Structure of Organic Thin Films Grown on Surface-modified Tantalum Oxide

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We fabricated an ordered monolayer film of a long-chain fatty acid or a perfluorofatty acid onto an anodized tantalum oxide (Ta_2O_5) amorphous surface by the Langmuir–Blodgett (LB) method, and grew a pentacene or C_{60} thin film on it. Remarkable improvements of morphology and crystallinity of the organic thin films were observed on the CH_3-terminated monolayer film of the fatty acid.

Organic semiconductors have drawn much attention due to their electronic functionality and mechanical flexibility. Development of organic field effect transistors (OFETs) using such soft materials is of great importance and its investigation has spread world-wide.[1,2] In most of such OFETs, thermally oxidized SiO_x films on conductive Si substrates have been used as the gate dielectric. However, the dielectric constant (k) of the SiO_x layer is rather low so that it is difficult to inject a large amount of carriers into the organic layer with low gate voltages. Recently, many groups have reported the characteristics of the OFETs which were fabricated on high-k gate insulators.[2,3] We have also succeeded in fabricating OFET using an anodized tantalum pentaoxide (Ta_2O_5) layer as the high-k gate dielectric.[4]

Another problem still remains if we use the high-k gate dielectric. The surface of the oxide layer is amorphous, so that a single-crystalline organic thin film never grows on the anodized Ta_2O_5 surface. It is reported that the performance of OFETs is mainly affected by the quality of the initial organic layer on the gate dielectric.[5,6] Therefore, the improvement in the crystallinity of the dielectric surface is expected to reduce the defects or the domain boundaries in the organic layer, and improve the working characteristics of OFETs. As for the SiO_x surface, organosilane self-assembled monolayers (SAMs) are used to introduce the ordered structure, and improvement in the OFET performance has been reported.[7–10] To our knowledge, however, no SAMs onto the Ta_2O_5 surface has been reported so far. In the present study, we focused our attention on the modification of the amorphous Ta_2O_5 surface by the LB films of long-chain fatty acids, which provides an artificial two-dimensional crystalline film on the solid substrates.[11] Then, we grew pentacene and C_{60} thin films on the modified Ta_2O_5 surfaces, and investigated the crystallinity of the grown films.

A 0.1 mm-thick Ta sheet was purchased from Furuuchi Chemical Corporation. A mirror-like anodized Ta_2O_5 surface was obtained following the previously reported processes.[4] The Ta substrate cut from the sheet was electrolytically polished in an aqueous HF solution (50%):concentrated $H_2SO_4 = 1:9$ (v/v) mixed electrolytic solution. The polished substrate was anodized in a KI solution ($2 \times 10^{-4}\,mol\cdot L^{-1}$) at 300 V, which produced a 600 nm-thick anodized Ta_2O_5 layer on Ta. Octadecanoic acid ($C_{18}A$, Tokyo Chemical Industry Co., Ltd.) and perfluorooctadecanoic acid ($PFC_{18}A$, Fluorochem Ltd.) were purified by repeated recrystallization from hexane or chloroform, respectively. $C_{18}A$ was dissolved in benzene and $PFC_{18}A$ was dissolved in a trifluoroacetic acid:chloroform = 1:4 (v/v) solution to make the spreading solutions with the concentration of $1 \times 10^{-4}\,mol\cdot L^{-1}$. Their monolayers were spread onto an aqueous subphase (pH = 6.8) containing $CdCl_2$ ($3 \times 10^{-4}\,mol\cdot L^{-1}$) and $KHCO_3$ ($5 \times 10^{-5}\,mol\cdot L^{-1}$) in Milli-Q water ($R = 18.2$ MΩ). Monolayers in the form of the cadmium salts (CdC_{18} and $CdPFC_{18}$) were deposited by the LB method on the Ta_2O_5/Ta substrates at 15 °C with the surface pressure of $25\,mN\cdot m^{-1}$ using a Lauda FW-1 film balance. The k of the dielectric layer was only slightly reduced (less than several %) by the deposition. Pentacene (Aldrich, 98%) or C_{60} (99.99%) molecules were evaporated from a Knudsen cell onto the Ta_2O_5/Ta substrate at room temperature under the ultrahigh vacuum (ca. 10^{-7} Pa). The evaporation rate and the final film thickness were set to $1.0\,nm\cdot min^{-1}$ and 100 nm, respectively. The wettability of the bare and modified Ta_2O_5 surfaces was observed by measuring the water contact angle. Surface morphology and crystallinity were investigated by atomic force microscopy (AFM) and X-ray diffraction (XRD).

The anodized Ta_2O_5 surface was smooth, and the root-mean-square roughness value of it was below 0.2 nm, which was as small as that of the thermally oxidized SiO_x. The anodized surface showed hydrophilicity with the water contact angle of 29°, and it was expected that the LB monolayer exposing the outermost layer of the hydrophobic group would be easily deposited on it. Actually, CdC_{18} and $CdPFC_{18}$ monolayers were deposited with good transfer ratios (almost unity). The water contact angles were 103 and 104° for the CdC_{18} and $CdPFC_{18}$ monolayers, respectively, and hydrophobic nature of these modified surfaces was confirmed. The values of contact angles agree well with the previously reported ones.[12,13] AFM observation also showed very flat surfaces of the deposited monolayer films. Thus, we were able to obtain CH_3- or CF_3-terminated well-ordered Ta_2O_5 surfaces by the LB method. We think that the LB monolayer did not change the structure during the growth of pentacene and C_{60} films, because they were grown at room temperature.

Figure 1 shows AFM images of the pentacene and C_{60} thin films on the above-mentioned surfaces. On the bare Ta_2O_5 surface, the pentacene film had very large domains with a dendritic shape similar to that on the SiO_x surface, and the layer-by-layer growth was clearly observed. The domain size of the C_{60} film, however, was far smaller than that of the pentacene film. The nucleation density was very high, and there were quite a number of domain boundaries. It was not expected to grow a C_{60} film with good crystallinity on the bare surface. On the CH_3-terminated Ta_2O_5 surface, we observed large domains of pentacene, which had the similar size with those on the bare Ta_2O_5 surface. It seemed that the nucleation density was a little smaller, but the

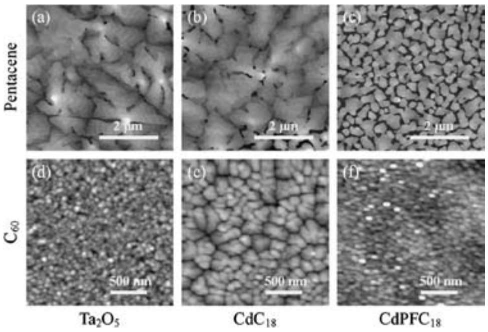

Figure 1. AFM images of the organic thin films. Pentacene and C_{60} films were grown on (a and d) bare Ta_2O_5 surfaces, (b and e) CdC_{18} LB film surfaces, and (c and f) $CdPFC_{18}$ LB film surfaces, respectively.

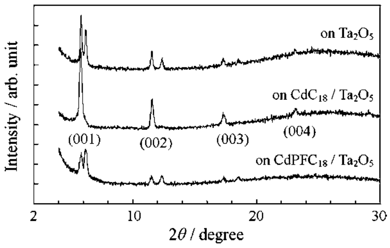

Figure 2. XRD patterns of pentacene thin films grown on the bare Ta_2O_5 surface and the LB film surfaces.

change was not so dramatic. On the other hand, the morphology of the C_{60} film greatly changed on the CH_3-terminated surface. Larger C_{60} domains with lower nuclear density were observed in the AFM image as compared with the film on the bare Ta_2O_5 surface. Therefore, it was suggested that the well-ordered C_{60} thin film grew on the CH_3-surface. On the CF_3-terminated surfaces, both pentacene and C_{60} films formed far smaller domains than on the CH_3-terminated surfaces. Especially, there were a very large number of domain boundaries in the pentacene film.

Figure 2 shows XRD patterns of the pentacene thin films on the various surfaces. Diffraction peaks assigned to (001), (002), (003), and (004) were found in each pattern. Two phases coexisted in the pentacene films on the bare and CF_3-terminated surfaces. They correspond to the thin film phase and the bulk phase with interplanar spacing (d) of 1.5 and 1.4 nm for the (001) reflection, respectively.[14] For the film on the CF_3-terminated surface, the peak intensities were weakened and the bulk phase was dominant. In contrast, the pentacene film consisted of only the thin film phase on the CH_3-terminated surface. Figure 3 shows XRD patterns of the C_{60} films. No diffraction peak was observed on the bare and CF_3-terminated surfaces, suggesting the growth of amorphous films. On the CH_3-terminated surface, however, there appeared a sharp peak with the corresponding d spacing of 0.8 nm for the (111) reflection, and an additional (222) reflection peak, indicating the growth of a highly-oriented C_{60} film.

These results imply that the c-axis ordering of the pentacene and C_{60} thin films was greatly improved by fabricating on the CdC_{18} LB films. The CH_3-terminated surface shows the lipophilicity, and the surface free energy is close to that of the organic molecules. So both pentacene and C_{60} molecules are enough wettable with the CH_3-terminated surface. Then, the formation of larger domains is favored at the initial growth stage on the CH_3-terminated surface due to the sufficient molecule–substrate interaction, and the crystallinity of the organic thin films can be improved.

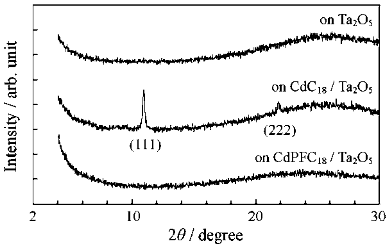

Figure 3. XRD patterns of C_{60} thin films grown on the bare Ta_2O_5 surface and the LB film surfaces.

In the case of the bare Ta_2O_5 surface, it has some lipophobicity so that C_{60} molecules, which have no C–H bond, are not enough wettable and form an amorphous film. In contrast, pentacene molecules are wettable on Ta_2O_5 and form highly c-axis-oriented layer-by-layer domains. Meanwhile, the CF_3-terminated surface provides the lowest surface free energy with the higher water and oil resistances. On it, the intermolecular interaction dominates over the molecule–substrate interaction. Then, many small domains are formed at the initial stage of the growth, because most impinging molecules nucleate not at the side step edges of preexisting domains, but just onto the domain surfaces. Thus, aggregated small domains with a large number of domain boundaries are formed even for pentacene molecules.

In conclusion, we succeeded in introducing ordered structures onto amorphous Ta_2O_5 surfaces by the LB method. The crystallinity of organic films, especially of the C_{60} film, was greatly improved by the surface modification with the CdC_{18} film. This method is effective for the improvement of the high-k gate surfaces, on which good SAMs could not be grown due to the lack of appropriate self-assembling molecules.

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