A$$
nucleation in conjunction with specific molecular interactions which determine growth mode. The rate of nucleation \( N \) (stable-nuclei time\(^{-1}\)) scales exponentially with the energetic barriers of desorption \( (E_{\text{des}}) \), molecular diffusion on the substrate \( (E_s) \), and nucleation \( (\Delta G') \), by the relationship\(^{[17,38]} \)

\[
N \sim \exp \left( \frac{E_{\text{des}} - E_s - \Delta G'}{kT} \right)
\]

where \( k \) is Boltzmann’s constant and \( T \) is substrate temperature. \( \Delta G' \) arises from the surface and entropic effects of stabilizing a cluster of molecules at the critical cluster size; at this size, the enthalpic benefit of adding another molecule to the cluster outweighs the energetic penalty associated with creating a new solid surface with a corresponding increase in surface free energy. \( \Delta G' \) is a strong function of \( \psi_{\text{mol-substrate}} \). A greater \( \psi_{\text{mol-substrate}} \) means a smaller energetic barrier for nucleation. Hence, smaller crystals but a larger number of nuclei (more 2D growth and higher first monolayer coverage) are observed on the substrate with the largest \( \psi_{\text{mol-substrate}} \): the LB-50 surface (see SI for submonolayer AFM showing pentacene nucleation density). In fact, the nucleation density of submonolayer (nominally 1 nm) pentacene is four times greater on the crystalline LB-50 surface compared to the amorphous OTS-V surface (see Supporting information).

Moreover, assuming that \( E_{\text{des}} \) and \( E_s \) are similar for both surfaces (since the surface roughness is comparable and chemical identity is the same), the calculated barrier to nucleation \( \Delta G' \) on LB-50 film is nearly 60% of that on OTS-V. As previously mentioned, 2D growth dominates when \( \psi_{\text{mol-substrate}} \) is greater than \( \psi_{\text{interlayer}} \). Together, these energetic considerations qualitatively explain the growth mode as a function of OTS density (since typically \((\Delta G' \gg |E_s| \text{ and } |E_{\text{des}}|)\)\(^{[17,38]} \). Moreover, these results highlight that there is still some confusion as to how grain boundaries

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Figure 7. Nominally 3 nm thin film of pentacene deposited under identical conditions as used in TFT fabrication (0.3 A\(^{-1}\) s\(^{-1}\) at 60 °C) on a) OTS-V b) OTS-20, c) LB-35, d) LB-50. The line corresponds to the line profile shown directly below each AFM image. The growth mode of pentacene tends to be more and more 2D as the OTS density increases.

Figure 8. AFM of nominally 2 nm C\(_{60}\) deposited under identical conditions as used for TFT fabrication on a) OTS-V (the coverage is ca. 30%), and on b) LB-50 (the coverage is ca. 80%)
precisely affect charge-carrier mobility. The higher nucleation density on the LB-50 films would presumably give rise to many more grain boundaries, but the strong tendency toward 2D growth engenders a well connected and highly conductive first monolayer. The physics of film growth between nucleation and coalescence is complex. It is plausible that the coalescence of 3D islands may give rise to more severe and detrimental grain boundaries (deeper energetic traps) than 2D islands. Our results indicate that the number of grain boundaries may not be as critical as the nature (severity) of the grain boundaries. Future work is on-going to address this issue. Nevertheless, from a technological standpoint our results indicate that a general approach for realizing desirable thin film morphology, which gives rise to high mobility, is to use a densely packed surface-modifying layer whose terminal groups interact favorably with the depositing semiconductor.

6. Conclusions
In conclusion, we have shown the importance of phase and order of the organic dielectric surface modification layer for achieving 2D semiconductor film growth and high charge-carrier mobility in pentacene and C60, two of highest performing organic semiconductors. AFM and GIXD provide the first complete picture for the effect of both crystalline order and growth mode of the vital first few semiconductor monolayers on OTFT performance. These results give insight into several new and important issues relevant to engineering high performance devices. Specifically, pentacene’s and many other semiconductors’ thin-film growth is highly sensitive to the precise nature of the surface. We show that an increase in density of the methyl terminated surface modification layer results in primarily two-dimensional growth of subsequently vacuum-deposited organic semiconductors. These changes in nucleation and growth give rise to a substantial improvement in the charge-transport characteristics in a variety of materials, and suggest that this approach is generally important for the optimization of OTFT performance and may also have implications on thin film growth in a variety of organic and inorganic materials

7. Experimental
Materials: Octadecyltrimethoxysilane (OTMS, 95%, purchased from Gelest Inc.) was purified by distillation and octadecyltrichlorosilane (OTCS, 99%, purchased from Gelest Inc.) was used as received. Device substrates consisted of thermally grown silicon oxide having a capacitance per unit area (C1) of 10 nF cm⁻². Pentacene was purchased from Sigma–Aldrich and sublimed twice prior to usage. C60 was purchased from Alfa Aesar (99.5%) and used as received. For ellipsometry and GIXD experiments, silicon wafers with 2–3 nm of native oxide were used. Prior to OTS treatment the wafers were cleaned with piranha (70:30 H2SO4: H2O2) for 60 min and then with ozone plasma (Jetlight UV-Ozone Cleaner Model 42–100 V) for 10 min.

Fabrication of LB Films: A OTMS solution (1 µg mL⁻¹ in chloroform) was prepared in a nitrogen glovebox and filtered (0.2 µm pore size). The trough (Nima model 612D) was filled with Millipore water (pH = 3) prepared using concentrated hydrochloric acid (38% HCl). The OTMS films were compressed (20 cm² min⁻¹) with respect to change in trough area to the desired surface pressure and then Blodgett transferred (1 mm min⁻¹) to the Si/SiO2 substrate. The substrates were cleaned sequentially with toluene, isopropanol, acetone, distilled water, and isopropanol again and then dried using a nitrogen gun (99.9% pure).

Characterization: The Grazing Incidence Xray Diffraction (GIXD) spectrum was obtained using a Nicolet 6700 Fourier Transform Infrared Spectrometer (FTIR) using a germanium crystal. A Sopra Bois-Columbes ellipsometer with a Physik Instrumente laser (He–Ne, λ = 632.8 nm, angle of incidence of 70°) and detector were used for OTS thickness measurements. Thickness was calculated from Ψ and Δ values and measured for five areas on the substrate. The following input refractive indices were used: air, n0 = 0; alkylsilane, n1 = 1.450; native silicon oxide, n2 = 1.460, silicon, n3 = 3.873, k = 0.016.

The AFM images of organic semiconductors were collected using a Digital Instruments MMAFM-2 scanning probe microscope. Tapping mode AFM was performed on the samples with a silicon tip with a frequency of 300 kHz.

High Resolution AFM: The OTS substrates were washed sequentially with ethanol (99.99% pure from Gold Shield Chemical Co.) and mili-Q water (18.3 MΩ) two times at room temperature (296 K) and allow to air dry before characterization using AFM. The OTS substrates were characterized in Decahydronaphthalene solution (99.9%, Sigma Aldrich).

The optimum imaging area to visualize local domain is 100 nm x 100 nm under AFM. Thus, the cursor profile and RMS value were obtained using RHK-based imaging processing software at 100 x 100 nm area. For statistical analysis, both domain sizes (FWHM), separation (center-to-center and edge-to-edge), and vertical height were measured quantitatively from over 10 cursor profiles per image, using characteristic features, at 300 nm x 300 nm areas. Repeated experiment yield similar results.

Grazing Incidence Xray Diffraction: GIXD was performed on the samples at the Stanford Synchrotron Radiation Laboratory (SSRL) on beam line 11-3 with a photon energy of 12.73 keV. A 2D image plate (MAR345) with effective pixel size of 150 µm (2300 x 2300 pixels) was used to detect the diffracted X-rays. The detector was 400.15 mm from the sample center. The angle of incidence was fixed at 0.1 µ. The GIXD data were analyzed using FIT-2D and PeakFit software programs.

The resolution for GIXD was calculated using

\[ \Delta Q_{xy} = \frac{2\pi d \tan(2\theta)}{\lambda D} \]  

Where:
- \( \Delta Q_{xy} \) is in-plane resolution (Å⁻¹)
- \( 2\theta \) is the scattering angle (degrees)
- \( \lambda \) is X-ray wavelength (Å)
- \( D \) is distance between the sample and the detector (cm)
- \( d \) is sample length (cm)

Solving gives: \( \Delta Q_{xy} = 0.06 \text{ Å}^{-1} \)

Electrical Characterization: A Keithley 2400 semiconductor parameter analyzer was used to test p-channel transistors in an ambient atmosphere, and n-channel transistors in a nitrogen glovebox.

The charge-carrier mobility (μ) was calculated by fitting the saturation transfer characteristics using

\[ I_{DS} = \frac{W C_{ox}}{2L} \mu (V_G - V_T)^2 \]  

where \( I_{DS} \) is the drain current, \( W \) the channel width, \( L \) the channel length, \( C_{ox} \) the capacitance of the oxide, \( V_G \) the gate voltage, and \( V_T \) the threshold voltage.
Acknowledgements

Portions of this research were carried out at the Stanford Synchrotron Radiation Laboratory, a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences. The authors acknowledge helpful discussion with Y. Ito, R. Stoltenberg, R. Lowe, M. Wang, M. Roberts, and C. Reese. Y. H. T. acknowledges University of California, Davis, provided 2007 Summer Graduate Student Researcher Award. This work was partially supported by the Stanford Center for Polymeric Interfaces and Macromolecular Assemblies (NSF-Center MRSEC), NSF DMR Solid State Chemistry, Air Force Office of Scientific Research, the Stanford School of Engineering, and a Sloan Research Fellowship. Supporting Information is available online at www.afm-journal.de or from the author.

Received: November 22, 2008
Published online: May 7, 2009