



Effect of Surface Energy on Pentacene Growth and Characteristics of Organic Thin-Film Transistors

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Fluorinated hybrid materials were synthesized for a solution-processable gate insulator. The surface energy was modified by perfluoroalkyl chains contained in the hybrid gate insulator itself. We investigated the initial morphology and growth mode of pentacene and the characteristics of organic thin-film transistors (OTFTs) to determine how these characteristics depend on the surface energy. Pentacene growth was changed from a layer-by-layer mode to a three-dimensional (3D) island growth mode at low surface energy. Tightly and uniformly grown pentacene grains at 3D island mode induced good OTFT performance, but the carrier mobility was degraded at very low surface energy due to the large amount of grain boundaries.
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Organic thin-film transistors (OTFTs) attract great interest due to their ease of processing, low cost, and wide applicability. The characteristics of OTFTs are very dependent on the gate insulators because the majority of the charge carriers in the OTFTs are located close to the interface between the gate insulator and the organic semiconductor.¹⁻³ The surface energy of the gate insulator has an effect on the initial growth behavior, the morphology, and the crystallinity of the pentacene layer; these are critical performance factors for OTFTs. The hydrophobic surface of the gate insulator, which induces the pentacene crystallinity and the interconnection between pentacene grains, enhances OTFT performance. To this end, surface treatments on the gate insulator using hexamethyldisilazane, octadecyltrichlorosilane, and other self-assembled monolayers (SAMs) were employed.⁴⁻⁶

In this study, we considered methacrylate siloxane hybrid materials (hybrimers) simply synthesized by a sol-gel process of organoalkoxysilane. The perfluoroalkyl chain was introduced in the design of the hybrimer to tune the surface energy of the gate insulator. Instead of using an additional surface treatment on the gate insulators, we added long perfluoroalkyl chains to the hybrimer gate insulator. These chains were concentrated on the insulator surface, leading to better growth of the pentacene. We added various amounts of perfluoroalkylsilane to the hybrimer to control the surface energy of the gate insulator. Next we observed the growth behavior of the pentacene on the hybrimer gate insulator. We investigated the electrical characteristics of the fabricated OTFT to determine how these characteristics depend on the content of perfluoroalkyl chains.

Experimental

We synthesized fluorinated hybrid materials (hybrimers) via a sol-gel process using 3-(trimethoxysilyl)propyl methacrylate, titanium(IV) butoxide, and 1H,1H,2H,2H-perfluorodecyltrimethoxysilane (PFAS). Instead of using an additional surface treatment, we added long perfluoroalkyl chains to the hybrimer gate insulator itself. These chains were concentrated on the insulator surface, leading to better growth of the pentacene. To control the surface energy of the gate insulator, the amounts of PFAS, which contained the hydrophobic perfluoroalkyl chain, were adjusted as follows: 0 (MTF0), 1 (MTF1), 5 (MTF5), and 10 mol % (MTF10) of total alkoxides in the precursor solution, respectively. Figure 1 shows a schematic of the synthesis process and the structure of the fluorinated hybrimer. The siloxane networks constituted the core of the hybrimer, with organic arms branching out from the core. The organic arms were composed of methyl methacrylate and perfluoroalkyl chains.

The synthesized hybrimers were spin coated on indium tin oxide coated glass. They were exposed to UV lights (220–260 nm, Hg/Xe

lamp) for 2 min in air and were thermally cured at 150°C for 2 h in vacuum. The film thickness was controlled to about 300 nm. The pentacene was deposited on the hybrimer gate insulators by thermal evaporation at a rate of 0.4–0.5 Å/s under a pressure of 1×10^{-6} Torr. Au was used as source and drain electrodes and deposited on the pentacene thin-film layer by thermal evaporation through a shadow mask. The OTFTs had a channel length (L) of 50 μm and a channel width (W) of 3000 μm .

Results and Discussion

The surface energies of the hybrimer gate insulators were determined by the Owens–Wendt surface energy calculation using deionized (DI) water and diiodomethane. Table I shows the contact-angle data of DI water and diiodomethane and the surface energy of gate insulators. γ^d and γ^p represent dispersion and polar components of the surface energy. The surface energy of the gate insulator (γ) is the sum of γ^d and γ^p .

The hybrimer gate insulators become hydrophobic as the PFAS content increases. The surface energy of the MTF0 hybrimer, 43.5 mJ/m^2 , was reduced down to 25.6 mJ/m^2 upon adding 1 mol % of PFAS. This drastic change in the surface energy indicates that most of the long perfluoroalkyl chains are located on the surface, not in the bulk, of the hybrimer thin film. Finally, the surface energy was reduced to 17.9 mJ/m^2 for the hybrimer with 10 mol % PFAS.

The dielectric constant was calculated from the film thickness and capacitance at 100 kHz using a metal–insulator–semiconductor structure. The dielectric constant values of MTF0, MTF1, MTF5, and MTF10 were 5.42, 4.91, 4.85, and 4.79, respectively. Their dielectric constant values of hybrimers were higher than that of SiO_2 due to titanium oxide formed in the gate insulators. As the concentration of the perfluoroalkyl chain increased, the dielectric constant decreased, owing to fluorine in the perfluoroalkyl chain.

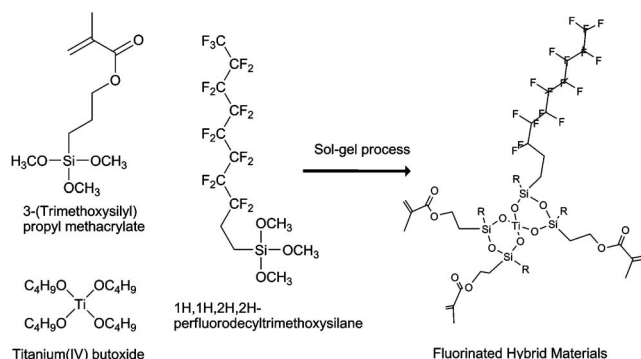


Figure 1. Schematic diagram of the synthesis and the structure of the fluorinated hybrimer.

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Table I. Contact angles and surface energies of the hybrimer gate insulators. The surface energy of pentacene is 38.3 mJ/m². The dispersion and polar components of the energy are 35.3 and 3.0 mJ/m², respectively.

Gate insulator	Contact angle (°)		γ^d (mJ/m ²)	γ^p (mJ/m ²)	γ (mJ/m ²)
	DI water	Diiodomethane			
MTF0	72.4	39.3	36.7	6.8	43.5
MTF1	93.2	67.2	22.9	2.7	25.6
MTF5	98.6	76.0	18.4	2.2	20.6
MTF10	102.7	80.6	16.1	1.7	17.9

The root-mean-square (rms) roughness of four gate insulators with different PFAS contents was measured by atomic force microscopy (AFM). The values were approximately 0.3 nm regardless of hydrophobicity. Because the rms roughness of thermally grown SiO₂ was about 0.4 nm, the hybrimer thin films were considered to have sufficiently low values of surface roughness. Therefore, the surface roughness of hybrimers would not give different effects on the pentacene growth and the morphology.

The morphologies of pentacene thin films that were grown on hybrimer gate insulators were observed using AFM. Because the major movement of the charge carrier occurs at the first or second layer of a pentacene thin film, it is important to survey the initial growth of the pentacene layer on the gate insulators. Pentacene thin films with very low thicknesses of 3 and 8 nm were deposited on hybrimer gate insulators. Because the d-spacing of the thin-film phase pentacene was 1.54 nm, the 3 nm thick pentacene constituted two layers. Figure 2a shows the 3 nm thick pentacene on the MTF0. The surface of the gate insulator is not fully covered by the pentacene. There are large-sized grains on the surface of MTF0, and small grains are located on the large grains. This is a result of the second layer of pentacene being grown before the first layer growth is complete; inconsistent growth causes defects and voids to occur between the first and second layers. The height profile supports the analysis of grain morphology. The layer-by-layer structure of the pentacene thin film is seen, along with the height of each layer at 3.5 nm, and the presence of large-sized grains formed on the wafer surface with smaller grains deposited on the large grains.

The different aspects are shown when the 3 nm thick pentacene is grown on the fluorinated hybrimer gate insulators (Fig. 2b-d). The pentacene is grown uniformly and we cannot see the layer structures. The height profile shows that the grain shape is not a layer-

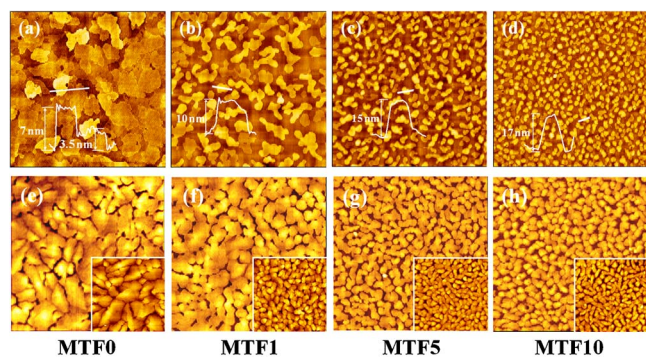


Figure 2. (Color online) Morphologies (5 × 5 μm) of pentacene thin films grown on hybrimer gate insulators with different levels of surface energy. The pentacene thickness is 3 nm for (a)–(d) and 8 nm for (e)–(h). Insets in (a)–(d) are height profiles of the white line measured by AFM and insets in (e)–(h) are morphologies (5 × 5 μm) of 50 nm pentacene deposited on the gate insulators.

by-layer structure but is an island structure. As the surface energy decreases, the grain size of pentacene decreases and its height increases. Each pentacene growth starts from a small core, and these small grains grow until they fill the surface of the gate insulators. Each pentacene grain is observed in a tightly packed formation and grains are merged into each other, as shown in Fig. 2f-h. This kind of three-dimensional (3D) island growth mode is the well-known Volmer–Weber growth mode, and the layer-by-layer growth mode is the Frank–van der Merwe mode.^{7,8} The growth modes are determined by the following relationship

$$\gamma_p + \gamma_i \leq \gamma_g \quad (\text{Frank–van der Merwe mode, layer-by-layer}) \quad [1]$$

$$\gamma_p + \gamma_i > \gamma_g \quad (\text{Volmer–Weber growth mode, 3D island}) \quad [2]$$

where γ_p is the surface energy of the pentacene, γ_g is the surface energy of the gate insulator, and γ_i is the interfacial free energy. Using work of adhesion ($W_{pg} = \gamma_p + \gamma_g - \gamma_i$), the γ_i term is eliminated, then the equation is represented as $W_{pg} > 2\gamma_p$ for layer-by-layer growth and $W_{pg} < 2\gamma_p$ for 3D island growth.⁹ The work of adhesion is calculated by the following relationship⁹

$$W_{pg} = 4 \left[\frac{\gamma_p^d \gamma_g^d}{\gamma_p^d + \gamma_g^d} + \frac{\gamma_p^p \gamma_g^p}{\gamma_p^p + \gamma_g^p} \right] \quad [3]$$

where the superscripts d and p represent the dispersion and polar components, respectively, of the surface energy.

Then the work of adhesion of MTF0 is 80.6 mJ/m², which is higher than $2\gamma_p$ (76.6 mJ/m²), so it follows the layer-by-layer growth mode. For perfluoroalkyl-chain-contained gate insulators, the works of adhesion are 61.3, 53.4, and 48.6 mJ/m² for MTF1, MTF5, and MTF10, respectively. As a result, they follow the 3D island growth mode.

Thus, the different growth modes are due to the effect of the different surface energies on the initial growth mode of the pentacene thin-film layer. If the surface energy of the gate insulator is high, pentacene molecules like to attach to the insulator and form a layer-by-layer structure. On the contrary, if the surface energy of the insulator is low, pentacenes prefer to gather each other and form a 3D island.

We confirmed that surface energy and pentacene growth mode influence the performance of OTFTs. OTFTs using several hybrimer gate insulators were fabricated and their electrical properties were characterized. Figure 3 gives the transfer characteristics with a drain–source voltage (V_{DS}) of –40 V. The gate voltage was swept continuously with a 0.5 V step, with values ranging from +20 to –40 V. The electrical parameters are calculated from a plot of $(I_D)^{1/2}$ vs V_G relationship in the saturation regime. The electrical characteristics are listed in Table II.

The results show that the carrier mobility is influenced by the surface energy of the gate insulator. The carrier mobility is proportional to the grain size; some groups believe that this effect is due to the traps at the grain boundaries.^{10,11} Alternatively, other studies have concluded that small grains on low surface energy insulators induce large carrier mobility due to the improved morphology of the grains and the increased adhesion between organic semiconductor and insulator layers.^{12–14} In the current study, we observed the effects of both the grain size and the surface energy. In the MTF0 hybrimer gate insulator, carriers in the pentacene can move freely because the pentacene grain is large and the grain-boundary density is low; this induces the high carrier mobility. The carrier mobility for the MTF1 hybrimer gate insulator is 1.1 cm²/V s, which is similar to the MTF0 hybrimer gate insulator. The pentacene on the MTF1 hybrimer gate insulator has a smaller grain size and more grain boundaries compared to the pentacene on the MTF0 hybrimer gate insulator. Nevertheless, the uniformly and closely packed pentacene grain can cause the charge carriers to hop from one pentacene grain to another effortlessly, which enhances the carrier mobility. However, for the MTF5 and MTF10 hybrimer gate insulators with

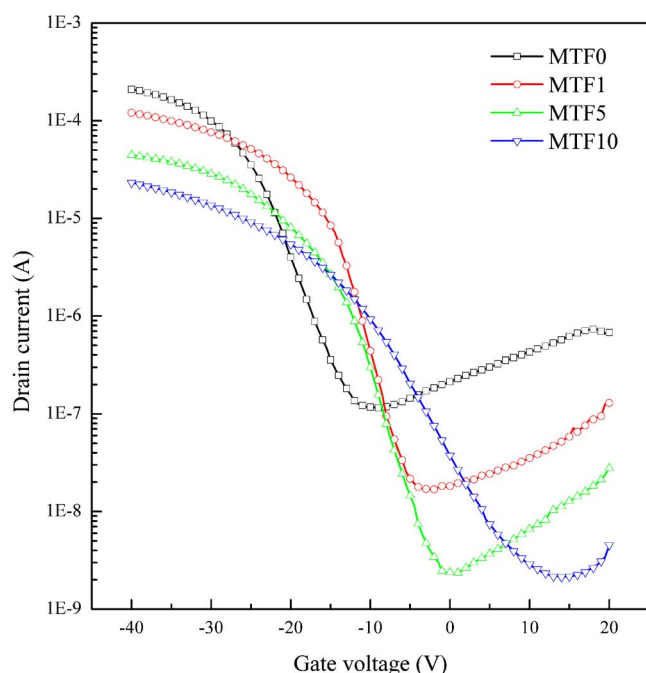


Figure 3. (Color online) Transfer characteristic of OTFTs with several hybrimer gate insulators.

high perfluoroalkyl content, the grain size is too small at a very low surface energy. This results in a decrease in carrier mobility because the grain boundaries act as trap sites in charge transport and limit the carrier mobility in OTFTs.

The on/off ratio of the OTFT with the fluorinated hybrimer gate insulator is on the order of 1×10^4 . Conversely, the OTFT with the MTF0 hybrimer gate insulator has a ratio on the order of 1×10^3 , which is 1 order lower than the other cases. Although all of the hybrimer gate insulators have a similar range of leakage current (less than 40 nA/cm^2 at 1 MV/cm), the on/off ratio varies depending on whether they contain perfluoroalkyl chains or not. Thus, the problem is not related to the gate insulator itself but to the interface between the gate insulator and the pentacene. Irregular growth of pentacene results in defects and voids at the interface, then induces a large off current that leads to a low on/off ratio.

Table II. Electrical characteristics of OTFTs with several hybrimer gate insulators.

Gate insulator	Surface energy (mJ/m^2)	Thickness (nm)	Mobility ($\text{cm}^2/\text{V s}$)	V_{th} (V)	On/off ratio
MFT0	43.5	314	1.09	-17.8	$\sim 10^3$
MFT1	25.6	322	1.11	-9.1	$\sim 10^4$
MFT5	20.6	319	0.23	-8.0	$\sim 10^4$
MFT10	17.9	333	0.12	-3.2	$\sim 10^4$

The threshold voltage is also affected by the surface of the hybrimer gate insulators. As the content of the perfluoroalkyl chain increases, the threshold voltage decreases due to the different carrier densities on the surface of the hybrimer gate insulator. The SAMs with fluorine groups on SiO_2 gate insulators are shown to accumulate holes in the transistor channel. Thus, the threshold voltage of OTFTs treated with SAMs has been shifted to the positive gate voltage compared with OTFTs using bare SiO_2 .¹⁵ Therefore the perfluoroalkyl chain on the surface of the hybrimer gate insulators would be useful for operating OTFTs at low voltage.

Conclusion

We have synthesized the fluorinated hybrimer gate insulators for application in OTFTs. Without using an additional surface modification to the gate insulator, the surface energy was easily modified by varying the content of perfluoroalkyl chains contained in the hybrimer gate insulator. The pentacene growth behavior and the grain morphology vary with the surface energy of the hybrimer gate insulators. At a certain surface energy, pentacene growth was changed from a layer-by-layer mode to a 3D island growth mode. Large pentacene grains lead to higher mobility than small grains, but the large grain growth mode (layer-by-layer mode) causes some defects and voids at the interface between pentacene and gate insulators; then they induce low electrical properties. On the contrary, in the small grain growth mode (3D island mode), uniformly and closely packed pentacene grain causes higher electrical properties. It also shows good mobility in spite of the small grain size. However, too small grains lead to low mobility due to the high grain-boundary density.

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References

- S. C. Lim, S. H. Kim, J. H. Lee, M. K. Kim, D. J. Kim, and T. Zyung, *Synth. Met.*, **148**, 75 (2005).
- D. Knipp, R. A. Street, A. Volkel, and J. Ho, *J. Appl. Phys.*, **93**, 347 (2003).
- K. P. Pernstich, S. Haas, D. Oberhoff, C. Goldmann, D. J. Gundlach, B. Batlogg, A. N. Rashid, and G. Schitter, *J. Appl. Phys.*, **96**, 6431 (2004).
- A. Di Carlo, A. Bolognesi, F. Piacenza, H. Maresch, and B. Stadlober, *Appl. Phys. Lett.*, **86**, 263501 (2005).
- Y. Yang, K. Shin, and C. E. Park, *Adv. Funct. Mater.*, **15**, 1806 (2005).
- S. M. Pyo, Y. J. Lee, J. H. Jeon, and M. H. Yi, *J. Appl. Phys.*, **99**, 073711 (2006).
- J. H. Van der Merwe, *Interface Sci.*, **1**, 77 (1993).
- D. J. Eaglesham and M. Cerullo, *Phys. Rev. Lett.*, **64**, 1943 (1990).
- S. Y. Park, T. Kwon, and H. H. Lee, *Adv. Mater. (Weinheim, Ger.)*, **18**, 1861 (2006).
- C. S. Kim, S. J. Jo, J. B. Kim, S. Y. Ryu, J. H. Noh, H. K. Baik, S. J. Lee, and Y. S. Kim, *Appl. Phys. Lett.*, **91**, 063503 (2007).
- S. C. Lim, S. H. Kim, J. H. Lee, M. K. Kim, D. J. Kim, and T. Zyung, *Synth. Met.*, **148**, 75 (2005).
- A. Di Carlo, F. Piacenza, A. Bolognesi, B. Stadlober, and H. Maresch, *Appl. Phys. Lett.*, **86**, 263501 (2005).
- G. Horowitz and M. E. Hajlaoui, *Synth. Met.*, **122**, 185 (2001).
- M. Yoshida, S. Uemura, T. Kodzasa, T. Kamata, M. Matsuzawa, and T. Kawai, *Synth. Met.*, **137**, 967 (2003).
- S. Kobayashi, T. Nishikawa, T. Takenobu, S. Mori, T. Shimoda, T. Mitani, H. Shimotani, N. Yoshimoto, S. Wogawa, and Y. Iwasa, *Nature Mater.*, **3**, 317 (2004).