Molecular dynamics simulations of graphoepitaxy
of organic semiconductors, sexithiophene, and pentacene:
Molecular-scale mechanisms of organic graphoepitaxy

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1. Introduction

The performance of organic semiconductor devices largely depends on the condensed state of semiconductor molecules such as molecular packing and crystallinity as well as the property of the molecule itself. In the case of thin films, in-plane orientation control is important in the following two aspects. One is that well-oriented thin films show a high charge mobility because of low grain boundary resistance even in polycrystalline films. The other is that molecular crystals have large anisotropy in charge mobility, and it is important to adjust the in-plane orientation showing the largest mobility in the direction connecting the source and the drain. However, substrates for the thin film growth are ordinarily amorphous (gate insulators), and conventional “epitaxy” technology cannot be used for controlling the in-plane orientation of thin films. To overcome such a problem, some techniques, for example, using friction-transferred polymer films or photo-aligned polyimide films, have been proposed for obtaining well-oriented films of organic semiconductors. In these techniques, the surfaces of amorphous substrates are covered beforehand with oriented polymers, which work as the templates for the oriented growth of organic semiconductors.

The author, together with some collaborators, tried to apply graphoepitaxy to obtain in-plane-oriented thin films of organic semiconductors on amorphous substrates from 2005 to 2010. Graphoepitaxy, in-plane-oriented thin film growth on artificial microstructures, was discovered in the 1970s in some inorganic materials. In 2006, about thirty years later than extensive studies of graphoepitaxy in inorganic and metallic materials fields, we first reported “organic” graphoepitaxy observed using α-sexithiophene (6T; C24H14S6). In the experiments, periodic microgrooves were fabricated on thermally oxidized silicon substrates by electron beam lithography and dry etching, and 6T thin films were grown on the substrates by molecular beam deposition. We confirmed that graphoepitaxy really occurred in 6T thin films by using AFM images (analysis of in-plane orientation of each crystalline grain based on the external form of the grain) and grazing-incidence X-ray diffraction. More interestingly, in-plane orientation changed 90° depending on the surface conditions; the c-axis was parallel to the direction of the grooves on a hydrophobic surface with hexamethyl-disiloxane (HMDS) treatment while the c-axis was perpendicular to the groove direction on a hydrophilic surface (b–c plane of 6T crystals was on the surface). After that, the author showed that the edge of the metal electrodes also causes oriented growth (graphoepitaxy) like periodic microgrooves fabricated on the substrate surface. Although the author described the possible mechanism of the organic graphoepitaxy based on the experimental results in Refs. 9–11, the real cause still remains a mystery.

Recently, the author has carried out molecular dynamics (MD) simulations to clarify the mechanisms of organic graphoepitaxy at the molecular level. MD simulations have already been applied to organic semiconductors, mainly to the research on pentacene (C22H14). However, they have not been applied to the study of “graphoepitaxy” of organic semiconductors, to the best of the author’s knowledge. First, in this study, MD simulations of orientation adjustment at the groove edge were carried out. These simulations well reproduced the experimental results partially, but some uncertainty remained. The simulated results strongly suggested that dynamic deposition processes, such as adsorption, desorption, diffusion, and nucleation, should be involved when considering the factors determining the in-plane preferred orientation observed in the experiments. Thus, the author also simulated the deposition process of molecules. Since it was found that the simulation of the deposition processes of 6T was difficult because of the softness of 6T molecules, we used pentacene for the simulations of the deposition processes. The MD simulations of pentacene provided quite important knowledge to understand the thin film formation of organic semiconductors, for example, the process that produces the standing configurations of molecules.
2. Experimental methods

2.1 Models of substrates

Models of the grooved substrates for MD simulations were prepared as shown in Fig. 1. 90 silicon (Si) atoms and 180 oxygen (O) atoms were put in a cubic cell (1.6 × 1.6 × 1.6 nm$^3$). The density of this cube filled with Si and O atoms was 2.19 g/cm$^3$, which almost corresponded to the density of amorphous SiO$_2$ under ambient temperature and pressure. These atoms in the cubic cell were completely mixed at 5,000 K using the NTV ensemble (the volume of the cell was fixed) and temperature was decreased to 300 K to obtain the stable structure at room temperature. For calculating the interaction among Si and O atoms in SiO$_2$, the set of the potentials proposed by Demiralp et al. was used. Periodic boundary conditions were applied in the X-, Y-, and Z-directions, and the Ewald method was used for calculating Coulomb interactions. The arrangement of Si and O atoms after MD simulations is shown in Fig. 1(a). To make hydrophilic and hydrophobic surfaces, some Si atoms near the surface of one side/top plane of the unit cube [Fig. 1(a)] were replaced with Si–OH or Si–OSi(CH$_3$)$_3$ as shown in Figs. 1(b), 1(c), 1(f), and 1(g). The trimethylsiloxy group, –OSi(CH$_3$)$_3$, is the functional group formed by the HMDS treatment. The stable structure and partial charge (Mulliken charge) of these functional groups were calculated in advance using Gaussian 09 with the Hartree–Fock method using 6-31G(d) basis sets as shown in Figs. 1(d), 1(e), 1(h), and 1(i). These calculations were carried out using a larger molecular assembly first to obtain the appropriate partial charge, and the parts of Si–OH and Si–OSi(CH$_3$)$_3$ were extracted after the calculation. The total charges of Si–OH or Si–OSi(CH$_3$)$_3$ were +1.1016 and +1.1303, respectively. In the unit cells shown in Figs. 1(b) and 1(c), the partial charge of the Si atoms in SiO$_2$ was set as +1.1016 (the same as that of Si–OH) to achieve the charge neutrality of the substrate (the partial charge of O atoms in SiO$_2$ was set as −0.5508, i.e., oppositely charged, and the value was half of that of Si atoms). In the unit cells shown in Figs. 1(f) and 1(g), the partial charge of the Si atom in SiO$_2$ was set as +1.1303 [the same as that of Si–OSi(CH$_3$)$_3$] to achieve the charge neutrality of the substrate (the partial charge of O atoms in SiO$_2$ was set as −0.56515, i.e., oppositely charged, and the value was half of that of Si atoms).
The size of the substrate (for example, the number of unit cells in the Y-direction) was changed depending on the purpose of the simulations. In this paper, substrates are sometimes named as “Y2 substrate”, “Y3 substrate”, and “Y6 substrate”, depending on the number of stacked cells.

### 2.2 Model of 6T and pentacene molecules

The optimum structure and partial charge (Mulliken charge) within a molecule of 6T and pentacene were calculated using Gaussian 09 in advance, with the Hartree–Fock method using 6-31G(d) basis sets. The results of the calculations are shown in Fig. 2. In most cases, in this study, these optimized molecular structures were kept during simulations (rigid model) except in the simulations of dynamic deposition processes.

#### 2.3 Interactions between atoms and molecules

Although the structure of 6T crystals was investigated by molecular mechanics using the MM3 force field model, there has not been any report of MD simulations investigating the crystalline state of 6T to the best of the author’s knowledge. There is a report that focused on the adsorption of 6T molecules on Ag(111) surfaces by MD simulations, but the simulations were largely different from the present case where many 6T molecules are standing on inert surfaces and form a bulklike crystal structure. In the case of pentacene, many papers on MD simulations have been published but the force field model used was case-by-case; the MM3 potential was used in Refs. 12 and 15, the Buckingham potential model with a Coulombic contribution for the interaction between rigid pentacene molecules (and DREIDING parameters for the interactions between pentacene molecules and silica substrates) was used in Ref. 13, and the AMBER force field was used in Ref. 14.

To calculate intramolecular and intermolecular interactions, in this study, the Dreiding force field, a simple generic set of force equations and parameter values, was used. Intramolecular interaction comprises the following four energy terms, bond stretch, angle bend, torsion, and inversion (out-of-plane) angle:

\[
E_{\text{bond}} = \frac{1}{2} K(r - R_0)^2, \\
E_{\text{angle}} = \frac{C}{2} \left( \frac{\sin^2 \theta}{\theta_0} \right)^2, \\
E_{\text{torsion}} = \frac{1}{2} V [1 - \cos(n(\phi - \phi_0))], \\
E_{\text{inversion}} = \frac{1}{2} K_{\text{inv}} (\psi - \psi_0)^2,
\]

where \(K, V, K_{\text{inv}}\) are force constants, \(r\) and \(R_0\) are the actual bond distance and equilibrium bond distance between two atoms, respectively, \(\theta\) is the angle that three atoms form, \(\phi\) is the dihedral angle, and \(\psi\) is the angle called inversion (out-of-plane) angle. When the structure of each molecule was treated as a rigid body, the intramolecular interactions described using Eqs. (1)–(4) were not calculated.

To describe intermolecular interactions (van der Waals force), the Lennard-Jones potential

\[
E = D_0 \left[ \frac{R_0}{r} \right]^{12} - 2 \left( \frac{R_0}{r} \right)^6
\]

or the Buckingham potential

\[
E = A_{ij} \exp(-B_{ij}r) - \frac{C_{ij}}{r^6}
\]

was used. In both cases, Coulomb interactions working between two charges \(q_iq_j/(\varepsilon_0r)\) were all integrated and added to the intermolecular interaction; Coulomb interactions were calculated by the Ewald method when periodic boundary conditions were applied in the X-, Y-, and Z-directions. However, when periodic boundary conditions were not applied, the Ewald method was not used but a simple summation of Coulomb interactions between charges within the cut-off distance \(R_c\) (1 or 2 nm, depending on the case) was carried out. In previous papers, there seems to have been a tendency to use the Buckingham potential more frequently than the Lennard-Jones potential for describing the van der Waals interactions in molecular crystalline systems. In
this study, both the Buckingham potential and Lennard-Jones potential were used and results were compared (the results were not very different from each other).

The Si and O atoms in amorphous SiO\textsubscript{2} substrates were not moved during all the simulations carried out in this study, by fixing the velocity of these atoms as zero. The functional groups placed on the substrate surfaces, Si–OH and Si–OSi(CH\textsubscript{3})\textsubscript{3}, were treated as rigid bodies in most simulations. However, these functional groups were freely moved in some simulations using the Dreiding force field and the effect of the movement was confirmed. In such cases, the desorption of the functional groups from the substrates was prevented by fixing the root Si atoms, by giving the Si atoms a huge mass.

### 2.4 Other factors, software, and hardware

The temperature of the system was controlled by the classical velocity scaling method.\textsuperscript{21} The average velocity of the molecules is always scaled to adjust the temperature derived from the total kinetic energy to the given temperature. The modeling of the substrates and molecules and all MD simulations in this study were carried out using SCIGRESS, a molecular modeling software package produced by Fujitsu Limited, and a workstation, Fujitsu CELSIUS M740 with a Xeon(R) E5-1650v3 processor. The time required for calculation ranged from 3\textasciitilde{}12 hours in all simulations except for the preliminary tests for the hydrophilic nature of the SiOSi(CH\textsubscript{3})\textsubscript{3} surface, which took roughly one day.

### 3. Results and discussion

#### 3.1 Preliminary tests investigating the effect of functional groups

The substrate surface was functionalized by replacing some Si atoms with Si–OH or Si–OSi(CH\textsubscript{3})\textsubscript{3}. However, it was unclear whether these functional groups, –OH group or –OSi(CH\textsubscript{3})\textsubscript{3} group, showed the expected properties, that is, hydrophilic or hydrophobic nature. Prior to the simulations using organic semiconductor molecules, the effect of these functional groups was checked using water (H\textsubscript{2}O) molecules. As shown in Fig. 3, the water droplet comprising 1,000 H\textsubscript{2}O molecules was placed on the grooved or flat substrates and MD simulations were carried out. In the simulations, the TIP5P potential\textsuperscript{22} was used to calculate the intermolecular interaction between H\textsubscript{2}O molecules. On the –OH substrates, H\textsubscript{2}O molecules spread wide along the substrate surface [Figs. 3(a) and 3(b)], which indicated high wettability. On the –OSi(CH\textsubscript{3})\textsubscript{3} surface, on the other hand, H\textsubscript{2}O molecules formed a massive aggregate [Figs. 3(c) and 3(d)], which indicated low wettability.

The different behaviors of water droplets on the two kinds of substrates with different surface treatments can be attributed to the degree of polarity (dipole moment) of the surface and water molecules, which is consistent with the distribution of partial charges in molecules. In general, the affinity of one substance for another substance is larger when those two substances have similar degrees of polarity than when they have different degrees of polarity. The preliminary simulations shown here well reproduced such general tendency of hydrophilic/hydrophobic nature caused by the difference in polarity, and it was confirmed that the substrate models prepared in this study could be used for the further investigation of the interaction between organic semiconductor molecules and the surface of the groove wall.

#### 3.2 Simulations of orientational adjustment at the edge of the groove (6T)

As described in the introduction, one of the most interesting phenomena observed in our previous experiments was the change in the in-plane orientation of 6T thin films depending on the surface conditions in the grooved substrates. On inert substrates such as amorphous SiO\textsubscript{2} substrates, a long monoclinic square pole unit cell stands perpendicular to the surface (the b- and c-axes are on the surface and the long a-axis is almost perpendicular to the surface). 6T molecules also stand on the substrates but their molecular long axes are slightly inclined at an angle of 23.5° with the a-axis of the monoclinic unit cell.\textsuperscript{23} The in-plane orientation (b–c plane) rotated 90°, a c-axis \perp groove (b-axis \parallel groove) on the hydrophilic surface and a c-axis \parallel groove (b-axis \perp groove) on the hydrophobic surface (HMDS-treated surface).\textsuperscript{10} If this experimental result can be reproduced by MD simulations, it will become firm evidence showing the capability of MD simulations for the study of organic graphoepitaxy.

In this challenge, we carried out two types of simulations. One is the MD simulations without periodic boundary conditions. In this case, a wider substrate model (“Y” substrate) was used and 120 molecules of 6T (2 layers of 60 molecules) were put at the central part near the groove wall, as shown in Fig. 4. Since the molecules are far from the ends of the substrate in the Y-direction, there is almost no effect of the ends on the 6T molecules. In Fig. 4, the initial arrangement of molecules was set as the molecular plane was parallel to the groove wall. The temperature of the system (average velocity of 6T molecules) was kept at 380 K, which corresponded to the substrate temperature set in previous experiments. In 2–3 ps, the arrangement of 6T molecules quickly changed and a herringbone packing structure appeared (see the online supplementary data at http://stacks.iop.org/JJAP/57/03EG04/mmedia). The herringbone packing can clearly be seen when the molecules are viewed from an upper part. The direction of the herringbone
packing (the direction of the arrowlike shape that molecular planes form) corresponds to the c-axis of the bulk crystal structure (as described above, the longest axis of the monoclinic unit cell corresponds to the a-axis, and the b–c plane is on the surface). This means that the c-axis of the 6T crystal (molecular cluster) is parallel to the groove wall in Fig. 4.

Figure 5 shows the variations of the results when the initial arrangement of the 6T molecules before MD simulations was changed every 10°, against the groove wall. Both results using the OH-terminated and HMDS-treated substrates are shown. The result of 0° of the HMDS-treated one is the same as that shown in Fig. 4. These twenty simulated results clearly show the dependence of final orientation on the initial arrangement. In both cases of hydrophilic (terminated by –OH) and hydrophobic [terminated by –OSi(CH3)3], the c-axis tends to be parallel to the groove wall when the initial direction is 0 or 10° while the c-axis tends to be perpendicular to the groove when the initial direction is 80 or 90°. It is very interesting that when the initial arrangement is tilted (20–70°), the c-axis tends to be inclined about 45° to the groove wall.

Figure 6 shows some results of MD simulations when periodic boundary conditions were applied in the X-, Y-, and Z-directions, by using the narrow “Y2” substrates. In this case, the relationship between the initially arranged angle and the c-axis’s direction after MD simulations was slightly different from the results shown in Fig. 5. For example, even in the case where the initial angle was 60°, the molecules moved in the Y-direction with the rotation of the molecular plane (molecules move to the next periodic cells as shown by the green arrows in Fig. 6), and the final in-plane orientation became the c-axis ⊥ groove (see the online supplementary data at http://stacks.iop.org/JJAP/57/03EG04/mmedia). As can be seen in the polygonal line graph in Fig. 6, internal energy decreases during the adjustment of the in-plane molecular orientation (during the azimuthal rotation of the b- and c-axes of 6T) even after the formation of the herringbone packing (the herringbone structure partially appeared at 2 ps and completed at 5 ps), and this clearly indicates that the in-plane orientation of the c-axis ⊥ groove represents a local energy minimum. Such relationship between the in-plane orientation and energy will be discussed again in the section of the MD simulations of pentacene.

When the angle of initial arrangement is 0 or 10°, the final in-plane orientation was the c-axis || groove. When the initial angle was 60, 70, 80, or 90°, the final in-plane orientation was the c-axis ⊥ groove. The range of the initially arranged angle to achieve the c-axis ⊥ groove is wider in the case using periodic boundary conditions than in that not using periodic boundary conditions. In the case where periodic boundary conditions are used, some force is given along the groove (Y-direction) and it probably causes the difference in the simulation results.

Anyway, regardless of the application of periodic boundary conditions, the tendency was almost the same; three angles, 0, ∼45, and 90° (the angle that the c-axis of 6T makes with the groove wall), are stable in both cases of
hydrophilic and hydrophobic surface conditions. Figure 7 shows the histogram of the number of crystal grains of 6T against the azimuthal (in-plane) angle experimentally observed using hydrophilic substrates (only UV/ozone treatment)\(^9\) and using hydrophobic substrates (HMDS-treated)\(^10\) reported in our previous papers. These histograms show, in both substrates, that three kinds of components, 0, \(\sim 45\), and 90°, exist, although the volume ratios of the three components are different in the hydrophilic and hydrophobic substrates. This means that the results of the simulations are right in a sense, that is, these three components are stable against the groove wall.

Further investigation is needed to completely elucidate the mechanism of the in-plane orientational change observed in the experiments. One possibility is that we need to further optimize the parameters in the force field (interaction between atoms and molecules) to reproduce the experimental results more accurately. As I explained in the section of preliminary simulations using water molecules, the surfaces of two kinds of substrates have different degrees of polarity and they must give, more or less, different effects on the interaction between the groove wall and the 6T molecules. Another possibility is that the deposition processes of molecules, that is, adsorption/desorption, diffusion, aggregation, nucleation, etc., affect the initial arrangement of the molecules when nucleation starts and they determine the final crystallographic orientation (0, \(\sim 45\), or 90°). To check on the latter possibility, MD simulations of deposition processes were carried out, and their results are described in the following sections.

3.3 Simulations of the deposition processes of 6T
To investigate the effect of deposition processes on the final in-plane orientation, MD simulations of deposition processes...
were performed, first using 6T molecules. The molecules were produced one by one at the upper part of the groove (X- and Y-coordinates where the molecules produced were random) with some applied velocity (with kinetic energy corresponding to 380 K) toward the bottom of the groove. Figure 8 shows the results of deposition on OH-terminated and HMDS-treated grooved substrates. In these simulations, each molecule has intramolecular degree of freedom (not rigid model) to reproduce the deposition process under near-natural conditions. In both simulations, 6T molecules flexibly bent and were intertwined with each other. Consequently, 6T molecules did not form any nuclei, which seemed to grow into crystals.

3.4 Simulations of the deposition processes of pentacene

As described in the last section, it was found that 6T is not appropriate for the MD simulations of the deposition and crystallization processes because 6T molecules are sufficiently soft to flexibly bend. Therefore, we changed the kind of molecule for the simulations into pentacene. Compared with 6T, pentacene has a rigid molecular backbone and does not bend so easily. In fact, it was found that pentacene molecules form herringbone packing spontaneously during the simulations of deposition processes.

Figure 9 shows the simulated deposition process of 400 molecules of pentacene using the “Y3” substrate with the –OSi(CH₃)₃ functional group on the surface under periodic boundary conditions (see the online supplementary data at http://stacks.iop.org/JJAP/57/03EG04/mmedia). At the initial stage of deposition, pentacene molecules basically lay down on the surface (bottom of the groove). The lying form is more stable than the standing form when molecules are isolated because of the interaction between atoms of the molecules.
Fig. 10. (Color online) Result of the MD simulation after the deposition of 400 pentacene molecules using the OH-terminated “Y3” substrate. One cross section showing the herringbone packing of standing pentacene molecules is also shown.

and the substrate. At around 150 ps, a large cluster consisting of lying pentacene molecules started to grow in the upper direction. Also at 150 ps, some standing molecules appeared (shown with a circle in Fig. 9). These standing molecules also formed a herringbone packing as shown in the figure, and the a-axis (the direction of the arrows of herringbone packing) was parallel to the direction of the groove wall. Figure 10 shows the simulation result of the deposition of 400 molecules of pentacene on the OH-terminated surface. Also, in this case, the a-axis of the pentacene cluster that appeared in the simulation was parallel to the groove wall. These simulation results suggest that pentacene tends to show graphoepitaxy, i.e., the a-axis || groove wall (b-axis ⊥ groove wall) regardless of surface conditions.

In the previous experimental works of the graphoepitaxy of pentacene, in-plane orientation, a-axis || grooves (b-axis ⊥ grooves), was reported, and this is consistent with the results of the MD simulations described above. One problem is that in the study of the orientational growth of pentacene using atomic steps formed on Si(111) substrates with a low miscut angle, (110) planes were parallel to the atomic steps. However, this different result can be explained on the basis of the truncation energy calculated using molecular mechanics with the MM3 force field by Shimada et al. In their study of the oriented growth of pentacene on step-bunched Bi- terminated Si(111) surfaces, the energy increase induced by truncation plotted versus the angle from the a-axis had “two” minima at 0° (a-axis || step edge direction) and 53°. The result using the atomic steps [(110) planes are parallel to the atomic steps] in Ref. 27 can be attributed to the second minimum (53°) of the truncation energy. It is considered that the in-plane orientation of 0° (a-axis || steps) is predominant when using grooves fabricated by lithography.

It can be said that the MD simulations of deposition processes performed in this study showed two important aspects of the thin film growth of organic semiconductors. One is that the in-plane orientation of graphoepitaxy can be reproduced by MD simulations. The other is that we can reproduce the formation of thin films comprising “standing” molecules. The standing structure of molecules on inert substrates such as SiO2 is a general tendency and this tendency is explained using a kinetic model based on the adsorption and reevaporation of molecules as well as thermodynamics. However, it is difficult to reproduce this structural feature by MD simulation. In fact, the author tested many simulations, but the standing structure has not been achieved using “flat” substrates. It is considered that nucleation is a stochastic process and it is too difficult to achieve in the limited time of MD simulations. The limited number of molecules in MD simulations, as well as the limited time, is probably another cause that makes the simulations of nucleation difficult. On the other hand, crystalline aggregates comprising standing molecules partially form during simulations when the “grooved” substrates are used. It suggests that the wall of the groove assists the formation of the standing component during film formation. This aspect is a bit different from our common view regarding nucleation and growth processes during thin film formation. However, there are many kinds of defects on the surface even on the flat substrates and there is some possibility that such defects assist the formation of crystalline grains consisting of “standing” molecules just like on the grooved substrates.

4. Conclusions

In this study, MD simulations have been applied to the study of organic graphoepitaxy for the first time to clarify the mechanism of organic graphoepitaxy at the molecular level. In the simulations using 6T molecules, three stable azimuthal angles, 0, ~45, and 90° (the angle that the c-axis of 6T makes with the groove wall) existed. This is well consistent with the previous experimental data. However, MD simulations could not explain the difference in the volume ratio of those three components (0, ~45, and 90°) observed in the experiments, that is, the component c-axis || grooves (b-axis || grooves) were predominant on the hydrophilic surface whereas the component c-axis || grooves (b-axis ⊥ grooves) were predominant on the hydrophobic surface. There are two possible causes of this discrepancy between the results of MD simulations and experiments. One is that the optimization of the force fields (parameters of interaction potentials) has not yet been achieved to reproduce the experimental results completely. The other cause is that the in-plane orientation of graphoepitaxy is determined depending on all the processes of film growth including deposition processes. To check on the latter possibility, MD simulations of the deposition processes were carried out. Although MD simulations of 6T molecules did not work well because of the softness of the 6T molecules, MD simulations of pentacene could reproduce the actual graphoepitaxy partially.

Throughout this study, understanding of the mechanism of organic graphoepitaxy at the molecular level has been deepened. In particular, the factors that determine the in-plane orientation of the thin films have been clarified to some extent. The author believes that these efforts to understand the mechanisms will improve the quality of graphoepitaxial films and lead graphoepitaxy to practical applications to organic devices.
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