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**Visualization of molecular packing and tilting domains and interface effects in tetracene
thin films on H/Si(001)**

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Visualizing molecular crystalline domains and influence of substrate defects are important in understanding the charge transport in organic thin film devices. Vacuum evaporated tetracene films of four monolayers on hydrogen-terminated Si(001)-2x1 substrate, as a prototypical system, have been studied with ex situ atomic force microscopy (AFM), transverse shear microscopy (TSM), friction force microscopy (FFM), and low-energy electron microscopy (LEEM). Two differently oriented in-plane lattice domains are found due to the symmetry of the substrate lattice, with no visible azimuthal twist between adjacent molecular layers in surface islands, indicating significant bulk-like crystallization in the film. Meanwhile, two types of subdomains are observed inside of each in-plane lattice domain. The subdomains are anisotropic in shape, and their sizes and distribution are highly influenced by the substrate atomic steps. TSM and FFM measurements indicate that these subdomains result from molecule-tilt orderings within the bulk-like lattice domains. TSM evidently shows a sensitivity to probe vertical molecule-tilt anisotropy for the molecular crystals, in addition to its known ability to map the lateral lattice orientations.

1. Introduction

In current search for novel materials, organic semiconductors are attracting much interest because they possess intriguing properties that can be manipulated by molecular design and have promising applications in building low-cost devices on large and flexible substrates [1–9]. Organic thin films serve as active layers in devices, microscopic or nanometer scale structures in the layers may critically impact the device performance. Particularly organic field-effect transistors (FETs) appear as interface devices: the charge transport is film thickness dependent, and a few molecular layers next to the molecule-substrate interface can dominate the charge transport. For a-hexathienylene [10, 11] and dihexylquaterthiophene [12], the FET channel current has been reported to be confined in the first two molecular layers. Whereas the hole mobility in the FETs of polyacene (pentacene [13–16], tetracene [17]) have been reported to have a saturation coverage of six or eight monolayers (ML). The origin of such variance in the thickness-dependent transport properties, and the mechanism of charge transport in organic materials have not been well understood.

Organic molecules are highly anisotropic in shape and generally weak in interaction inside the bulk. Molecular crystals commonly possess two-dimensional (2D) layered structures with pi-orbital overlap bonding within the layers and van der Waals interaction between the layers. During the film growth, thermodynamic driving forces induce molecular crystallization maximizing the p-orbital overlap, while kinetic limitations may trap molecular layers in states away from equilibrium disrupting the pi-orbital overlap network. The resulting film consists of a large amount of crystalline domains (and domain boundaries) with different sizes and orientations. Charge carrier mobility depends on domain size, as domain boundaries pose

barriers to charge transport in the molecular layers [6], and spatial charge distribution can be modulated by growth mode [16]. With charge transport being most efficient in the direction of pi–pi stacking, the mobility also depends on domain orientation and their relative orientations with respect to neighboring domains. Visualizing these domains in the coalesced molecular layers is therefore crucial in understanding the insight of charge transport, which, however, has been challenging [6].

Lateral force imaging with atomic force microscopy (AFM) offers promising ways for the investigation. In friction force microscopy (FFM) [18], cantilever twisting is dominantly induced by the dissipative (frictional) forces. Frictional anisotropy associated with molecule-tilt anisotropy has been visualized in studies of organic chain-like molecules [19, 20]. In transverse shear microscopy (TSM), cantilever twisting is due to shear forces that are transverse to the scan direction [21–23]. TSM of individual pentacene grains has been realized for the ultrathin films (up to the second molecular layer), which was attributed to the elastic anisotropy [22–24]. However, the lowest noticeable mobility in polyacene FETs often happens for the films with nominal coverage more than two monolayers (MLs) [13, 17], the crystalline domains at such minimum mobility thickness and beyond have not been studied in real space, though it is desirable to know the structure–function relationship. Moreover, influence of substrate defects to the domain structures has not been previously visualized.

In the present study, we have employed multiple microscopy techniques including AFM, FFM, TSM, and low-energy electron microscopy (LEEM) for real-space imaging of crystalline domains of organic films, using a tetracene film on H/Si(001)-2x1 at ~4 ML as a prototypical system. Tetracene (C₁₈H₁₂) consists of four fused-benzene rings [25], and is a promising polyacene in organic FETs and light-emitting devices [17, 26, 27]. The hydrogen-terminated

Si(001)-2x1 surface provides a structurally well-defined and inert substrate template [28, 29]. Our previous work demonstrates that tetracene films can form a layered structure (i.e., standing molecules on the ab-plane) on silicon substrates, with roughening transition from quasi-layer-by-layer growth to mound-type island growth (as a result of the Ehrlich–Schwoebel barrier at the terrace edges [30]) on top of the third molecular layer [31–33]. We observe that there is a coverage-dependent structure phase transition for the film (i.e., the initial film is rather disordered in molecule-tilting and significant bulk-like crystallization happens from ~3ML) [33]; and that the lowest measurable mobility in tetracene film FETs occurs at ~3 ML coverage [17]. Our grazing-incidence X-ray diffraction (GIXD) data [34] show that the film lattice is commensurate with the substrate lattice along the longer base vector of the ab-plane unit cell (i.e., the a-direction), and incommensurate along the b-direction (which is perpendicular to the a-direction here). The tetracene films are thus considered partially commensurate with the substrate lattice [34], different from the common epitaxy categories defined in Ref. [35]. In this work, we describe the observation of different types of domain structures for the tetracene films of ~4 ML coverage. There are two major domains (in-plane lattice domains) orthogonally oriented with each other due to the partially commensurate registrations with the substrate lattice. Different from pentacene ultrathin films reported, the TSM image contrast is found insensitive to the individual layers of surface islands in the major domain, indicating significant bulk-like crystallization throughout the film. We report two newly observed subdomains (molecule-tilt domains) inside each major domain. The subdomain size and distribution are sensitively influenced by substrate atomic steps. These findings reveal rich internal structures induced by different molecular tilting that are associated with substrate defects, even though they collectively follow the same 2D registration guided by the substrate lattice ordering.

2. Experimental

2. 1. Sample preparation

The growth of tetracene (98%, Sigma–Aldrich) films was carried out at Guelph at room temperature by thermal evaporation in a vacuum chamber (base pressure of $\sim 3 \times 10^{-9}$ Torr) using an alumina crucible heated in a tungsten basket [31, 33]. The deposition rate was ~ 1 nm/min, as monitored by a quartz crystal microbalance. In this study, we limited the film nominal thickness at ~ 4 ML. The substrate silicon wafers (Virginia Semiconductor) have miscut angle $< 0.03^\circ$ along a direction off surface normal [001] axis toward [110]. The wafers were cleaned via resistive heating at ~ 1470 K for ~ 1 min in a separate chamber (base pressure of $\sim 1 \times 10^{-10}$ Torr). Monohydride Si(001)-2x1 substrate was obtained by back-filling the chamber with molecular hydrogen ($\sim 10^{-6}$ Torr) for 30 min, during which a hot tungsten filament (~ 1800 K) was used to generate atomic hydrogen while the silicon substrate was kept at ~ 600 K [29, 33]. The H/Si(001)-2x1 surface typically showed atomic steps and alternating 2x1 and 1x2 lattice structures in adjacent terraces due to the degeneracy in energy, with monohydride dimer rows running along [110] and [-110] directions, respectively [29, 33]. Samples can be transferred between the two chambers in vacuum.

2. 2. Scanning probe microscopy

An ex situ AFM (Agilent Technologies 5500) was operated at Guelph in contact-mode under ambient conditions. To simultaneously obtain AFM topography and lateral-force images of a surface, vertical deflection and lateral twist of the AFM cantilever were monitored, respectively, via the intensities of the four segments of the photo diode. Lateral-force imaging was operated in two ways: (i) TSM mode – the tip scan direction was parallel to the cantilever

axis, so that cantilever twisting was due to the shear forces that are transverse to the scan direction; (ii) FFM mode – the tip scan direction was perpendicular to the cantilever axis, such that cantilever twisting was dominantly due to the dissipative (frictional) forces. The commercial sample holder was slightly modified with a home-made attachment, so that sample azimuthal orientation relative to the cantilever axis can be adjusted with a precision less than 10° . AFM probe were silicon tips (Nanosensors PointProbe Plus, model PPP-CONT), with a constant normal load of ~ 1.7 nN in experiments. The images were analyzed using software Gwyddion.

2. 3. Low energy electron microscopy

LEEM measurements (base pressure of 5×10^{-10} Torr) were carried out ex situ in the Elmitec SPE-LEEM III situated at the beamline U5UA of the National Synchrotron Light Source at Brookhaven National Laboratory. The incident electron beam was slightly tilted from the film surface normal (i.e., tilted bright field imaging mode [36]) using electron energy of ~ 1.9 eV, such that a surface-sensitive diffraction spot can be selected for LEEM imaging. The m-beam low-energy electron diffraction (LEED) patterns were also recorded in the LEEM experiments, using electron energies of 9–10 eV. In this LEED operation, an aperture was placed in the path of the electron beam, limiting the beam size to 2 μm in diameter, and thus detecting the diffraction data from a local surface area.

3. Results and discussion

3. 1. Major domains

When AFM topography imaging was performed on the tetracene film of ~ 4 ML, mound-type 3D surface islands were monitored by the cantilever deflection data (Fig. 1a). These islands appear to have an elongated shape along substrate lattice orientations, consistent with our

previous work: the film is commensurate with the substrate lattice along the a-axis (the longer base vector of the ab-plane unit cell of the film) [33, 34]. AFM imaging of a smaller area on the same film is shown in Fig. 1b. A close inspection (Fig. 1c) of the white frame inside Fig. 1b reveals terraced surface islands, with identical molecular height for each layer as shown in the AB line profile (underneath Fig. 1c). Figure 1d shows a TSM image of the same surface area as shown in Fig. 1a, the cantilever twist contrast between two differently orientated domains of the film is accentuated. In contrast with the conventional AFM image shown in Fig. 1a, where the surface morphology of the film is pronounced, this TSM image ignores the height profiles of the surface but presents a network of two dominant domains (hereafter referred to as the “major domains”). The TSM contrast between the two domains is indicated in the CD line profile. The two major domains appear equal in population in this commensurate film (Fig. 1d).

In TSM imaging, the degree of cantilever twist is dependent upon the scan angle (ϕ) relative to the film crystalline lattice directions [21–23]. Our rotational TSM data (Fig. 2) consistently suggest that the two major domains are due to the symmetry of the substrate lattice; and that they are of the same molecular organization but differ in orientation by 90deg. When scan direction is along ($\phi=0\text{deg}$) or perpendicular ($\phi=90\text{deg}$) to the substrate lattice, the shearforce contrast between the two domains is negligible. When $\phi=45\text{deg}$ and $\phi=135\text{deg}$, the TSM contrast appears about the strongest. Comparing $\phi=45\text{deg}$ and $\phi=135\text{deg}$ cases shown in Fig. 2 (in practice, the switching between the two cases was facilitated by rotating the sample by 90deg while leaving the cantilever orientation unchanged), we note that the contrast levels for the two major domains appear interchanged from one case to the other. Therefore, there is 180deg-rotation symmetry in TSM imaging of the major domains: when the sample is azimuthally rotated by 180deg underneath the tip, the TSM contrast level for each major domain

appears unchanged. In this work, we mostly use $\theta_i=45^\circ$ in TSM imaging for the best contrast unless otherwise specified.

Above results appear similar to those reported for pentacene monolayer films [23]. Given that pentacene and tetracene possess similar bulk molecular crystalline structures (i.e., the “herringbone” molecular packing) [37, 38], we attribute the two kinds of major domains to two kinds of in-plane lattice domains that are orthogonal to each other in our tetracene films. However, the TSM contrast for tetracene domains is found not layer-dependent in the terraced surface islands within a same major domain (e.g., Fig. 1d), demonstrating significant bulk-like crystallization through the layers in the tetracene films of ~ 4 ML, consistent with the structure data obtained in our previous work [33].

A combined LEEM and u-beam LEED study directly confirms the identical crystallinity for the two major domains, and the orthogonality between their orientations by tilting slightly away from the sample surface normal, such that a surface-sensitive diffraction spot of this thin film is selected for the LEEM imaging [36]. Similar to the TSM image shown in Fig. 1d, two kinds of major-domains appear on the LEEM screen (Fig. 3a). Once the tilted-beam in LEEM is further tuned while azimuthally rotated by 90° , another thin film diffraction spot (orthogonally located from the previous case) is selected for imaging. Indeed, the operation leads to the domain pattern inverted on the screen (Fig. 3b). After performing the u-beam LEED measurements on each kind of major domains, as shown in Fig. 3c and d, we further confirm that the two corresponding diffraction patterns are identical in unit-cell, but orthogonally oriented to each other.

3. 2. Subdomains

Strikingly, small scale TSM imaging of the tetracene films brings out two subdomain structures inside a major domain (Fig. 4). Figure 4a shows an AFM topography image of a rather flat terrace area. The vertically narrow (dark) area represents the terrace vacancies or the lower terrace area, and a small portion of (bright) higher terrace is nearby the right frame edge. TSM images of the same surface location are shown in Fig. 4b (forward-scan) and Fig. 4c (backward-scan). The major domain boundary is a winding curve from lower-left corner to the top-right corner in both TSM images, and two types of subdomains exist in two shades in each major domain. For example, in Fig. 4c, subdomain-1 and -2 are inside of the upper-left major domain and subdomain-3 and -4 inside of the lower-right major domain. But the contrast between the two shades is smaller than the contrast between the two major domains, as the relative contrasts shown by the CD and EF line profiles (associated with Fig. 4b and c, respectively). The subdomains appear inverted in contrast between forward-scan and backward-scan images (i.e., Fig. 4b and c, respectively). Again, in Fig. 4, both TSM contrasts for subdomains and major domains are insensitive to the height of molecular layers, indicating bulk-like crystallization across the layers of the film.

3. 3. Effects of substrate steps on subdomains and major domains on surface islands

Substrate atomic steps play an important role in forming subdomain boundaries. In an AFM topography image shown in Fig. 5a, substrate steps meandering diagonally are perceptible, for examples, at locations indicated by arrows and dotted lines. When the dotted lines are overlaid onto the corresponding TSM image (Fig. 5b), we see that there is a high probability for subdomain boundaries outlining the contours of the substrate steps.

Clearly, subdomains are significantly altered by the presence of the substrate steps, due to molecular misalignments caused by these atomic steps.

In contrast, the sizes of major domains are found insensitive to substrate roughness such as the atomic steps, presumably, they would be primarily dependent upon the nucleation density hence upon the kinetic growth conditions. Major domains are random in shape and about several tens of micrometers in size due to the coalesced nature of the film.

To alleviate the reader's concern about the dark feature which is nearly vertically distributed in the forward-scan TSM image (Fig. 5b), we present the backward-scan TSM image in Fig. 5c. The dark feature belongs to a different major domain from the type in the surrounding area. Not only its inverted bright appearance in Fig. 5c indicates such interpretation, the CD and EF line profiles taken from Fig. 5b and c, respectively, also consistently demonstrates the same relative contrasts between subdomains (i.e., subdomain-1 and -2 in the surrounding major domain, and subdomain-3 and -4 in the other major domain) as those measured from the line profiles in Fig. 4.

The orientation of a major domain determines the orientation of the surface islands contained within. As shown in the AFM topography (Figs. 1a and 6a) and corresponding TSM (Figs. 1d and 6b) images, all the islands within a single major-domain have their long-axis oriented along a same direction. Since pentacene islands on silicon have been found elongating along the a-axis direction as driven by kinetic processes in growth [36], a similar kinetic driving force could be expected in tetracene case. We may thus interpret that tetracene surface islands preferentially elongate along the a-axis direction, as indicated by white hollow arrows in Fig. 6a.

Why should subdomains appear dramatically different in size (from ~100 nm to 10 μ m) in different major domains in Fig. 6b? We note that subdomains tend to be anisotropic in shape (e.g. Fig. 6b), being elongated along the direction perpendicular to the respective island orientation (i.e., perpendicular to the white hollow arrows Fig. 6a). In other words, if the surface

islands preferentially grow along the a-axis due to kinetics in growth, then the subdomains would tend to elongate along the b-axis (which is perpendicular to the a-axis in the film [34]). On the other hand, substrates were chosen to have step anisotropy in this study (i.e., with a specific miscut angle). The step lines are perceptible in an enlarged frame taken from the dashed frame in Fig. 6a – the substrate steps are generally along the frame diagonal direction, which is indicated in the schematic representation underneath. Combining these two aspects, we believe that it is the subdomain elongating growth anisotropy together with substrate step anisotropy that leads to various subdomain sizes. Since all the images in Fig. 6 are acquired from the same surface area, thus they all have the same step anisotropy as shown in Fig. 6a. Notice that in the upper-left (darker) major domain in Fig. 6b, the subdomains are elongating perpendicular to the (top) white hollow arrow in Fig. 6a, they have high probability to be confined or interrupted by the step lines, leading to short and small sub-domains. Meanwhile, in the lower-right (brighter) major domain in Fig. 6b, the subdomain elongating direction is perpendicular to the bottom white hollow arrow in Fig. 6a (i.e., approximately parallel to the step lines), such that the subdomain elongating growth is not highly disturbed by the steps, leading to much longer and larger subdomains.

Figure 7 provides further AFM topography (Fig. 7a) and the TSM (Fig. 7b) data to show the same results as mentioned above. In Fig. 7b, the subdomains in the left (darker) major domain are elongating perpendicular to the subdomains in the right (brighter) major domain. With the substrate steps generally running along the diagonal direction of the squared white frame (from lower-left to upper-right), much smaller subdomains appear in the darker major domain (see the ovaled area) than the subdomains in the brighter major domain (see the squared area) due to the influence of the steps.

3. 4. Subdomain: Molecule-tilt ordering

To address the nature of the subdomains, we performed FFM operation (Fig. 6c) in conjunction with TSM imaging (Fig. 6b) of the tetracene film. As shown in the FFM image (Fig. 6c), there is little contrast between the two kinds of major domains, unlike the TSM image in Fig. 6b. However, subdomains are clearly visible in both TSM (Fig. 6b) and FFM (Fig. 6c) images, validating our approach that we may understand the nature of subdomains via FFM imaging.

We believe that the physical origin of subdomains is related to the nature of molecule-tilt ordering. First, the subdomains should be part of the crystalline structure, but different from the in-plane molecular organization. For a given major domain, all subdomains inside share the same in-plane lattice, and there are four possible molecule-tilt orderings. As depicted in Fig. 8, the four possible molecule-tilt cases fit for a given in-plane unit cell orientation: if one uses case 1 as a standard, cases 2–4 can be reproduced from case 1 through 180° rotation around a, b, and the ab-plane normal ($a \times b$) direction, respectively.

Second, we observe that there is 180°-rotation symmetry in both TSM and FFM imaging of the subdomains: upon rotation of the sample underneath the probe by 180°, the subdomain contrast patterns appear unchanged. Because of this 180°-rotation symmetry for the subdomains, the two cases with tilting vectors projected to the ab-plane being anti-parallel to each other are effectively indistinguishable in TSM and FFM images. In other words, the four molecule tilt cases would appear as two groups (A and B in Fig. 8) in the images, depending on the tilting azimuth. We therefore propose that the observed two subdomains are these two groups shown in Fig. 8. Because the subdomains have the in-plane symmetry equivalent structure and orientation, they cannot be resolved in our LEEM and diffraction measurements.

Lastly, frictional anisotropy due to molecule-tilt anisotropy has been reported in FFM studies of organic chain-like molecules [19, 20], the highest friction was found when the FFM tip scan direction perpendicular to molecule tilt azimuth, and the lowest friction when the scan direction parallel to molecule-tilt azimuth. The enhanced friction is caused by enhanced penetration of the tip into the film, owing to a mismatch between tip scan direction and molecule-tilt orientation. We interpret our FFM data with this frictional anisotropy mechanism, in combination with our proposed model for subdomains (Fig. 8). When the FFM tip scans at $\phi_i=45^\circ$ with respect to the a- or b-axis (Fig. 8), the scan line (red dotted line) is almost parallel to the tilt azimuth (green-arrow lines) for A-subdomains (i.e., the lowest friction configuration), but is almost perpendicular to the tilt azimuth for B-subdomains (i.e., the highest friction configuration), leading to nearly the strongest contrast between A- and B-subdomains, as the situation shown in Fig. 6c. When the tip scans parallel to the a- or b-axis (e.g., at $\phi_i=0^\circ$), zero friction contrast should occur between A- and B-subdomains, because of the similar medium frictions due to the similar mismatch between tip scan line and the molecule-tilt azimuths. Indeed, such scan angle- dependent subdomain FFM contrasts have been obtained in our FFM experiments, supporting our proposed model and understanding for the subdomains.

In Fig. 6c, identical subdomain contrast has been obtained simultaneously in both kinds of major domains under the same fixed $\phi_i=45^\circ$ for the FFM tip scan direction. The observation provides further evidence to support our model and analysis: Imagine that if subdomain A and B in Fig. 8 were rotated by 90° to mimic the other major domain configuration, the original tip scan line ($\phi_i=45^\circ$ dashed line in Fig. 8) would still be either nearly perpendicular or parallel to the tilt azimuths of the rotated-A and -B, leading to the same (strongest) friction contrast, though the contrast levels for A and B would be interchanged with the rotation.

Interestingly, in the TSM image (Fig. 6b), both major domains and subdomains in the thin film are clearly visualized. The fact that subdomains can be visualized by both TSM and FFM (Fig. 6c) suggests the existence of a transverse component of the friction forces acting on the tip during TSM imaging. Furthermore, subdomain contrast patterns in TSM and FFM images appear the same in one major domain, for example, in the lower-right major domain shown in Fig. 6c (TSM) and Fig. 6d (FFM). However, in the other major domain, the subdomain contrast patterns in TSM and FFM images appear inverted with each other (see the circled areas). Presumably, TSM has one more mechanism to induce the cantilever twist than FFM does, i.e., TSM data reflect two kinds of orderings (i.e., molecular lateral packing and vertical tilting), while FFM data reflect only one kind (i.e., molecular vertical tilting). These observed similarities and differences between TSM and FFM subdomain images will be insightful for further theoretical investigations on the mechanisms of TSM imaging [23, 39].

4. Conclusions

We have carried out real-space investigation of crystalline domain structures of a tetracene film on H/Si(001)-2x1 substrate at a ~ 4 ML coverage. We observe two differently oriented in-plane lattice domains (“major domains”) due to the symmetry of the substrate lattice, with no visible stacking twist between molecular layers along the depth of surface islands, consistent with our previous work [33] that significant bulk-like crystallization has been realized under the given coverage (~ 4 ML). Major domain determines the orientation of the surface islands contained within the domain, and the sizes of major domains are found insensitive to the substrate roughness such as atomic steps. We report two types of subdomains within each major domain, elongating perpendicular to that of the corresponding surface islands. Using AFM,

TSM, and FFM data, we attribute these subdomains to molecule-tilt orderings in the molecular layers. Subdomain size and distribution are sensitively influenced by substrate atomic steps, indicating that the change in molecule-tilt is highly susceptible to the molecular misalignments at the molecule–substrate interface. The observation of subdomains with both TSM and FFM demonstrates that TSM has substantial sensitivity to probe the vertical moleculetilt anisotropy (in terms of frictional anisotropy) for bulk-like molecular crystals, in addition to its known ability to visualize the lateral lattice orientations.

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FIGURES :

Figure 1: (a) A topography image of a ~ 4 ML tetracene film on H/Si(001)-2x1. The surface islands are oriented along the substrate lattice directions (marked at the upper left corner). (b) A small-scale AFM image of the same sample surface. (c) Close inspection of the framed area in (b) shows terraced islands, and identical molecular height for each layer is indicated in the AB line profile underneath (see double arrows). (d) A TSM image of the same surface area as shown in (a). The TSM contrast between the two major domains is indicated in the CD line profile.

Figure 2: TSM images of two major domains (marked as 1 and 2) acquired with different scan angle ϕ with respect to the substrate lattice directions (shown underneath the images). When scan direction is along ($\phi=0^\circ$) or perpendicular ($\phi=90^\circ$) to the substrate lattice, the TSM contrast between the two domains is negligible. When $\phi=45^\circ$, the TSM contrast between differentl oriented domains is close to the strongest, and if scan angle is further rotated by 90° (i.e., $\phi=135^\circ$), the contrast levels appear interchanged between the two major domains. There is 180° -rotation symmetry in TSM imaging of these domains.

Figure 3: Tilted bright-field LEEM images in (a) and (b) confirm the orthogonality between orientations of the two major domains. The corresponding m-LEED patterns individually collected from each major domain reveal identical unit-cells, but azimuthally orthogonal to each other, as shown in (c) (~ 9 eV) and (d) (~ 10 eV).

Figure 4: (a) A topography image of a ~ 4 ML tetracene film on H/Si(001)-2x1. (b) and (c) are the corresponding TSM forward-scan and backward-scan images of the same surface area, respectively, revealing a pair of subdomains (marked as 1 and 2, or 3 and 4) inside of each major domain area. Identical molecular height for each layer is indicated in the AB line profile underneath (see double arrows). The CD and EF line profiles of the TSM images (b) and (c), respectively, show the relative contrasts between major domains and subdomains.

Figure 5: (a) A topography image of a ~ 4 ML tetracene film on H/Si(001)-2x1 with visible silicon substrate atomic steps, as indicated by arrows and dashed lines. The corresponding TSM forward-scan image (b) and backward-scan image (c) of the same surface area reveal a variety of domain structures. The dashed lines in (a) and (b) refer to the boundaries of subdomains that highly match the contours of substrate steps. The vertically distributed dark features on the left part of the image in (b) belong to the other type of major domain. Identical molecular height for each layer is indicated in the AB line profile underneath (see double arrows). The relative contrasts between subdomains (1 and 2, or 3 and 4) and major domains are shown in the CD and EF line profiles taken from (b) and (c), respectively, and they are similar to those shown in the line profiles in Fig. 4.

Figure 6: (a) A topography image of a ~ 4 ML tetracene film on H/Si(001)-2x1 illustrates surface islands elongated along two orthogonally oriented directions (white hollow double arrows). An enlarged image of the dashed frame in (a) reveals substrate steps that are meandering along the diagonal direction (from upper-left to lower-right), as indicated by a schematic representation

underneath. TSM and FFM images of the same surface area are shown in (b) and (c), respectively. Major domains can only be revealed in TSM imaging, while subdomains are accentuated in both TSM and FFM data. Blue double-arrows in (c) indicate the preferred growth direction for subdomains, perpendicular to the elongating directions of the surface islands (i.e., blue double-arrows in (c) are perpendicular to white double arrows in (a)). In the lower-right major domain (boundary visible in (b)), the contrast pattern of subdomains is identical for both TSM (b) and FFM (c) images; while in the upper-left major domain, the contrast pattern appears inverted with each other between TSM (b) and FFM (c) images (see circled areas). The AB line profile taken from (b) is consistent with the TSM contrast data shown in Figs. 4 and 5. The CD line profile taken from (c) shows the FFM contrast between subdomains.

Figure 7: (a) A topography image of a ~4 ML tetracene film on H/Si(001)-2 $\times$ 1 reveals substrate steps generally running along the diagonal direction of the squared white frame (from lower-left to upper-right). Identical molecular height for each layer is indicated in the AB line profile on the right side (see double arrows). (b) A TSM image of the same surface area as shown in (a) presents domain structures. The subdomains in the left (darker) major domain (see the oval areas) are elongating perpendicular to the subdomains in the right (brighter) major domain (see the squared areas). These subdomains appear dramatically different in size between different major domains. The CD line profile taken from (b) is consistent with the TSM contrast data shown in Figs. 4 and 5.

Figure 8: Schematic diagram of two different subdomains. There are four possible molecule-tilt cases for a given lattice orientation in the ab-plane of the crystalline film. Based on the molecule-tilt azimuths (green arrows), the four cases will be imaged as two groups (A and B). Red dashed lines indicate FFM scan lines. The molecular structure of tetracene is indicated below the diagram.

Fig.1

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8