2 Phase Control of Molecular System Project

– Controlling of physical properties in molecular systems –

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In this project, electronic correlation in molecular crystal systems is investigated to elucidate novel phenomena such as superconductivity, ferroelectricity, and charge ordering. One of our goals is to elucidate the origins of physical properties from crystal structural information. With this aim, we performed crystal structure analyses of various molecular systems, including organic thin films, under different external conditions.

Recently, we succeeded in producing high-quality thin films made of organic materials and evaluated them using synchrotron radiation diffraction and reflectivity.[1] Here, we report the wafer-scale fabrication of an ultra-thin organic semiconductor film and determination of its layered structure using synchrotron radiated X-ray reflectivity.[2]

2-1 Semiconductive molecular bilayers realized using geometrical frustration

Single molecular bilayers (SMBs) are basic components of cell membranes, being the fundamental form of molecular nanostructures composed of biological lipids or synthetic amphiphiles. Although the realization of ultrathin, flexible, and stable artificial SMBs is expected to result in versatile applications, the inherent instability and fragility of SMBs due to the lateral mobility of their constituent molecules strictly limit their practical use. Here, we report the fabrication of unprecedented large-area, uniform, and strongly self-organized SMBs using the extended π-conjugated molecular skeleton of phenyl-[1]benzothieno[3,2-*b*][1]benzothiophene (Ph-BTBT) substituted by alkyl chains of variable length, Ph-BTBT-C_n. These SMBs were successfully produced by simple blade-coating of substrates with a solution containing two Ph-BTBT-C_ns with different alkyl chain lengths. The chain-length disorder did not perturb the in-plane crystalline order; instead, it effectively acted as a geometrical frustration to inhibit interlayer stacking and multilayer crystallization. The obtained SMBs exhibited efficient two-dimensional carrier transport, allowing for the operation of high-performance thin-film transistors (TFTs). This finding opens a new route to SMB-based ultrathin super-flexible electronics capable of biomimetic functions such as molecular recognition and energy harvesting.

The unique nature of SMBs lies in their nanometer-scale thickness, which is well-defined by the doubled length of their constituent molecules. This feature accounts for several unique physicochemical phenomena and mechanical flexibility that are important for determining the properties of cell membranes in living organisms. The SMBs are held together by weak intermolecular (or supramolecular) interactions between constituent molecules exhibiting internal lateral mobility, similar to the case of liquid crystals. Therefore, the SMBs characterized currently can only exist in the presence of water, as their structural stability is primarily ascribed to decreasing water interfacial energy. Thus, the unavoidable instability and fragility of artificial SMBs poses strict limitations on their uses in the current next-generation nanotechnology applications.

Here we present an alternative approach to produce highly stable and functional SMBs, utilizing an extended π-electron skeleton that considerably enhances the intermolecular attractive forces within the bilayers. Recently, some asymmetric rod-like organic molecules developed for soluble

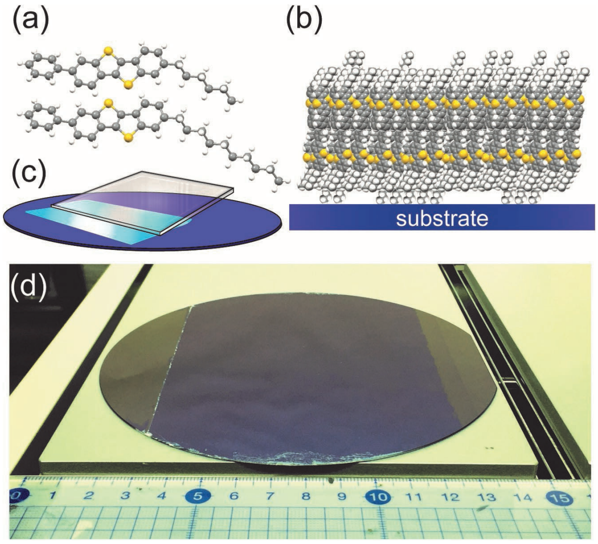

Fig. 1: Wafer-scale SMB formation. a, Chemical structure of Ph-BTBT-C$_n$. **b**, Schematic SMB diagram showing alkyl chain length disorder acting as a geometrical frustration to suppress interlayer stacking. **c**, Schematic of the blade-coating technique. **d**, Optical image of a wafer-scale (6-inch) SMB produced using a mixed solution of Ph-BTBT-C$_{10}$ and Ph-BTBT-C$_6$ with Φ_{long} = 0.1. The highly uniform film area was as large as 100 cm^2.

or printable organic semiconductors have been reported to exhibit very high layered crystallinity associated with the formation of bilayer-type layered herringbone packing motifs, as exemplified by Ph-BTBT-C$_n$ ($n \geq 5$) (Fig. 1a). The crystals of this compound feature bilayer units composed of antiparallelly aligned polar monomolecular layers, resulting in head-to-head contact of the π-electron cores (Ph-BTBT). Inter-bilayer interactions due to alkyl-alkyl (or tail-to-tail) contacts should be much weaker than intra-bilayer intermolecular interactions. The resulting high layered crystallinity enables efficient two-dimensional carrier transport and smooth channel/gate-insulator interface formation, eventually allowing for the realization of high-performance organic TFTs. However, these materials usually form thin flake-like crystals or crystalline thin films, composed of multiply stacked molecular bilayer units, with no method for producing the corresponding SMBs reported to date.

To realize strongly self-organized SMBs based on Ph-BTBT-C$_n$, we introduced geometrical frustration, preventing the multiple stacking of molecular bilayer units by taking advantage of the controllable nature of substituent alkyl chain lengths, as schematically presented in Fig. 1b. Two kinds of SMBs, Ph-BTBT-C$_n$ and Ph-BTBT-C$_{n'}$, with different alkyl chain lengths ($n > n'$) were employed. They were dissolved in chlorobenzene at various weight ratios of Φ_{long} (i.e., weight ratio of Ph-BTBT-C$_n$ in the mixed solute), with the total solute concentration in the solution remaining constant. The mixed solutions were blade-coated on a Si wafer covered with a 100-nm thermally grown silica layer, as schematically shown in Fig. 1c. In the case of single-component solutions (i.e., Φ_{long} = 0.0 or 1.0), the obtained films exhibited a notable inhomogeneous color distribution due to the uneven thickness distribution on the substrate. In striking contrast, utilization of mixed solutions allowed for the fabrication of a mono-colored ultrathin film with a constant thickness over the whole area, as exemplified by the case of Ph-BTBT-C$_6$ and Ph-BTBT-C$_{10}$ at Φ_{long} = 0.1 (Fig. 1d). The obtained film comprised a highly uniform SMB with a constant thickness over the whole 100-cm^2 substrate area, as depicted below.

Atomic force microscopy (AFM) measurements determined the film thickness to be 4.4 nm in the peripheral areas, as presented in Fig. 2a. The film height is coincident with the c-axis unit-cell length (or bilayer thickness) of Ph-BTBT-C$_6$, as revealed by the crystal structure analyses. Crossed nicols observation was used to analyze the optical anisotropy of the whole film, revealing that it was composed of a small number of mono-colored areas approximately 100 mm × 10 mm in size and the long side parallel to the coating direction, as shown in Fig. 2b. These areas exhibited distinct brightness contrast relative to each other, with the brightness changing from bright to dark or vice versa at every 45° interval of rotation around the axis normal to the substrate plane. The results showed the optical anisotropy to be uniform over the above-mentioned mono-colored areas, which were assumed to correspond to single-crystalline domains.

Figure 2c shows an expanded high-resolution AFM image of the obtained film, revealing crystalline molecular order consistent with the in-plane crystal lattices of Ph-BTBT-C$_6$ or Ph-BTBT-C$_{10}$. Figure 2d shows a thin-film X-ray diffraction pattern associated with the in-plane crystalline order. A single sharp Bragg reflection was observed by scanning Φ with 2θ fixed at 20.343° (corresponding to the 020 reflection of Ph-BTBT-C$_6$); however, it was not observed in the case of 2θ = 20.463°

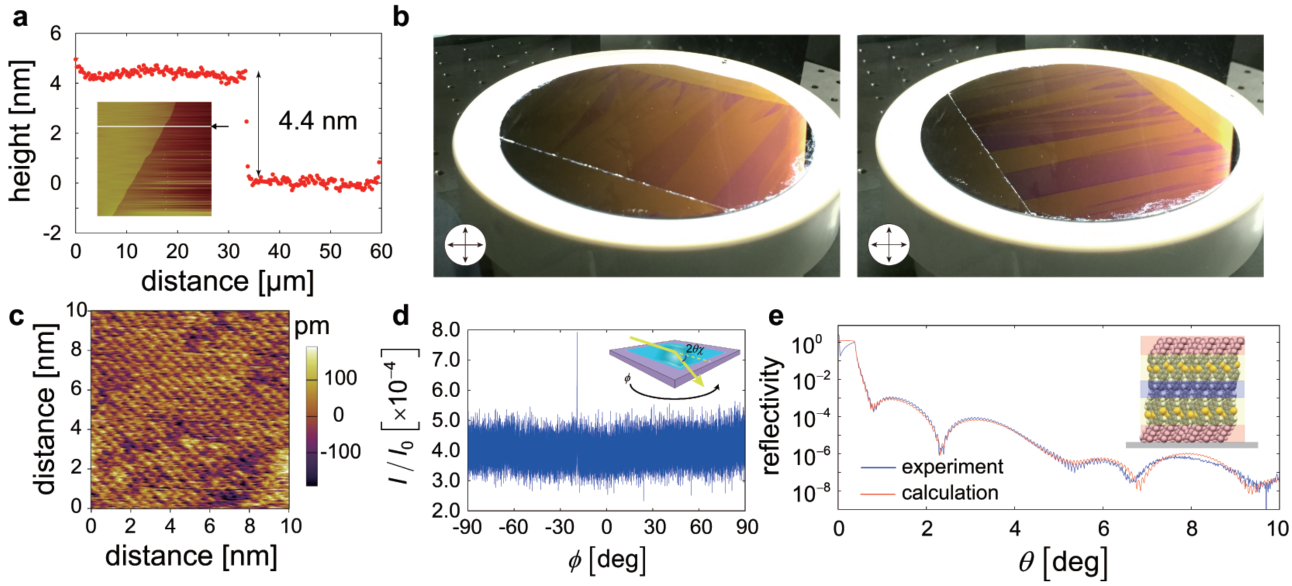

Fig. 2: SMB thickness uniformity and crystallinity. a, AFM height profile. **b**, Crossed nicols polarized images of a wafer-scale SMB. **c**, High-resolution AFM image of an SMB produced using a mixture of Ph-BTBT-C_{10} and Ph-BTBT-C_6 with $\Phi_{\mathrm{long}} = 0.03$. **d**, Thin-film X-ray diffraction pattern of the above SMB, collected by scanning the Φ angle with 2θ fixed at 20.343°, corresponding to the (020) diffraction of Ph-BTBT-C_6. **e**, X-ray reflectivity spectrum of the same SMB, compared with the spectrum simulated under the assumption that the SMB features head-to-head contacts only (inset).

(corresponding to the 020 reflection of Ph-BTBT-C_{10}), indicating that the characterized film area comprised a single-crystalline domain whose in-plane lattice constant was close to that of Ph-BTBT-C_6. The single-crystalline nature is also confirmed by the corresponding polarized absorption spectra (extended data—Fig. 2). The X-ray reflectivity spectrum in Fig. 2e could be well-fitted by a simulation based on electron density mapping analyses under the assumption that the SMB is composed of antiparallelly aligned polar monomolecular layers with head-to-head contact of the π-electron cores, as schematically shown in the inset. We also confirmed that the assumption of the other alignments (e.g., tail-to-tail contact) does not reproduce the experimental data (Fig. 3). Notably, the head-to-head molecular alignment in the SMB is very consistent with our scenario that the introduction of chain-length disorder prevents multiple stacking of the molecular bilayer units through geometrical frustration, while minimizing the influence on the intra-bilayer crystallization.

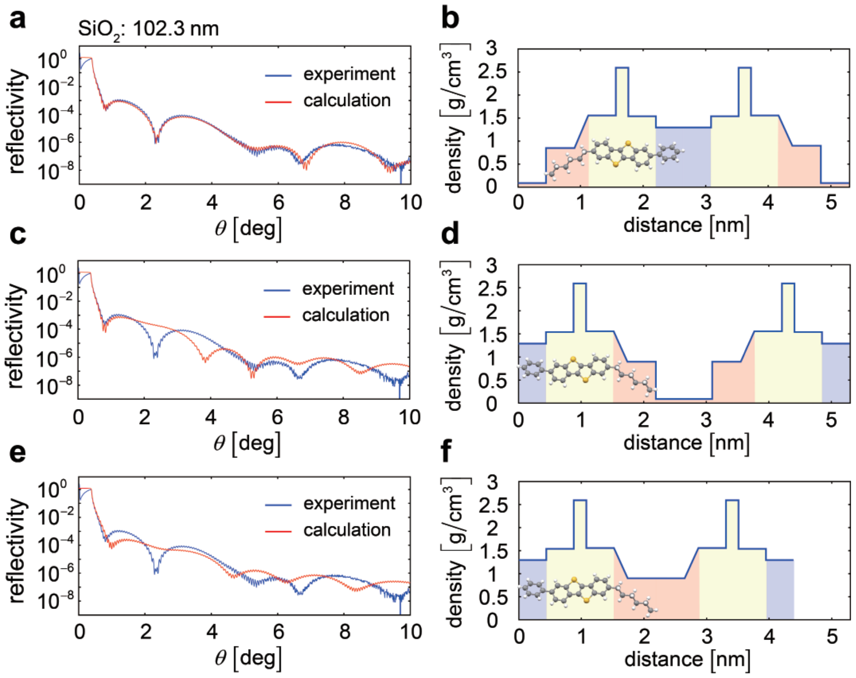

Fig. 3: Experimental and simulated X-ray reflectivity spectra. The X-ray reflectivity spectrum of the SMB film was compared to the spectrum simulated assuming that the SMB featured tail-to-tail contacts between Ph-BTBT-C_{10} polar monomolecular layers.

Recent molecular dynamics simulation studies revealed that solution-based, non-epitaxial

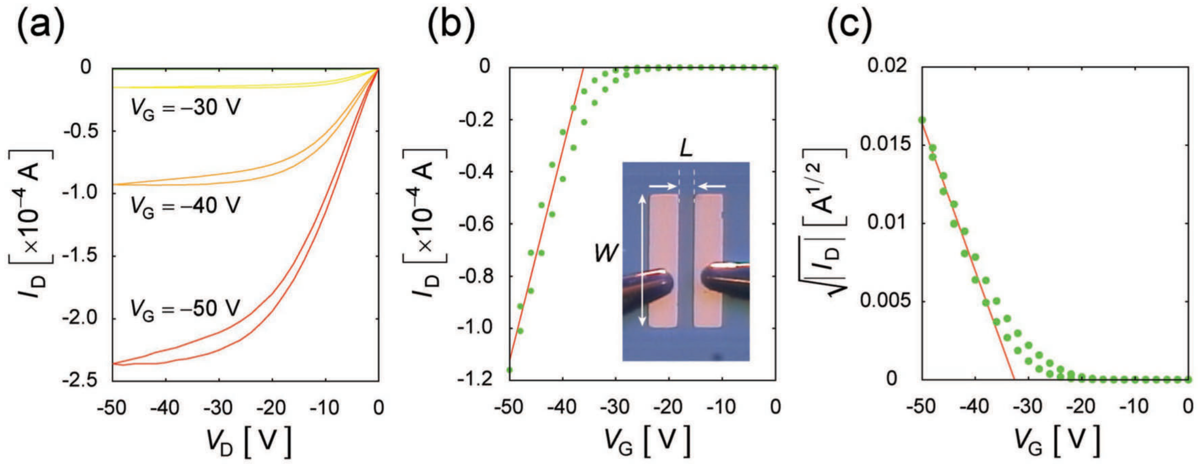

Fig. 4: Characteristics of SMB-TFT devices. a, Output characteristics. **b**, Transfer characteristics in the linear regime, and **c**, in the saturation regime. Device mobilities were determined as μ_{lin} = 2.0 cm^2 V^{-1} s^{-1} and μ_{sat} = 6.5 cm^2 V^{-1} s^{-1}.

growth of large-area, single-crystalline thin films becomes possible for highly layered-crystalline small-molecule organic semiconductors via stepwise ordering at air-solution interfaces. This implies that the above process should also be applicable to any wettable surface. Notably, we found that SMBs could also be produced on non-(silica/Si) surfaces, such as Au films. These ultrathin films with atomic- or molecular-scale thicknesses have recently attracted considerable attention for their applicability to super-flexible or wearable electronic devices. However, it has not thus far been possible to manufacture such ultrathin films with wafer-scale area size. Note that no cracks were observed in the wafer-scale SMBs produced in this study. Additionally, the strongly self-organized nature of semiconducting organic molecules should allow carrier transport through the SMB. Figure 4 presents the output and transfer characteristics of bottom-gate top-contact TFTs based on SMBs, revealing typical mobilities of 2.0 cm^2 V^{-1} s^{-1} in the linear regime and 6.5 cm^2 V^{-1} s^{-1} in the saturation regime. Notably, these values are about 33% lower than those of single-crystalline Ph-BTBT-C$_{10}$ TFTs with channels composed of a larger number of layers. This result could be ascribed to the limited thickness of the carrier transport media in the SMB-based TFTs. Nonetheless, this observation also indicates that the above change in the device characteristics can be employed as chemical sensors for such as highly sensitive molecular recognitions.

In summary, we have successfully developed a technique for manufacturing strongly self-organized SMBs that have uniformity of both molecular-level thickness and in-plane molecular order over a six-inch wafer-size scale. These SMBs were produced easily and reproducibly by a simple blade-coating technique based on the extended π-electron skeleton of Ph-BTBT substituted by alkyl chains of variable length. This process was enabled by introducing the effect of geometrical frustration by chain-length disorder on the supramolecular layered crystallization in the solution phase under ambient conditions. The uniformity, stability, and size scale are unprecedented compared to other artificial SMBs produced by conventional self-assembly processes. The obtained SMBs also afford TFTs that exhibit excellent device characteristics, exceeding those of amorphous Si TFTs. These findings should open a new route to SMB-based ultrathin super-flexible electronics.

References

[1] T. Hamai, S. Arai, H. Minemawari, S. Inoue, R. Kumai, T. Hasegawa, Phys. Rev. Appl., **8**, 054011 (2017).
[2] S. Arai, S. Inoue, T. Hamai, R. Kumai, T Hasegawa, Adv. Mater., **30**, 1707256 (2018).