Impact of graphene-molecular interaction on collective orientation barrier for organic film growth

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Organic electronic devices comprising organic semiconductor (OSC) films, such as organic thin-film transistors and organic photovoltaics, have long attracted attention because of their low cost, low weight, flexibility, and ecofriendliness.1–4 However, the performance of such devices needs to be improved for practical applications. Controlling the molecular orientation of OSC films is essential for optimizing their characteristics and improving the device performance. Because OSC films have anisotropic molecular structures with pi-conjugated planes, their carrier mobility and optical properties depend on their molecular orientation.5,6)

The collective orientation barrier (COB) has been proposed as an index of the molecular orientation control.7) The COB is an energy barrier that all molecules need to overcome to form a standing orientation during film growth and represents the ease of standing orientation formation. The COB was estimated by determining the temperature-dependent increase in the formation of a standing-oriented component using p-polarized multiple-angle incidence resolution spectroscopy (pMAIRS).8,9) It was found to be approximately 0.02 eV for pentacene (PEN) on SiO2,7) where PEN molecules generally form a standing orientation during growth at ambient temperature. The COB value is expected to vary with the substrate surface, OSC material, and deposition rate. However, it has not yet been investigated in greater detail.

Graphene (Gr) is a promising two-dimensional material for flexible and transparent organic electronic device applications as it has outstanding electrical, optical, and mechanical characteristics.10,11) The six-membered ring structure of Gr has a high affinity with pi-conjugated planes in OSCs with polycyclic aromatic hydrocarbon structures. Several studies have reported that Gr acts as a template to promote the formation of lying-oriented crystallites of OSC molecules.5,12–15) The interaction between PEN and Gr is expected to be larger than that between PEN and SiO2. Specifically, computational studies have estimated that when PEN molecules are oriented parallel to the substrate, the PEN/SiO2 interaction energy is 0.22 eV16) whereas that of PEN/Gr is 1.5 eV.17) Therefore, PEN/Gr is adopted as a suitable system for comparison with PEN/SiO2 to verify the effect of the molecular-substrate interaction on the COB. This study investigates the temperature-dependent molecular orientation variation in the PEN/Gr system, estimates the COB via pMAIRS, and compares it with the result of the PEN/SiO2 system.

A Gr/SiO2 substrate was prepared by transferring a Gr monolayer onto a naturally oxidized silicon wafer (consigned to Graphene Platform). The substrates were cleaned twice using acetone for 10 min and heated at 680 K for 2 h in a vacuum for polymeric residue removal. PEN (Tokyo Chemical Industry, sublimed grade) was used as purchased. PEN thin films were grown via vacuum deposition on Gr/SiO2 substrates under a base pressure below 1 × 10−6 Pa with a deposition rate of 0.1 nm s−1. Different substrate temperatures were tested during deposition: 273, 298, 302, 313, 323, 338, and 348 K. The film thickness was monitored using a quartz crystal microbalance and was 20 nm for all samples. After deposition, the substrate temperature was gradually returned to ambient temperature in a vacuum.

The surface morphology was investigated via tapping-mode atomic force microscopy (AFM; Hitachi High-Tech E-sweep NanoNavi). The molecular orientation in the films was investigated via two-dimensional grating incidence X-ray diffraction (2D-GIXD) and pMAIRS. 2D-GIXD measurements were performed on the BL46XU beamline at SPring-8. A monochromatized X-ray with a 0.1 nm (12.398 keV) wavelength irradiated the sample surface at an angle of approximately 0.12°. The diffraction was observed using a two-dimensional detector (PILATUS 300 K) with a distance of approximately 175 mm. The pMAIRS measurements were performed using a Thermo Fisher Scientific Nicolet 8700 FT-IR spectrometer equipped with automatic MAIRS equipment with a Harrick Scientific PGW-U1R wire-grid polarizer. A liquid-N2-cooled mercury-cadmium-telluride detector was used for data collection. The incident angle was changed from 9° to 44° in 5° steps.18) In-plane (IP) and out-of-plane (OP) spectra were obtained using the MAIRS equation. The orientation angle ϕ was obtained as:

\[ \varphi = \tan^{-1} \sqrt{2A_{IP}/A_{OP}}, \]

where ϕ is the angle from the surface normal, and \( A_{IP} \) and \( A_{OP} \) are the peak intensities of the IP and OP spectra, respectively.8,9) \( n^* \) is the number of standing oriented molecules.
molecules in the film, \(N\); total number of molecules in the film) for each film was obtained as

\[
\frac{n^s}{N} = \frac{[S]}{[S] + [L]} = \frac{[S]/[L]}{1 + [S]/[L]} = \frac{2A_{IP}/A_{OP}}{1 + 2A_{IP}/A_{OP}} = \frac{1}{1 + \cot^2 \varphi},
\]

where \([S]\) and \([L]\) indicate the concentration of standing- and lying-oriented molecules, respectively. The COB value, \(E_{COB}\), was estimated as

\[
\frac{n^s}{N} \propto \exp\left(-\frac{E_{COB}}{k_B T}\right),
\]

where \(k_B\) and \(T\) are the Boltzmann constant and substrate temperature, respectively.

Figures 1(a)–1(d) respectively show the surface morphologies of PEN films with an area of \(5 \times 5 \ \mu m^2\) on Gr/SiO_2 substrates grown at 273, 298, 313, and 348 K (hereafter referred to as Films A, B, C, and D, respectively) as obtained from AFM measurements. Films A and B exhibited flat, block-shaped grains with trenches. These resemble the horizontally oriented crystals observed on highly oriented pyrolytic graphite,\(^{19}\) suggesting that Films A and B have a lying orientation. The streaky pattern in the grains of Film A differs slightly from the elongated dotted pattern in the grains of Film B, indicating minor differences in the film formation processes. Films C and D contained island grains with step-terrace structures; these resembled the standing-oriented islands observed in the PEN/SiO_2 system.\(^{2,7,16}\) Film C also contained narrow, block-shaped grains, suggesting that lying-oriented crystallite fragments existed in Film C.

2D-GIXD measurements were performed to confirm the molecular orientation of crystallites in the PEN/Gr films. The 2D-GIXD patterns obtained from Films A–D are shown in Figs. 2(a)–2(d), respectively. The horizontal and vertical axes show the scattering vector in the \(q_r\) and \(q_z\) directions, respectively. Miller indices with subscript \(L\) and \(S\) correspond to the reflections of the lying- and standing-oriented crystallites, respectively.

Fig. 1. (Color online) (a)–(d) \(5 \times 5 \ \mu m^2\) surface morphologies of PEN/Gr Films A–D as obtained via AFM, respectively. The scale bar in (d) represents 2 \(\mu m\).

Fig. 2. (Color online) (a)–(d) 2D-GIXD patterns of Films A–D, respectively. The horizontal and vertical axes show the scattering vector in the \(q_r\) and \(q_z\) directions, respectively. Miller indices with subscript \(L\) and \(S\) correspond to the reflections of the lying- and standing-oriented crystallites, respectively.
circles. The peaks $\nu_z$ observed in the wavenumber region of $912–904$ cm$^{-1}$ were assigned to the CH out-of-plane bending vibration mode of an aromatic ring whose dipole moment was directed perpendicular to the $\pi$-conjugated plane of a PEN molecule.26) The relative intensities $I_{IP}/I_{OP}$ of $\nu_z$ peaks indicated the degree of molecular orientation, and the orientation angle $\varphi_z$ calculated from Eq. (1) indicated the tilt angle of the dipole moment of PEN from the surface normal, as illustrated in Fig. 3(b). The results indicate that the larger the $\varphi_z$ value, the greater is the proportion of standing-oriented components in a film. The obtained $\varphi_z$ values were $32^\circ$, $31^\circ$, $46^\circ$, and $62^\circ$ for Films A–D, respectively. These results indicated that Films A and B mainly comprised similar amounts of lying-oriented components; Film C had an intermediate orientation with lying- and standing-oriented components coexisting; and Film D mainly comprised standing-oriented components. The degree of lying orientation in Films A and B seemed saturated in light of previously reported 2D-GIXD results.5,13) By contrast, the $\varphi_z$ of $62^\circ$ obtained from Film D was $10^\circ$ smaller than that for a standing-oriented PEN film on SiO$_2$.27) This indicated the presence of a minor amount of lying-oriented components in Film D, as shown in Fig. 2(d).

Next, we discuss the wavenumber positions of peak $\nu_z$ [Fig. 3(a)]. The peak positions in the OP spectra were observed at $912$ cm$^{-1}$ except in Film D, whereas those in the IP spectra were observed at $904$ cm$^{-1}$. This peak splitting can be attributed to both the Berreman effect and polymorphism. The former is known as transverse optic-longitudinal optic (TO-LO) splitting,27) which is observable in the LO sensitive mode, such as reflection absorption measurements and the OP mode of pMAIRS.28) Polymorphism can cause peak position shifts owing to different molecular packings.19,29,30) The IP peak positions of $904$ cm$^{-1}$ derived from standing-oriented components agree well with the “thin film” phase position,29,30) which is consistent with the 2D-GIXD results. The OP peak positions of $912$ cm$^{-1}$ derived from lying-oriented components is consistent with the lying-oriented film on graphite,19) and may be assigned to that of the “single crystal” phase affected by TO-LO splitting.

These results demonstrated the temperature-dependent molecular orientation variation of PEN/Gr films. PEN/Gr films had a lying orientation during growth below $298$ K, and their degree of standing orientation increased with temperatures in the $298–348$ K range. From the pMAIRS results, the $n^*/N$ values for all PEN/Gr films were calculated using Eq. (2), and an Arrhenius plot was generated (Fig. 4). In Fig. 4, the logarithms of $n^*/N$ for PEN/Gr and that for PEN/SiO$_2$ obtained from Ref. 7 are plotted as a function of the inverse temperature. The inset shows a magnified view of the plot for PEN/Gr in the $0.003 < 1/T < 0.004$ range, where plots obtained from Films A–C are indicated by A–C, respectively. The $n^*/N$ value of PEN/Gr monotonically decreased with $1/T$ and showed linearity except for plot A. No significant change in $n^*/N$ was observed between plots A and B, as shown in the inset. This suggested that the degree of lying orientation saturated at temperatures below $298$ K ($1/T > 0.0034$), where the standing orientation formation was hindered by the Gr-molecular interaction being stronger than the kinetic energy. A regression analysis was performed in the $1/T < 0.0034$ range (plot A was neglected), and $E_{COB}$ was

Fig. 3. (Color online) (a) pMAIRS spectra of Films A–D, where the black-closed and blue-open circles indicate OP and IP spectra, respectively. The corresponding fitted curves have the same colors as the circles, where the peak fitting was performed using a Gaussian function. The orientation angle $\varphi_z$ of Films A–D is shown. (b) Schematic of the orientation angle $\varphi_z$ for PEN on the substrate.

Fig. 4. Arrhenius plot of $\ln(n^*/N)$ as a function of inverse temperature for the PEN/Gr and Pen/SiO$_2$ systems. The inset shows magnified plots of PEN/Gr in the range of $0.003 < 1/T < 0.004$, where A–C indicate plots obtained for Films A–C, respectively.
estimated from the gradient and using Eq. (3). $E_{\text{COB}}$ for the PEN/Gr system was estimated as 0.2 eV. A similar orientation variation was observed in the PEN/SiO$_2$ system, the temperature range of which was lower and broader than that of the PEN/Gr system. $E_{\text{COB}}$ of the PEN/Gr system was 10 times larger than that of the PEN/SiO$_2$ system (0.02 eV). This proved that higher energy was required to form standing-oriented crystallites on Gr than on SiO$_2$. Given that the interaction energies were 1.5 and 0.22 eV for PEN/Gr and PEN/SiO$_2$, respectively, the approximately 10 times difference in COB between them is plausible.

Figure 5 shows a schematic of the temperature-dependent variation of the film structure observed in the ((a)–(c)) PEN/Gr and ((d)–(f)) PEN/SiO$_2$ systems studied in Ref. 7. A system adopts a lying orientation when it cannot cross the COB at low temperatures. The formation of standing-oriented components is thermally activated upon crossing the COB at high temperatures. Although such orientation change was observed both in the PEN/Gr and PEN/SiO$_2$ systems, the formation processes of the lying orientation were different. In the PEN/SiO$_2$ system, there only exists a weak van der Waals interaction between the molecule and substrate. Small-sized, lying-oriented crystallites were found at extremely low temperatures of approximately 105 K, at which molecular diffusion and nucleus growth may be negligible [Fig. 5(d)]. At an intermediate temperature, both standing and lying orientations formed while the crystallite size was small [Fig. 5(e)]. By contrast, in the PEN/Gr system, the formation of large, block-shaped, lying-oriented crystallites was found at approximately room temperature, as seen in Films A and B, at which molecules may diffuse while retaining a lying-oriented configuration owing to the π–π interaction between Gr and molecules. $^{17}$ The flat shape of lying-oriented grains indicated that the growth proceeded in the layer-by-layer mode [Fig. 5(a)]. $^{31}$ At high temperatures where fast diffusion can allow rotation to the standing configuration by breaking through the π–π interaction with the Gr surface, the formation of standing-oriented crystallites can competitively occur with the formation of lying-oriented crystallites [Fig. 5(b)]. This corresponded to the coexistence of standing- and lying-oriented crystallites found in Film C. In Film C, standing-(island) and lying-oriented (block-shaped) grains with sizes of the order of several micrometers formed separately. Such grain sizes were obviously larger than the 10-nm-sized grains observed in the PEN/SiO$_2$ system [Fig. 5(e)].$^{7}$ This indicated that the competitive nucleation and growth of lying- and standing-oriented crystallites in the PEN/Gr system proceeded as molecules diffused to grow. As the molecular mobility increased further, the formation of the standing orientation became dominant in both systems [Figs. 5(c) and 5(f)]. This corresponded to Film D. While standing-oriented (island) grains were observed in the morphology of Film D [Fig. 1(d)], the 2D-GIXD and pMAIRS results suggested the existence of lying-oriented components as a subcomponent. It was believed that small lying-oriented crystallites were occasionally formed at the boundary of standing islands.$^{32}$ Most importantly, the $E_{\text{COB}}$ can be consistently estimated, although the formation scenario of the lying orientation differs between the PEN/Gr and PEN/SiO$_2$ systems. This revealed that the COB is valuable to quantitatively understand the difficulty of forming a standing orientation during growth.

In conclusion, the molecular orientation variation in the PEN/Gr system in the temperature range of 273–348 K was investigated via AFM, 2D-GIXD, and pMAIRS. At temperatures below 298 K, flat and block-shaped lying-oriented crystallites were dominantly formed. At higher temperatures, the formation of the standing orientation was thermally activated. In particular, at 348 K, the formation of the standing orientation was found to be preferred. The COB was estimated to be 0.2 eV from the temperature-dependent increase in the formation ratio of the standing orientation as evaluated via pMAIRS. This value is 10 times larger than that of the PEN/SiO$_2$ system, thus quantitatively indicating the effect of the π–π interaction between the molecule and the Gr substrate. This study found that the COB is valuable for understanding and controlling the molecular orientation of organic films.

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