# Influence of Surface Energy and Roughness of Substrate on Thin Pentacene and $C_{60}$ Films Prepared by Vacuum Deposition

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Substrate surface roughness predominantly influenced grain size of pentacene in vacuum-deposited thin films while surface energy of the substrate did not, i.e., larger pentacene grain was obtained on a substrate with lower roughness instead of lower surface energy. On the other hand, grain size of $C_{60}$ deposited in the same manner was influenced by both surface energy and roughness, i.e., large $C_{60}$ grain was obtained on substrates with lower surface roughness and energy.

Among organic electronic devices, organic field-effect transistors (FETs) have become a main target to be developed for current sources of thin display panels.[1–6] In this application, a large transistor current is necessary, which may be realized mainly by improvement of FET mobility and also partially by shortening channel length of the transistors to several micrometers. Recently we have reported a facile fabrication method for channel patterns of organic FET, in which channel lengths are less than 5 µm, by using wet-spun PEDOT/PSS microfibers.[7] Pentacene-based FETs fabricated on the channel patterns showed very large drain current.[3] Very recently we have applied this channel-patterning technique to low-voltage pentacene/HfSiO FET[4] operating at driving voltage as low as $-10$ V and to pentacene/$C_{60}$ FET[5] which exhibits ambipolar FET characteristics in air atmosphere.

In the above-mentioned organic FETs, thin films of organic semiconductors such as pentacene and $C_{60}$ are prepared by vacuum deposition. In this deposition method, the thin films are formed as grains of the organic semiconductors. Commonly it is believed that larger grain size results in higher FET hole or electron mobility. The grain size, however, can be influenced by physical characteristics of the substrate surface and substrate temperature in addition to the deposition conditions such as deposition rate. However, to date few systematic studies on the influence of substrate conditions such as surface energy and roughness on pentacene or $C_{60}$ grain sizes have been reported.

Herein we report the results of systematic investigation of the influence of substrate surface energy and roughness on grain sizes of pentacene and $C_{60}$ in thin films prepared by vacuum deposition, coupled with atomic force microscopic (AFM) measurements.

Heavily doped n-type silicon wafers with thin $SiO_2$ layer (350 nm) or thin HfSiO layer (100 nm) were washed in pure water and acetone, and finally UV–ozone treatment was carried out in order to remove organic contaminants. A self-assembled monolayer (SAM) of octadecyltrichlorosilane (OTS) was then prepared on the UV–ozone-treated substrate by immersion. A 30 nm pentacene or $C_{60}$ layer was thermally deposited in vacuum on the SAM-free or -formed substrate. We evaluated the SAM formation on the $SiO_2$ or HfSiO surface by a combination of measurement of water contact angle and Zisman plot.[8] Surface roughness of the SAM-free or SAM-formed substrates and grain sizes of the pentacene or $C_{60}$ were estimated by tapping-mode AFM measurements. Pentacene FET was fabricated on the OTS-SAM formed $SiO_2$/Si substrate, and the FET characteristics were measured by a semiconductor parameter analyzer (4200-SCS Keithley).

We evaluated surface energy of the SAM-free or SAM-formed HfSiO or $SiO_2$ surfaces by measurement of water contact angle. The water contact angle on the surface of the HfSiO drastically increased from 34 to 109° by immersing the surface in OTS–hexane solution for 10 min. The contact angle further increased to 113° and saturated at around this value after 3 h. We calculated the critical surface tension of the SAM formed HfSiO surface with contact angle of 113° to be 19 mN/m from a Zisman plot.[4] The value of the critical surface tension is basically consistent with that of methyl groups in perfect octadecylamine SAM, 22 mN/m.[8] The change of contact angle was quite similar to the case of $SiO_2$ surface whose contact angle saturated at 111° by immersing in the OTS for 4 h, and the critical surface tension is measured to be 17 mN/m similarly by a Zisman plot.[4]

To evaluate roughness of the substrate surfaces, we carried out AFM measurements. The AFM height images showed values of the surface roughness ($R_a$), which were 0.11 and 0.80 nm for the SAM-free $SiO_2$ and HfSiO, respectively. After the SAM formation the roughness did not evidently change, i.e., 0.12 and 0.50 nm for the $SiO_2$ and HfSiO, respectively. The results indicated that the SAM treatment does not much improve the surface roughness.

We have deposited 30 nm-thick pentacene layers on SAM-free or SAM-formed $SiO_2$ substrate. The average grain sizes ($S_g$) of the deposited pentacene crystals were 498 and 458 nm, respectively, as shown in Figures 1A and 1C. Similarly we also deposited the pentacene layer on the SAM-free or SAM-formed HfSiO substrate, and the $S_g$s were 116 and 87 nm, respectively (Figures 1B and 1D). The experimental fact indicates that the surface energy little influences the $S_g$ of the vacuum-deposited pentacene crystal since surface energy was so much different between the SAM-free and SAM-formed surfaces, i.e., contact angles of water were 34 and 116° (corresponds to critical surface tension of 19 mN/m) for $SiO_2$, and 7 and 111° (17 mN/m) for HfSiO, respectively.[4] We also carefully analyzed the influence of the surface roughness on the $S_g$. On both SAM-formed $SiO_2$ and HfSiO substrates the $S_g$'s were 458 and 87 nm, respectively, as mentioned. The critical surface tensions were 19 and 17 mN/m, respectively, indicating both substrate surfaces are covered with a monolayer of methyl groups.[8] In other words, ones can reasonably regard that the both surfaces are the same

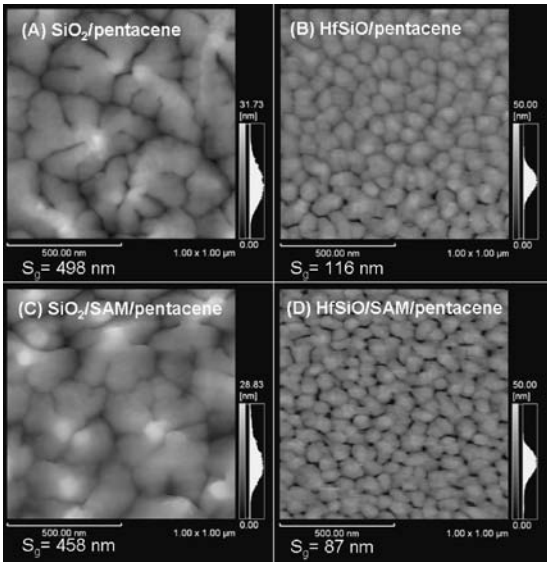

**Figure 1.** AFM images of pentacene grains on various substrate surfaces for vacuum-deposition of pentacene. (A) On SAM-free $SiO_2$; (B) On SAM-free HfSiO; (C) On SAM-formed $SiO_2$; and (D) On SAM-formed HfSiO.

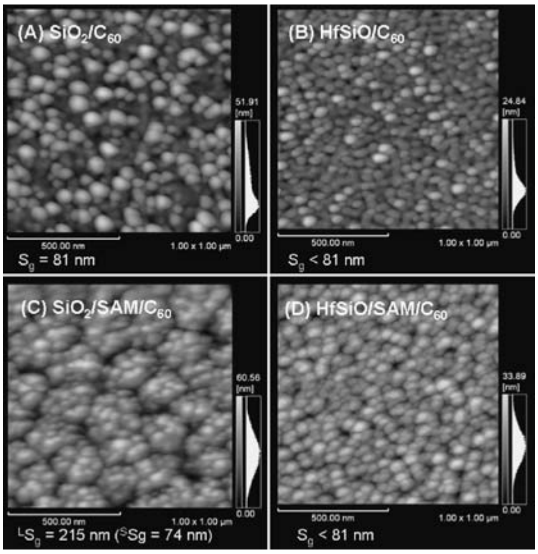

**Figure 2.** AFM images of $C_{60}$ grains on various substrate surfaces for vacuum-deposition of $C_{60}$. (A) On SAM-free $SiO_2$; (B) On SAM-free HfSiO; (C) On SAM-formed $SiO_2$; and (D) On SAM-formed HfSiO.

substance surfaces but with much different surface roughness, i.e., 0.1 and 0.5 nm for the SAM-formed $SiO_2$ and HfSiO substrates, respectively. Accordingly, it is concluded that the roughness predominantly influences the $S_g$ of the vacuum-deposited pentacene crystals, while the surface energy does not.

On the other hand, the influence of the surface energy and roughness on $S_g$'s of the deposited $C_{60}$ crystals were much different from the case of pentacene. Two kind of grains, i.e., smaller primary grain and much larger grain (${}^{L}S_g = 215$ nm) aggregated by the smaller primary grains (${}^{S}S_g = 74$ nm), were observed, as shown in Figure 2. Both surface energy and roughness little influenced the primary grain size. However, the larger grains formed only on the SAM-formed $SiO_2$ substrate which has less surface energy and roughness (Figure 2C). The larger grains transferred into denser and single grains accompanying reduction of total size. Intermolecular interaction among $C_{60}$ molecules is much stronger than that of pentacene.[9] Therefore, the different influence on the $C_{60}$ and pentacene is easily understood, however, it is not well explained at this stage.

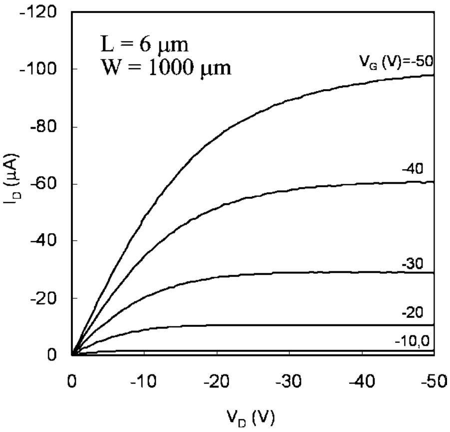

**Figure 3.** Output characteristics of pentacence FET fabricated on SAM-formed $SiO_2$/Si substrate.

We have fabricated a pentacene FET by deposition of thin pentacene film on the SAM-formed $SiO_2$/Si which corresponds to $S_g$ of 458 nm (Figure 1C) and compared with our previous pentacene FET[4] fabricated on HfSiO/Si which corresponds to $S_g$ of 87 nm (Figure 1D). Figure 3 shows the output characteristics of the present pentacene FET, indicating good saturation with a high mobility of $0.2\,cm^2\,V^{-1}\,s^{-1}$ and on/off current ratio of $4 \times 10^5$. The value of mobility is much higher than the previous FET[4] whose mobility is $0.02\,cm^2\,V^{-1}\,s^{-1}$. It should be noted that the mobility is not solely dependent on the grain size while other factors such as molecular orientation regarding the dielectric surface also strongly influences the mobility.[2]

## References

1 H. Yan, Z. Chen, Y. Zhang, C. Newman, J. R. Quinn, F. Dötz, M. Kastler, A. Facchetti, *Nature* **2009**, *457*, 679.
2 C. D. Dimitrakopoulos, P. R. L. Malenfant, *Adv. Mater.* **2002**, *14*, 99.
3 H. Yan, T. Kagata, Y. Mori, Y. Harashina, Y. Hara, H. Okuzaki, *Chem. Lett.* **2008**, *37*, 44.
4 H. Yan, T. Kagata, S. Arima, H. Sato, H. Okuzaki, *Phys. Status Solidi A* **2008**, *205*, 2970.
5 H. Yan, T. Kagata, H. Okuzaki, *Appl. Phys. Lett.* **2009**, *94*, 023305.
6 S. C. Lim, S. H. Kim, H. Y. Chu, J. H. Lee, J.-I. Lee, J. Y. Oh, D. Kim, T. Zyung, *Synth. Met.* **2005**, *151*, 197.
7 H. Okuzaki, Y. Harashina, H. Yan, *Eur. Polym. J.* **2009**, *45*, 256.
8 H. W. Fox, W. A. Zisman, *J. Colloid Sci.* **1950**, *5*, 514.
9 K. Itaka, M. Yamashiro, J. Yamaguchi, M. Haemori, S. Yaginuma, Y. Matsumoto, M. Kondo, H. Koinuma, *Adv. Mater.* **2006**, *18*, 1713.

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