Collective orientation barrier in growth of organic thin films revealed by pMAIRS

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We used *p*-polarized multiple-angle incidence resolution spectrometry (pMAIRS) to investigate a collective orientation barrier (COB) in the growth of organic semiconductor (OSC) films. We demonstrate a temperature-dependent variation in the growth of pentacene (PEN) on SiO₂ films as a model system. The molecular orientation varied from lying to standing as the growth temperature increased. This change suggests that the formation of a standing orientation is thermally activated compared with the lying state. The nucleation of standing-oriented islands occurs by molecular self-assembly at sufficiently high temperatures. Conversely, molecules deposit in a flat-lying state at low temperatures owing to hindrance of the kinetic barrier to reorientation from lying to standing states. The COB is defined as a collective energy barrier for the reorientation processes throughout the growth. The COB is quantitatively estimated from an Arrhenius plot of the probability to form a standing orientation, derived from the dichroic ratio measured by pMAIRS. We found that the COB in the growth of PEN on the SiO₂ system was approximately 0.02 eV, which is a key parameter for determining the molecular orientation. A quantitative evaluation of the COB will be applicable to other systems and enable effective control over the molecular orientation of OSC films.

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I. INTRODUCTION

Organic-semiconductor (OSC) thin films function as active layers in organic electronic devices such as organic thin film transistors, organic light emitting diodes, and organic photovoltaics [1–6]. The performance of these devices strongly depends on the structure of the OSC films, including factors such as molecular orientation, morphology, and crystallinity [2,4–6]. Therefore, control over OSC film structure is important for optimizing device performance. Particular attention has been paid to control of molecular orientation because it directly affects charge carrier mobility and optical properties of films owing to the anisotropic characteristics of π -conjugated planes in OSC molecules [4,5,7].

Established growth processes of thin films are classified into three modes; layer-by-layer, layer-plus-island [Stranski-Krastanov (SK)], and island growth [8]. In the case of pentacene (PEN) on silicon dioxide (SiO₂) as a representative OSC film system, it has been reported that growth proceeds by the SK mode [9–11]. First, evaporated molecules adsorb and diffuse on a substrate in a lying state. Second, when a critical number of molecules meet, an island nucleates in a standing configuration by molecular self-assembly [9,12]. The standing orientation with the molecular long-axis nearly vertical to the substrate is thermodynamically stable because of the lower

surface energy of the (001) plane compared with other planes of the crystalline structure [13]. Next, an island grows by incorporation of adjacent molecules and coalescence with another islands. After completion of the initial layer, nucleation of subsequent layers proceeds by an island mode owing to weaker interactions among molecules than with the substrate [9–11]. This growth mechanism is strongly influenced by the growth conditions.

Specifically, the substrate surface, the deposition rate, and substrate temperature are essential parameters that determine the growth of OSC films [9–11,14–16]. The substrate surface determines the nature of interactions with molecules, whereas the deposition rate and substrate temperature determine the density of diffusing molecules and the kinetic energy of adsorbed molecules, respectively. These parameters can affect growth behaviors, such as the growth mode, nucleation, and molecular orientation. For instance, it has been reported that the growth mode can be switched to island mode by lowering the surface energy of the substrate [15] and the nucleation density increases together with the deposition rate [16]. Furthermore, recent studies have reported that OSC molecules can be induced to adopt a lying orientation on SiO₂ rather than a standing orientation by lowering the substrate temperature [17,18]. Hence, nucleation in the standing orientation should be prevented during growth owing to limited kinetic energy at low temperature. Because an isolated molecule initially lies on its surface to maximize van der Waals interactions with the substrate, there is a kinetic barrier to switching the configuration from a lying to standing state. The concept of such a kinetic barrier has been proposed as a reorientation barrier in a previous study [19].

The reorientation barrier was defined as a microscopic energy barrier for molecule reorientation from a lying-down

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to standing-up state in the nucleation process [19]. It has also been suggested that this microscopic reorientation barrier is substrate-dependent and strongly influences the nucleation and the growth processes at the initial layer. However, such reorientation processes occur not only on the substrate surface but also on top of the molecular layers. Hence, the kinetic barrier for reorientation depends on the circumstances of the growth. For example, a reorientation barrier might be higher for lying than standing oriented molecules because of π - π interactions between the molecules. If both standing and lying orientations coexist in the initial layer, a reorientation barrier in the second layer will differ depending the nature of the first layer. The final film structure is formed by crossing various kinds of energy barriers for reorientation in nucleation processes. Therefore, we define a collective orientation barrier (COB) as a barrier energy that molecules collectively overcome for formation of a standing orientation throughout the growth processes, which governs the probability to nucleate standing oriented islands. Because the COB parametrizes the determination of the molecular orientation, there is a need to study the COB so that it can be applied to optimize OSC film structures.

The purpose of this study is to investigate the COB as a key parameter for controlling molecular orientation in the growth of the OSC films. We report the temperature-dependent variation of the film structures of PEN on SiO₂, as a model system, grown at a fixed deposition rate. Film structures, such as morphology and molecular orientation, are investigated by atomic force microscopy (AFM), two-dimensional grazing incidence x-ray diffraction (2D-GIXD), and *p*-polarized multiple-angle incidence resolution spectrometry (pMAIRS) [20]. We focus on the change in growth mode arising from the effects of a kinetic barrier to the reorientation processes. Furthermore, we evaluate the COB with the use of pMAIRS, which is a powerful method for quantitatively estimating the degree of molecular orientation in organic thin films. pMAIRS measurements yield both in-plane (IP) and out-of-plane (OP) vibrational spectra simultaneously, which give a dichroic ratio of IP to OP components of a vibrational mode. The dichroic ratio of vibrational modes related to the π -conjugated planes of OSC molecules enables an estimate of the concentration of standing and lying molecules in a film. We examined the temperature dependence of the concentration of the standing orientation in PEN films to deduce a COB from the Arrhenius behavior.

II. EXPERIMENT

A naturally oxidized silicon wafer (SiO₂) was used as the substrate. The substrates were cleaned in solvent (acetone, 10 min, two times). PEN (sublimed grade) was used as received. Thin films of PEN were grown by vacuum deposition on substrates under a base pressure below 1×10^{-6} Pa with a deposition rate of 0.1 nm s^{-1} . The substrate temperature was fixed during deposition (105, 125, 155, 173, 203, 253, and 318 K). The film thickness, monitored with a quartz crystal microbalance, was 20 nm for all samples. After deposition, the substrate temperature was gradually returned to ambient temperature under vacuum.

The PEN films were analyzed under ambient conditions after removal from the preparation chamber. The surface structure was investigated by AFM using E-sweep/NanoNavi (Hitachi High-Tech) in tapping mode. The average island size in the film was statistically determined from several $1 \times 1 \mu\text{m}^2$ topographic images. The molecular orientation of the films was investigated by 2D-GIXD and pMAIRS. The 2D-GIXD measurements were performed on the beam line BL46XU at SPring-8. Monochromatized x rays with a wavelength of 0.1 nm (12.398 keV) irradiated the sample surface at an angle of approximately 0.12° . The diffraction was observed with the use of a two-dimensional detector (PILATUS 300 K) with a detector distance of approximately 175 mm. The pMAIRS measurements were conducted on a Thermo Fisher Scientific Nicolet 8700 FT-IR spectrometer equipped with an automatic MAIRS equipment with a Harrick Scientific PWG-U1R wire-grid polarizer. A liquid-N₂ cooled mercury-cadmium-telluride (MCT) detector was used for data collection. The incident angle was changed from 9° to 44° in 5° steps [21]. The orientation angle φ was obtained from $\varphi = \tan^{-1} \sqrt{2A_{\text{IP}}/A_{\text{OP}}}$ [20], where φ is the angle from the surface normal and A_{IP} and A_{OP} are the peak intensities of the in-plane (IP) and out-of-plane (OP) spectra, respectively.

III. RESULTS AND DISCUSSION

A. Morphologies

Figure 1 shows representative $1 \times 1 \mu\text{m}^2$ AFM topographic images of PEN films on SiO₂ grown at 105, 203, 253, and 318 K (denoted as films A to D, respectively). The film morphologies varied with deposition temperature. Films B–D had uniform islands in each film. As revealed by the color scale bars, the roughness values of these films were within 30 nm, which is consistent with the nominal film thickness of 20 nm. Films C and D had mound-shaped islands with step-terrace structures although such step-terrace structures were hardly observed in the small grains in film B [22]. The step height of approximately 1.5 nm corresponds to the interplanar spacing of the (001) plane in the crystalline structure of PEN, as commonly observed in the thin-film phase [23]. The step height indicates that the islands comprised standing-oriented molecules. The island sizes of these films systematically increased with growth temperature. The average diameters of the islands in films B, C, and D were estimated to be 20, 150, and 750 nm, respectively. In contrast to films B to D, film A comprised nonuniform grains, having lateral diameters in the range of 50–300 nm and roughness values up to 150 nm, which was considerably greater than the nominal film thickness. The maximum of the height scale was exceeded by relatively large grains that seemed to accumulate on small grains.

The step-terrace structure of films C and D indicated that their film formation proceeded in the SK mode and established growth mechanisms [9–11]. By contrast, films A and B had almost no step-terrace structures in their grains, which suggested that these films grew by a different mechanism. Additionally, the temperature-dependent evolution of island sizes observed in films B–D was consistent with the diffusion-mediated growth model [24,25]. In this model, larger stable

FIG. 1. Temperature-dependent variation of film morphology ($1 \times 1 \mu\text{m}^2$) for PEN on SiO_2 . Films A–D correspond to growth temperatures of 105, 203, 253, and 318 K, respectively. Nominal thickness is 20 nm. Scale bar indicates 500 nm.

islands form at higher temperature owing to active diffusion whereas smaller separated islands form at lower temperature, owing to restricted diffusion causing binding of neighbor molecules rather than migration to distant existing nuclei. However, film A behaved differently from the other films in terms of grain size and the height scale. These different behaviors suggested that a different growth mode takes place in film A.

B. Molecular orientations

The 2D-GIXD patterns of films A to D are shown in Fig. 2(a). The $2\theta_{xy}$ and $2\theta_z$ axes corresponded to the in-plane and out-of-plane components of the scattering vectors, respectively. The 2D-GIXD patterns revealed a distinct variation in the distribution of 001 reflections among these films. Film A had a streaked 001 reflection only in the $2\theta_{xy}$ direction, whereas film B had dotted 001 reflections splitting into the $2\theta_{xy}$ and $2\theta_z$ directions and films C and D had dotted 001

reflections only in the $2\theta_z$ direction. Because the long axis of PEN molecules almost lies along the c^* axis in the unit cell, the distribution of 001 reflections reveals the orientation distributions of the long-molecular axis for each film. Thus, these results indicate that the long-molecular axis was mainly oriented almost parallel (lying) in film A, both parallel and vertical (coexistence of lying and standing) in film B, and almost vertical (standing) in films C and D. The streaked profile of the 001 reflection in film A indicates a spread of the orientation distribution of the lying crystallites. Additionally, the azimuth profiles of the 001 and 002 reflections for films B–D in the azimuth angle range of 60° – 120° are shown in Fig. 2(b) to compare the spread of the orientation distributions of the standing crystallites. Film B (red dotted line) had a broader distribution of both the 001 and 002 reflections than those of films C (black dashed line) and D (blue solid line). Although the 001 profile showed no clear differences between films C and D, the 002 profile had weak broad peaks at the bottom of the peak only for film C (indicated by black arrow).

FIG. 2. (a) 2D-GIXD patterns obtained from films A–D, where Bragg peaks are indexed by the Miller indices of the crystal lattice planes. (b) Azimuth profiles of 001 and 002 reflections for films B (red dotted line), C (black dashed line), and D (blue solid line). Black arrows in the 002 azimuth profile indicate weak broad peaks observed in film C.

TABLE I. Crystallite sizes calculated from peak width of 001 reflections along the $2\theta_{xy}$ and $2\theta_z$ axes in the 2D-GIXD patterns (Fig. 2) with the use of Scherrer's equation. The parameters $2\theta_{xy}$ or $2\theta_z$ respectively represent the in-plane or out-of-plane crystallite components.

Film	Crystallite sizes (nm)	
	$2\theta_{xy}$	$2\theta_z$
A	12.0	
B	11.9	13.9
C		22.7
D		24.6

The weak peaks were located approximately 15° from the peak top, which suggested the presence of a minor component at different tilt angles. Thus, the spread of 001 reflections indicates that the width of angular distributions of the standing crystallites decreased in the following order: film B > film C > film D.

We used 2D-GIXD to investigate the crystallite sizes. Table I shows the crystallite sizes determined from the peak width of the 001 reflections in Fig. 2(a) by the Scherrer equation. The crystallite sizes in the $2\theta_{xy}$ or $2\theta_z$ axes corresponded to those of lying or standing crystallites, respectively. The standing crystallite sizes of films B–D increased from 14 to 25 nm. Although the crystallite sizes of films C and D were almost saturated owing to the film thickness of 20 nm, the size increase of the crystallites was consistent with the lateral size increase of islands (Fig. 1). Conversely, the lying crystallite sizes of 12 nm for films A and B were the same although the grain sizes appeared larger in film A than in film B (Fig. 1). This observation suggests that enlargement of the lying crystallites in film A was not accompanied by crystallite growth, which is unlike the island growth process of a standing nucleus.

Further quantitative evaluation of the molecular orientation was performed by pMAIRS. Figure 3 shows pMAIRS spectra of films A–D in the range of $940\text{--}880\text{ cm}^{-1}$. Open and filled circles respectively correspond to the IP and OP spectra. Gaussian function fitting curves are overlaid on each spectrum. The peaks ν_z observed at $909\text{--}904\text{ cm}^{-1}$ were assigned to the C-H out-of-plane deformation vibration of aromatic rings [17,26]. The peak intensity ratio of IP to OP spectra, A_{IP}/A_{OP} , of ν_z varied considerably with growth temperature. Film A had a much weaker A_{IP} than A_{OP} , whereas film B had similar A_{IP} and A_{OP} intensities. Films C and D had a stronger A_{IP} than A_{OP} . The orientation angles ϕ_z of ν_z are denoted in Fig. 3 with a schematic explanation of ϕ_z . The value of ϕ_z consistently increased from 27° to 72° for films A–D. Although ϕ_z can also vary depending on the short-axis rotation of molecules, long-axis rotation dominated the variation of ϕ_z in these films according to the 2D-GIXD results. The orientation angle of 27° for film A indicated a lying orientation, whereas the value of 50° for film B was close to the magic angle (54.7°) and indicated the coexistence of similar amounts of lying and standing orientations. Both orientation angles of 67° and 72° for films C and D indicated a standing

FIG. 3. pMAIRS spectra for films A–D in the wave-number position of $940\text{--}880\text{ cm}^{-1}$ where IP (blue open circle) and OP (black filled circle) spectra are plotted with fitted curves (IP: blue solid line, OP: black solid line). Orientation angles ϕ_z of peak ν_z are denoted for each spectrum. Inset shows a schematic illustration of the orientation angle ϕ_z of a PEN molecule against a substrate (sub.).

orientation. The slight decline of ϕ_z for film C is attributed to the existence of a minor component with different tilt angles, as indicated in Fig. 2(b).

The pMAIRS spectra in Fig. 3 show a shift in the peak position of ν_z between the IP and OP spectra, particularly in films A and B. The peak positions of ν_z in films C and D were almost the same at 904 cm^{-1} in both the IP and OP spectra whereas those in films A and B split into 904 and $909\text{--}907\text{ cm}^{-1}$ in the IP and OP spectra, respectively. This peak splitting between the IP and OP spectra can be attributed to the Berreman effect, i.e., transverse-optic (TO)-longitudinal-optic (LO) splitting [27]. The TO-LO splitting is often found for surface perpendicular-sensitive measurements, such as the reflection-absorption spectrometry and the OP mode of pMAIRS [28] in which the LO mode is observable. Because the lying state of molecules clearly exhibited the LO mode in the ν_z vibration region, films composed of lying-oriented molecules show TO-LO splitting in pMAIRS spectra. Accordingly, the degree of the TO-LO splitting is relevant to the degree of lying orientation of films. Indeed, film A had the most apparent peak splitting and the difference corresponded to 5 cm^{-1} . Film B also had peak splitting; however, the difference was 3 cm^{-1} . Films C and D had no clear peak splitting. The peak position shift between the OP and IP

FIG. 4. Schematic illustration of temperature-dependent variation of film structures for PEN on SiO_2 . Film structure varies with temperature based on the assumption that the growth mode switches by overcoming a COB. At low temperatures, molecules grow in a lying deposition mode owing to kinetic hindrance of the COB. At intermediate temperatures, lying deposition and standing nucleation modes compete and the final film comprises small isolated grains with various orientations involving lying, standing, and intermediate orientations. At high temperature, molecules form standing nuclei of sizes that increase with temperature.

spectra is therefore attributed to the Berreman effect, which is induced by a lying orientation.

The pMAIRS spectra of films grown at 125, 155, and 173 K (denoted as films A_1 , A_2 and B_1 , respectively) are shown in Fig. S2 of the Supplemental Material [22]. Films A_1 and A_2 had small $A_{\text{IP}}/A_{\text{OP}}$ and the TO-LO splitting, and provided φ_z of 36° and 38° respectively, which indicated a lying orientation as well as film A. Film B_1 had similar intensities of A_{IP} and A_{OP} and provided φ_z of 59° , which indicated the coexistence of similar amounts of lying and standing orientations as well as film B. Therefore, we will consider films A_1 and A_2 as film A, and film B_1 as film B, when we discuss the film growth mechanisms.

The 2D-GIXD and pMAIRS results revealed an orientation transition of films A–D from the lying to standing orientation with an increase of the growth temperature. Film A mainly contained lying-oriented molecules and was unlike films B–D because these comprised standing-oriented molecules. The formation of a standing orientation suggested that nucleation occurs through reorientation processes involving a switch from a lying to a standing orientation. The ratio of the standing orientation increased with temperature as indicated by the increase of the orientation angle φ_z . This temperature dependence suggests that the reorientation processes are activated by thermal energy. The lying orientation of film A indicates that the low kinetic energy at low temperature inhibited the reorientation and caused the molecules to remain lying down. Furthermore, the coexistence of lying and standing orientations in film B suggests competition between nucleation of standing crystallites and retaining flat-lying states. For the standing molecules, the degree of orientation in films B–D differed [Fig. 2(b)]. The smaller islands in film B had a wider angular distribution of orientations than the larger islands in films C and D. These results indicate that the degree of orientation can be influenced by diffusivity during island growth. Under diffusive conditions, molecules can form large, well-oriented islands because they can adopt the optimal configuration.

C. Temperature-dependent variation of film growth

Figure 4 schematically illustrates the temperature-dependent variation of the film structures of PEN on SiO_2

based on the experimental results. Molecular orientation in films varied from lying to standing as the growth temperature increased. This difference in molecular orientation suggested that the growth mechanism depends on the temperature. For films C and D, molecules were mainly in a standing orientation. The growth of these films may proceed in the SK mode with a standing-up orientation and established growth mechanisms [9–11]. At the first step, adsorbed molecules diffuse on the substrate in a lying state and an island nucleates by meeting adjacent molecules through a reorientation into the standing configuration. The reorientation can occur by molecular self-assembly because the standing orientation is thermodynamically stable [13]. After the initial layer completely forms, subsequent layers grow on the top of the initial layer with standing orientation in the island mode.

By contrast, the lying orientation observed in films A and B indicates that some molecules retain a lying state rather than nucleate in a standing oriented island during growth. Because nucleation of the standing-oriented islands needs some driving force, a lying state is kinetically favored at low temperatures and forms initially upon adsorption of the molecules to the substrate. Under such low temperature conditions, lying molecules hardly diffuse on the substrate and incoming molecules deposit randomly on lying molecules or the exposed substrate. Although the interactions with substrate weaken as the coverage of lying molecules increases, incoming molecules are expected to take a lying orientation because of π - π intermolecular interactions and low kinetic energy. The formation of a standing orientation or retention of a lying orientation is decided based on the growth conditions. A temperature-dependent increase of the standing orientation is observed in films A–D suggesting that the nucleation of standing-oriented islands was thermally activated at a constant deposition rate. At low enough temperatures, the lying orientation mode mainly occurs and the final film structure comprised mostly lying molecules, as observed in film A. At intermediate temperatures, the lying orientation is retained or nucleation of the standing orientation occurs competitively, such that the final film structure comprised both two orientations as observed in film B. At high enough temperature, nucleation of the standing orientation mainly occurs, and the final film structure comprises standing oriented islands, as observed in films C and D.

The characteristics of the film morphology are attributed to the different growth scenarios. In the standing orientation mode, the temperature-dependent evolution of the island size can be explained by the diffusion-mediated growth model, as reported by Tejima *et al.* [24]. In this model, the nucleation density depends on the diffusivity of molecules and the deposition rate. When the deposition rate is constant, the island size increases with the growth temperature because island growth is promoted by high diffusivity. The island size evolution observed in films B–D was consistent with this model. Additionally, a surface morphology with step-terrace structure was apparent in films C and D, which indicates layered formation of standing-oriented monolayers. By contrast, in the lying orientation mode, molecules randomly deposited on the surface or on top of molecules without optimizing their arrangement. Such random stacking of lying molecules might contribute to the surface roughness. Although aggregation or

crystallization can occur with neighboring molecules in the vicinity of stacking layers, reorientation may be less likely owing to limited kinetic energy. Considering the surface morphology, gradual annealing effects should be considered because the AFM measurements were conducted at ambient temperature. The lying orientation in the bulk structure remained even after gradual annealing owing to kinetic hindrance of the deposited molecules [18], whereas molecules, particularly those around the surface, are relatively unstable owing to the small number of molecules deposited on them. Thus, aggregation of neighboring molecules only occurs easily in the surface layers. Film A (Fig. 1) had a rough surface with some of large grains, whereas the crystallite size of film A (Table I) was as small as that of film B. Thus, the lying molecules in the underlying layers retained their arrangement when deposited whereas molecules, particularly those around the surface, aggregated and formed islands.

Furthermore, when the lying and standing orientation modes compete during growth, small separated islands form, as observed in film B. Under such growth conditions, nucleation of standing islands competes with retention of the lying states. Consequently, an inadequate diffusivity to stabilize each configuration leads to the formation of small separated islands with various kinds of orientations, such as standing, lying, and their intermediate states.

D. Collective orientation barrier

We estimated the COB based on data obtained from pMAIRS measurements. We define the COB, E_{COB} , as the barrier energy that molecules in the PEN/SiO₂ system need to overcome for nucleation of standing-oriented islands throughout film growth. Therefore, at a fixed deposition rate, a E_{COB} determines the molecular orientation and the probability of nucleation of standing-oriented crystallites n^*/N depends on E_{COB} , where n^* and N correspond to the numbers of standing molecules and of all molecules, respectively. Furthermore, we assume that the system can be approximated to have only two components of standing (S) and lying (L) molecules where the tilted configurations are averaged to perfectly perpendicular (S) and parallel (L) states. In this assumption, the n^*/N can be estimated from pMAIRS spectra as

$$\frac{n^*}{N} = \frac{[S]}{[S] + [L]} = \frac{[S]/[L]}{1 + [S]/[L]} = \frac{2A_{\text{IP}}/A_{\text{OP}}}{1 + 2A_{\text{IP}}/A_{\text{OP}}}, \quad (1)$$

where [S] and [L] are the concentrations of standing and lying molecules in a system, respectively, and $A_{\text{IP}}/A_{\text{OP}}$ correspond to the intensity ratio of the C-H out-of-plane deformation vibration peak, such as ν_z . Because the E_{COB} controls the probability of nucleation, n^*/N can be written as

$$\frac{n^*}{N} \propto \exp\left(-\frac{E_{\text{COB}}}{kT}\right). \quad (2)$$

In Fig. 5 the logarithm of n^*/N obtained from the $A_{\text{IP}}/A_{\text{OP}}$ of ν_z is plotted as a function of inverse temperature. We note that the intensity ratio might include an analytical error to some extent owing to the Berreman effect, which can induce peak splitting and intensity enhancement [27,28]. Nevertheless, the logarithmic plot showed a linear trend, which enabled the estimation of E_{COB} . The least-squares fit provided

FIG. 5. Logarithm of the component ratio of standing molecules to all molecules $\ln(n^*/N)$ derived from Eq. (1) vs inverse temperature. Dotted line represents a least-squares fit. The correlation coefficient is 0.90.

$E_{\text{COB}} = 0.020 \pm 0.007 \text{ eV}$, where the error represents the 95% confidence interval.

This E_{COB} parametrizes the probability for molecules to select a standing orientation during film growth. We found that the E_{COB} was approximately 10% of the energy of the intralayer (of the order of 0.4 eV) and interlayer (of the order of 0.15 eV) interactions [13]. This indicates that PEN molecules on SiO₂ generally adopt a standing orientation at ambient temperature because of the small E_{COB} . If a system with a different substrate needs a larger E_{COB} than 0.02 eV to enable the molecules to adopt a standing orientation, a higher temperature will be required to form a standing oriented film.

The COB represents the total energy barrier for the various reorientation processes throughout film growth, such as molecules adopting standing orientation on the substrate, other standing molecules, and accumulated lying molecules. Investigating the COB is valid because the molecular orientation of an OSC film is determined by the simultaneous or collective motion of individual molecules. For instance, different processes such as forming standing orientation and retaining lying state may occur simultaneously during competitive film growth. Subsequently, the orientation of incoming molecules may be influenced by that of the underlying molecules. Although it is difficult to identify the behavior of individual molecules, one can predict the probability of a molecule adopting standing orientation by estimating the COB as a collective barrier energy. The COB depends on growth conditions, such as the surface energy of the substrate and deposition rate. Furthermore, this barrier is a characteristic value of molecules, which should be influenced by the molecular structure, such as chemical functional groups, molecular length, and intermolecular attractive forces. The proposed mechanism and experimental evaluation of the COB can be applied to orientation transitions observed in other OSCs. Knowledge of the value of this activation barrier optimizes can be used to control growth of thin films. Our pMAIRS-based method enables a quantitative investigation of the COB dependence on deposition conditions and

characteristics of the molecules, which will lead to a deeper understanding of thin-film growth.

IV. CONCLUSIONS

We have demonstrated the temperature-dependent variation of film structures for PEN on SiO₂ at a fixed deposition rate to investigate COB as a collective energy barrier for reorientation processes during growth with the use of pMAIRS. We observed that the molecular orientation of these films switched from a lying to standing orientation as the growth temperature increased. The characteristics of the morphology differ between lying- and standing-oriented films. These results suggest that the formation of a standing orientation is thermally activated rather than maintaining a flat-lying state and a kinetic barrier exists for the reorientation processes during growth. At higher temperatures, standing-oriented islands nucleate and form molecular layers by self-assembly and established growth mechanisms. Alternatively, at lower temperatures, molecules deposit on a substrate in the lying states because the reorientation process is kinetically inhibited. The standing or lying orientation mode competitively

occurs depending on the growth temperature throughout the formation of all layers. Therefore, we estimated the COB that governs the determination of the molecular orientation using pMAIRS. The probability of nucleation in standing orientations was quantitatively determined from the dichroic ratio of the C-H out-of-plane deformation vibration peak in pMAIRS spectra. The temperature dependence of the probability to nucleate in a standing orientation had an Arrhenius behavior and provides a specific value of the COB. We observed that the COB was approximately 0.02 eV, which is low enough for the PEN/SiO₂ system to overcome at ambient temperature. Because the COB can be experimentally evaluated by our method, it is effective to investigate the dependence of the barrier on the growth conditions or the characteristics of molecules. An understanding of the COB is essential for controlling the molecular orientation of OSC thin films and for improving device performances.

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