

論文内容の要旨

Preparation of Well-defined Organic Crystal Surfaces by Orientation Control and Layer-by-layer Surface Cleaning

(配向制御と分子層除去により構造を規定した有機結晶表面の作製)

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[Introduction]

Organic semiconductors are attracting much attention for their potential application for flexible, low-cost and printable devices. The carrier transport mechanism in organic materials, though, is not thoroughly understood while some report that polaron-band mechanism is the most probable in case of crystalline low-molecular-weight materials.

The most widely used method to elucidate electronic structure of solids is angle-resolved photoemission spectroscopy (ARPES). The ARPES gives us powerful insight into the carrier transport properties, including effective mass of carriers, inter-molecular transfer integrals, and charge-phonon coupling constant. Hence, band dispersion measurement is essential for studying carrier transport mechanism as well as establishing molecular design guidelines for novel materials. The ARPES study of organic semiconductors, however, is quite challenging and only performed in limited systems due to following reasons. First, conductivity of organic materials is very low without doping. Therefore, positive charges generated during photoemission accumulate on the surface, and make the spectrum shifted toward high binding energy direction. Second, since photoemission method is surface sensitive in general, the surface for ARPES studies should be clean, free from adsorbates or oxidized molecules. In order to satisfy this requirement, ARPES studies are generally performed with samples grown in-situ. Finally, as it is an "Angle-resolved" method, the sample should be single crystals.

In this research, I will demonstrate two novel methods to prepare well-defined organic surfaces which are suitable for surface sensitive characterization methods like ARPES. The first approach is to grow epitaxial film of organic molecules on conductive substrates with 1 monolayer thickness and control in-plane orientation to satisfy angle resolution. The second one is to prepare organic single crystals ex-situ, introduce it into the vacuum chamber, clean the surface, and then neutralize accumulated charges using electron shower.

[In-plane orientation control of organic epitaxial films on conductive substrates]

The requirement for the substrate is as follows. First, it should be conductive substrate as mentioned above. Second, the lattice mismatch between organic crystal and substrate need to be small. Finally, since the $\pi\pi$ overlap is essential for high performance of organic semiconductors, the molecules should be in "standing" orientation with its molecular plane perpendicular to the surface. This requires rather inert surface without strong interaction with molecular π orbital. The epitaxial growth of pentacene on Au or Cu single crystals, for instance, often results in "lying" orientation, in which the molecular long axis is parallel to the surface.

As for pentacene, which is a benchmark material of organic semiconductors, epitaxial growth of "standing" molecules was reported by us on Bi terminated Si(111)-($\sqrt{3} \times \sqrt{3}$) reconstructed surface. The lattice constant of reconstructed surface is 6.65 Å, which is close enough to those of pentacene ($a = 5.93$ Å, $b = 7.59$ Å). However, since the substrate has three-fold symmetry and pentacene crystals have triclinic lattice, there are 6 possible in-plane orientations for pentacene. This does not satisfy angle resolution. In order to reduce surface symmetry, we used vicinally cut substrates instead of flat ones. By bunching steps and producing periodic steps as high as 3 nm, we successfully controlled in-plane orientation of pentacene, reducing 6 orientations to 2. The pentacene monolayer film obtained in this method had thin-film phase structure, and band dispersion was studied. In this research, I demonstrate that orientation control using bunched steps is also applicable to other organic materials.

Experimental

The substrate is Si(111) with miscut toward $[11\bar{2}]$ direction. The sample was introduced into vacuum chamber (base pressure $\sim 3 \times 10^{-10}$ Torr) equipped with Knudsen cell, pyrometer, and Reflective High Energy Electron Diffraction (RHEED). First, the sample was flashed at 1260 °C for 20 s in order to obtain clean 1×1 surface. As it was cooled down, the 1×1 turned into 7×7 reconstruction at 860 °C, and confirmed by RHEED. From 960 °C to 860 °C was cooled gradually, at the rate of 6 °C/min, which gives smooth surface and bunched steps with ~ 3 nm height. All of processes above were performed under $< 2 \times 10^{-9}$ Torr conditions. One monolayer bismuth was then deposited from Knudsen cell at room temperature, and 1×1 image was confirmed.

In order to turn 1×1 Bi into $\sqrt{3} \times \sqrt{3}$ reconstructed surface, the sample was annealed after Bi deposition. It is known that depending on the annealing temperature, Bi coverage changes in the same $\sqrt{3} \times \sqrt{3}$ manner. When annealed at less than 400 °C, Bi coverage remains 1 ML and called

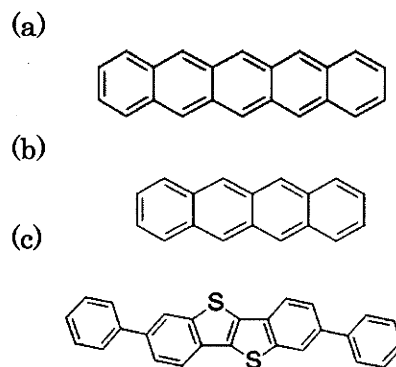


Fig. 1 The molecular structure of (a) pentacene, (b) tetracene, and (c) 2,7-Diphenyl[1]benzothieno[3,2-b][1]benzothiophene (DPh-BTBT).

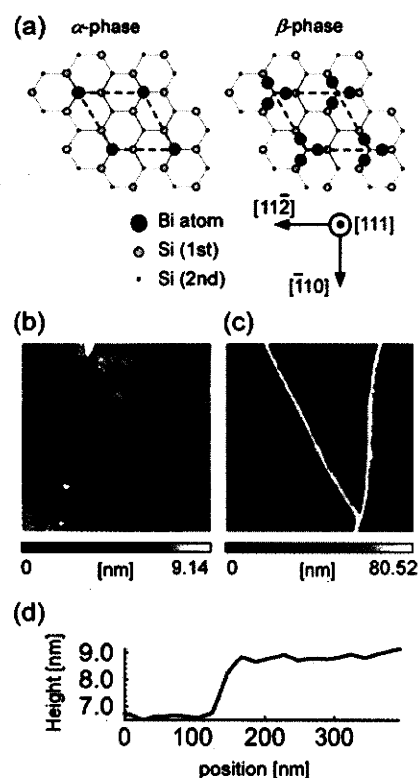


Fig. 2 (a) Schematic illustration of the Bi/Si(111)-($\sqrt{3} \times \sqrt{3}$) surface structures. (b) DPh-BTBT monolayer film grown on α -phase (1/3 ML). The cross section profile is shown in (d). (c) DPh-BTBT grown on β -phase (1 ML). Unlike α -phase, needle-like crystals were obtained.

β -phase. On the other hand, annealing at 450 °C and 590 °C lead to 0.66 and 1/3 ML, respectively. 1/3ML thickness Bi-Si is called α -phase. Since both α -phase and β -phase have $\sqrt{3} \times \sqrt{3}$ reconstructed surface, it is difficult to assign them using RHEED patterns. Therefore, the coverage of Bi was estimated using ex-situ X-ray Photoemission Spectroscopy (XPS) by comparing intensity ratio of Bi 4f_{7/2} and Si2p peaks.

Results and discussion

First, I report the difference in surface energy depending on surface reconstruction manners. Fig. 2 shows DPh-BTBT crystals grown on α -phase and β -phase Bi-Si(111)-($\sqrt{3} \times \sqrt{3}$). On α -phase, DPh-BTBT crystal grew in two-dimensional mode, resulting in monolayer films. When grown on β -phase, though, needle-like, three dimensional crystals were obtained. The same tendency was also observed in DNTT crystals. This result indicates that the surface energy of β -phase is smaller than that of α -phase.

Fig. 3 is the optical microscope image of DPh-BTBT needle-like crystal grown on vicinal substrate. When grown on flat Si(111) substrate, needle-like crystals grew in 6 directions. Even though the needle-like crystals are polycrystalline, molecular layers in the vicinity of substrates seem to be affected by lattice periodicity. In order to control in-plane orientation of the crystal, the DPh-BTBT was deposited onto vicinal Si(111) substrate terminated by Bi. It was found that even when DPh-BTBT form needle-like crystals, which are larger than steps on surfaces, in-plane orientation was controlled. The step height necessary to control orientation was found to be 4.4 nm. Interestingly, the direction of controlled crystal growth was perpendicular to the step edges. It means that crystals growing over steps are selected. This result indicates that steps do not work as obstacles of crystal growth, but they stabilize crystal growth or nucleus formation in certain direction.

On the other hand, the orientation of monolayer films on α -phase Bi-Si required steps more than 10 nm to be controlled. Figure 4 shows the Transverse shear microscopy (TSM) images of DPh-BTBT monolayer grown on stepped surfaces. The contrast in TSM image reflects the in-plane orientation of each grain. Figure 4 (b) shows clear contrast in and between grains while (d) shows no contrast. Moreover, Reflective High Energy Electron Diffraction (RHEED) analysis indicates that in-plane orientation was successfully limited down to at least two directions.

[Development of surface cleaning technique for organic single crystals]

The second approach is to clean the surface of ex-situ grown single crystals and neutralize positive charges. First, I will report the development of surface cleaning technique for organic crystals. Since many low-molecular-weight organic semiconductors have layered crystal structure, it was found that cleavage can be employed to obtain clean surface. However, cleaving crystal often require thick crystals. In our research, only crystals thicker than several hundred μm were cleaved successfully. These thick crystals, though, often have low conductivity and poor crystallinity. Therefore, we have to develop a novel surface cleaning technique suitable for crystals thinner than 1 μm .

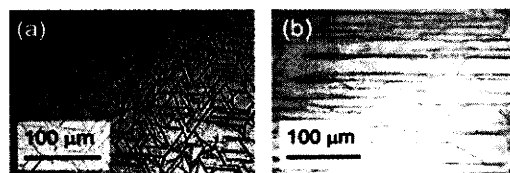


Fig. 3 The optical microscope images of (a) DPh-BTBT crystals grown of flat β -phase Bi-Si(111) surface, and (b) vicinally cut β -phase Bi-Si(111).

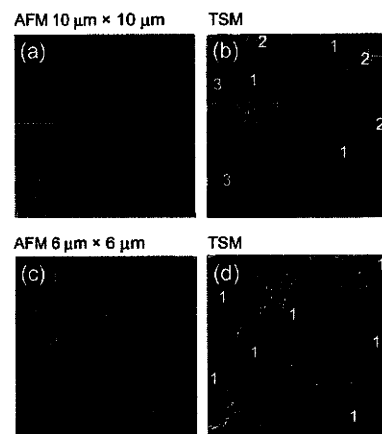


Fig. 4 The AFM and TSM images of DPh-BTBT films grown on (a, b) 4 nm steps and (c, d) 10 nm steps. The grains in the same contrast is indicated in (b) and (d).



Fig. 5 MCP-RHEED patterns of tetracene single crystal grown ex-situ. The incidence angle of electrons is $\sim 8^\circ$.

Experimental

The single crystal of tetracene was grown by Physical Vapor Transport (PVT) method, in which tetracene was sublimated inside quartz tube with two temperature zones and Ar gas flow. The tetracene single crystal, with typical dimension of $0.2 \times 2 \times 0.001 \text{ mm}^3$ was laminated onto Au (17 nm) / Ti (3 nm) / SiO₂ substrate. The surface morphology was investigated using RHEED equipped with micro channel plate on the screen (MCP-RHEED).

Results and Discussion

Typical terrace width of tetracene crystals were around several μm , and molecularly flat surface was obtained. The MCP-RHEED image of the surface, though, indicate that the top-most surface do not have crystalline order. Only when the incident angle of electrons was more than 8° , which means that probing depth was large, streaky patterns were obtained.

First, I show the effect of vacuum annealing on the disordered top-most surface of tetracene crystals. Fig. 6 show the surface of tetracene single crystal annealed in the vacuum of $\sim 10^{-8}$ Torr. It was found that vacuum annealing make the surface roughening, probably due to random molecule desorption from the surface. The MCP-RHEED image of vacuum annealed sample was spotty (Fig. 6 (a)), indicating that the surface has nm size bumps and holes.

On the other hand, when annealed under atmospheric pressure argon, layer-by-layer sublimation was achieved. The schematic image of experimental setup is shown in Fig. 7 (e). It was observed that the tetracene molecules sublimated from terraces with layer-by-layer mode, without random desorption and roughening. Moreover, the MCP-RHEED image of tetracene surface after blowing hot Ar gas was significantly improved and streaky image was recovered even when incidence angle was sufficiently low. This result suggests that contamination and disordered layer at top-most surface was successfully removed.

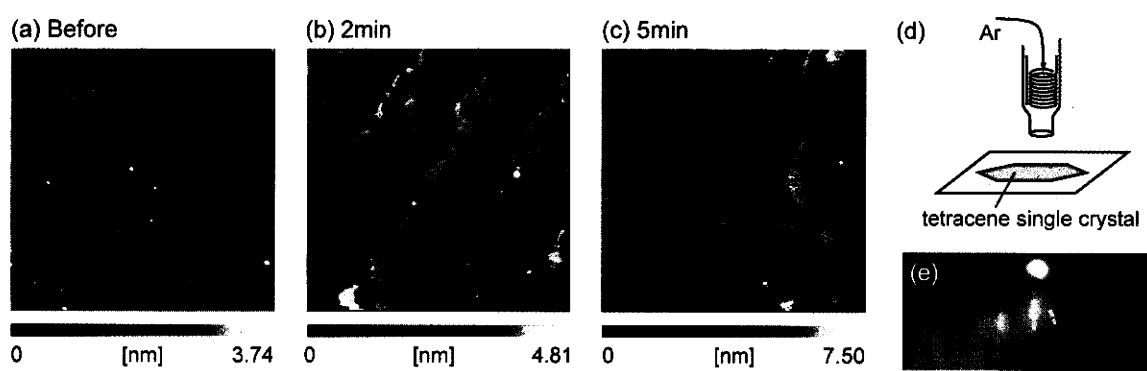


Fig. 7 (a-c) The AFM images of tetracene single crystal annealed in atmospheric pressure. (d) The schematic image of hot Ar annealing. (e) The MCP-RHEED pattern after annealing in atmospheric pressure Ar for 5 minutes. Streaky pattern was recovered.

[Conclusion]

In this research, I have demonstrated two novel methods to prepare well-defined samples suitable for surface sensitive characterization methods like ARPES of organic semiconductors. For the first approach, in which singly-oriented epitaxial film of organic molecules were grown on conductive substrate, it was found that the coverage of Bi greatly affects surface energy. The role of steps in orientation control was also studied, and it was assumed that periodic steps stabilize nucleus formation. In the second approach, the surface cleaning technique for organic crystals was developed. These methods will be widely used to prepare clean and highly crystalline organic surface in-situ, and promote researches on fundamental transport mechanism in organic functionalized materials.

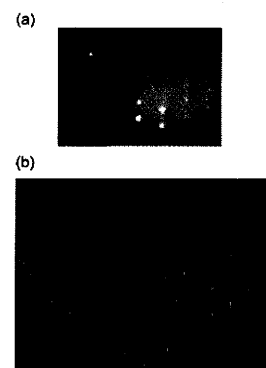


Fig. 6 (a) MCP-RHEED pattern and (b) AFM image of tetracene single crystal after vacuum annealing.