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PSEUDO-COMMENSURATE EPITAXY OF A NON-PLANAR MOLECULE OF ISOINDOLINE DERIVATIVE AT LIQUID-SOLID INTERFACE

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To understand epitaxial growth of organic molecules from a phenyloctane solution, mono-molecular layers of a non-planar isoindoline derivative formed on the graphite (0001) surface were investigated by STM. The observed images showed that the layer is composed of many small single-crystalline 2D domains, where the lattice orientation was analyzed with respect to the graphite surface lattice. As a result, the molecules adsorbed with its isoindoline frame to be parallel to the HOPG surface and the epitaxial orientations were slightly fluctuated around commensurate orientation from domain to domain. This is named pseudo-commensurate epitaxy, which is resulted from a size effect; that is, due to broadening of Laue functions appearing in an expression of lattice-lattice interaction energy at interface of deposited layer and substrate surface.

Keywords: epitaxy; pseudo-commensurate; STM; liquid-solid interface

INTRODUCTION

Epitaxial growth of thin films, in particular by vacuum deposition or molecular beam method, is one of the fundamental technique to control structures of the two-dimensional (2D) crystal in fabricating modern semiconductor devices. There have been many studies on the growth of inorganic crystalline layers on inorganic single crystals. In such cases, the orientation of layer is often explained by the lattice misfit between deposited films and substrates [1,2]. Recently, many organic molecular crystals hold an attraction for their optical, electronic and magnetic

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functionalities so that studies on epitaxy of organic molecules have been progressed mainly by scanning probe microscopy (SPM); for example, perylene derivatives on the gold (100) surface [3] and on graphite [4]. In these cases, the epitaxy was considered to be originated from lattice-lattice interaction between a molecular layer and a substrate surface. For vacuum-deposited mono-molecular layers, three modes of interfacial lattice correlation were observed as commensurate [5,6], point-on-line [4,7–9] and incommensurate epitaxy [10]. The lattice relation between an organic layer and a substrate surface can be described with lattice vectors of a molecular layer and a substrate surface as below.

$$\boldsymbol{a}_{\mathrm{m}} = \mathrm{s}\boldsymbol{a}_{\mathrm{g}} + \mathrm{t}\boldsymbol{b}_{\mathrm{g}}, \quad \boldsymbol{b}_{\mathrm{m}} = \mathrm{u}\boldsymbol{a}_{\mathrm{g}} + \mathrm{v}\boldsymbol{b}_{\mathrm{g}}, \tag{1}$$

where $\boldsymbol{a}_{\mathrm{m}}$ and $\boldsymbol{b}_{\mathrm{m}}$ are the lattice vectors of 2D molecular layer, and $\boldsymbol{a}_{\mathrm{g}}$ and $\boldsymbol{b}_{\mathrm{g}}$ are those of substrate surface. The epitaxy coefficients of s, t, u and v are parameters relating both lattices. In these equations, the commensurate epitaxy is characterized as that all of s, t, u and v are integers and the point-on-line epitaxy as that a pair of (s,u) or (t,v) are integers, whereas the incommensurate epitaxy can be defined as the case that the coefficients of s, t, u and v are non-integral values. The interfacial energy in these epitaxy modes has been discussed by Hoshino *et al.* [4,7,8] and by A. C. Hiller *et al.* [11]; highest stability of commensurate, secondary stability of point-on-line and no energy gain of incommensurate epitaxy. However, since molecules interact each other in the 2D lattice, this intermolecular interaction energy should be taken into account in addition to the interfacial lattice-lattice interaction. The epitaxial modes, therefore, depend on the balance between the lattice-lattice interaction and the intermolecular interaction in 2D layer [10].

The epitaxial growth of organic molecules has been mainly examined on the dry processes in vacuum so far. However, it is also important to know epitaxy by the wet process like epitaxy at solid-liquid interfaces, because organic molecules are occasionally deteriorated during heating in the dry process. Recently, 2D crystals of isoindoline derivatives with planar molecular shapes were reported on their epitaxy at liquid-solid interfaces [12], in which the planar molecules were concluded to form 2D mono-molecular layers and they exhibited so-called pseudo-commensurate epitaxy accompaning orientation fluctuation of 2D domains. The fluctuations of mono-molecular domains are well known at liquid-solid interfaces [13] which becomes clearer by observing moiré pattern [14]. The pseudo-commensurate epitaxy was considered to be typical in such orientation fluctuation with small 2D domains at liquid-solid interfaces.

In the present study, an isoindoline derivative of 1,1-diethoxy-3-imino-4,5,6,7-tetrachloroisoindoline (DEITCI) was examined by liquid-STM method on its 2D layer formation at liquid-solid interface. Due to the

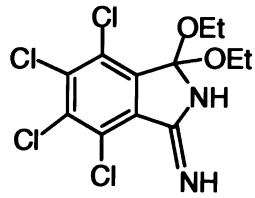

FIGURE 1 Chemical structure of DEITCI.

non-planar shape of the molecule, it is interesting to study the crystal growth at the liquid-solid interface, which will be discussed from the viewpoint of stabilization of interfacial energy.

EXPERIMENTAL

The (0001)-plane of highly oriented pyrolytic graphite, HOPG (Advanced Ceramics Corp., STM grade), was used as a substrate after being carefully cleaved in air. Excess amount of an isoindoline derivative, DEITCI (Fig. 1), was dissolved into phenyloctane. After a drop of the saturated solution was put on the cleaved graphite surface, constant tunneling current observation was carried out with a scanning tunneling microscope (STM), Digital Instruments Nanoscope IIIa with a low current STM head. Soon after an STM observation of DEITCI layers, an image of HOPG surface at the same area was also measured to determine the orientation relationship between the mono-molecular layer and HOPG. In order to examine the molecular adsorption on HOPG, the adsorption energy was calculated by the MM method for a single molecule on HOPG surface, where the molecular shape was estimated from PM3 method calculation of UniChem software package.

RESULTS AND DISCUSSION

Mono-Molecular Layer

From the phenyloctane solution used, the DEITCI molecules were very quickly adsorbed on the HOPG (0001)-surface to form mono-molecular layer. A typical STM image of DEITCI layer at the liquid-solid interface is shown in Figure 2, where small mono-molecular domains with some tens nm in diameter are formed as indicated by the white lines. The domain boundary can easily be distinguished through variations in moiré contrast. The moiré patterns indicate that the interface is incommensurate because

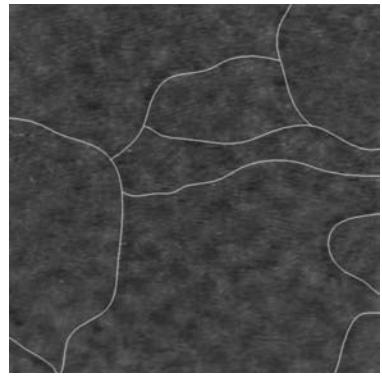

FIGURE 2 An STM image of DEITCI mono-molecular layer adsorbed on HOPG from phenyloctane solution. The bias voltage V_b was +399 mV and the tunneling current I_t was 30 pA. The scan size was 70 nm × 70 nm.

the patterns are spotty not linear [10]. Such domain structures are frequently observed at liquid-solid interfaces with small sizes depending on the molecules. Because a positive bias voltage was applied, the unoccupied molecular orbital corresponds probably to the STM image contrast. The moiré patterns were observed in each domains, but the patterns are not the same with each other. This suggests that there are several orientations of DEITCI relative to HOPG.

From high resolution imaging of STM, we examined 2D unit cell dimensions and the orientation with respect to the HOPG surface. A high resolution image of the DEITCI mono-molecular layer is shown in Figure 3 which was obtained under the condition of $V_b = +307$ mV and $I_t = 30$ pA. The 2D unit cell shown in the figure should contain one molecule from its size; $a \approx 0.92$ nm, $b \approx 0.88$ nm and $\gamma \approx 59°$. The γ is the angle between the a- and b-axes. The individual molecular image is composed of four strong contrasts as in other planar isoindoline derivatives already reported [12], in which the four contrasts correspond nearly to the lowest unoccupied molecular orbital (LUMO) of the molecules when the molecular planes are parallel the HOPG surface. Accordingly, the DEITCI molecules may be adsorbed their isoindoline molecular frame to be nearly parallel to the HOPG surface, even though the molecule is not planar.

In order to ascertain the adsorption feature of the molecule, the MM calculation was performed as shown in Figure 4. where three typically expected adsorptions on HOPG were estimated in their interaction energies, E_a. In the calculation the molecular shape was determined from PM3 calculation. The most stable energy was obtained in the case (a) of

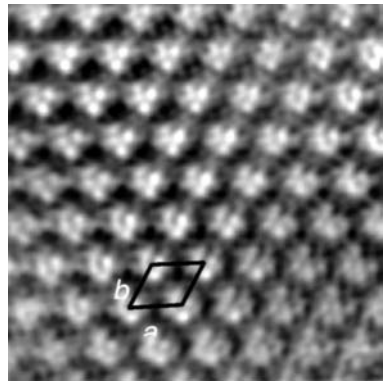

FIGURE 3 A high resolution STM image of DEITCI molecules adsorbed on HOPG. The unit cell contains a single molecule. The scan parameters are: 6.8 nm × 6.8 nm, $V_b = +307$ mV and $I_t = 30$ pA.

$E_a = -11.7$ kcal/mol, in which the molecule adsorbed keeping its isoindoline frame to be parallel to the HOPG surface as expected from the STM image contrast.

From careful determination of the epitaxy coefficients in Eq. (1) with respect to the HOPG, each domain has the different epitaxial coefficients at liquid-solid interface of DEITCI. As summarized in Table 1, the coefficients are fluctuated around integral values. This is a typical feature in the pseudo-commensurate epitaxy [12]; the unit cell of the 2D layer is likely to coincide commensurately on HOPG surface lattice but not realized due to intermolecular interaction in the 2D layer. The molecular packing in the averaged lattice is illustrated in Figure 5 where the molecules pack very closely; $\boldsymbol{a}_m = 4.1\boldsymbol{a}_g - 1.1\boldsymbol{b}_g$ and $\boldsymbol{b}_m = 1.1\boldsymbol{a}_g + 2.9\boldsymbol{b}_g$, and the calculated lattice parameters are $a = 0.92$ nm, $b = 0.88$ nm and $\gamma = 59°$. The epitaxy coefficients suggest that the mono-molecular layer is incommensurate but roughly commensurate, which indicates that each domain fluctuates

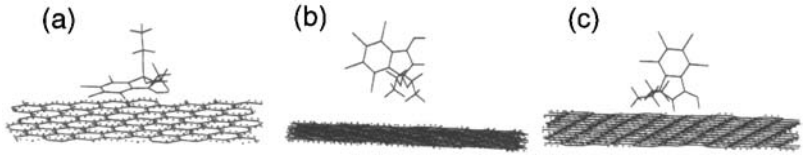

FIGURE 4 MM simulation of adsorption energy on HOPG in three cases; (a) the most stable orientation with $E_a = -11.7$ kcal/mol, (b) $E_a = -0.4$ kcal/mol and (c) $E_a = -4.0$ kcal/mol.

TABLE 1 Epitaxial Coefficients of DEITCI in Small Domains

	s	t	u	v
Domain-1	4.1	−0.9	1.1	3.1
-2	4.2	−1.1	1.3	2.6
-3	4.1	−1.1	0.8	2.9
-4	4.1	−1.0	0.9	3.2
-5	4.1	−1.0	1.1	3.2
-6	4.3	−1.2	1.3	2.8
Average	4.1	−1.1	1.1	2.9

around commensurate orientation; that is, basically optimal orientation is realized from the view of lattice-lattice interaction as discussed later.

Pseudo-Commensurate Epitaxy

The mono-molecular layers of DEITCI formed at the liquid-solid interface exhibit pseudo-commensurate. To understand such pseudo-commensurate epitaxy, the stabilization energy of the lattice-lattice interaction is considered. When the surface potential $V(\mathbf{r})$ of substrate is expanded in the Fourier series, to the first approximation,

$$V(\mathbf{r}) = -\sum_i A_i \cos(2\pi \mathbf{g}_i \cdot \mathbf{r}), \tag{2}$$

where $\boldsymbol{g}_i$ is a basic reciprocal lattice vector of a substrate surface and $\boldsymbol{r}$ is a positional vector in real space. The interaction energy between the molecular layer and the substrate can be represented,

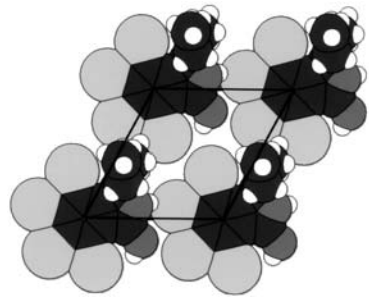

FIGURE 5 Packing model of DEITCI on HOPG.

$$E = \sum_{m=-M}^{M} \sum_{n=-N}^{N} V(m\mathbf{a}_m + n\mathbf{b}_m)$$
$$= -(2M+1)(2N+1)A_0 \qquad (3)$$
$$- \sum_i A_i \cdot \frac{\sin(2M+1)\pi \mathbf{g}_i \cdot \mathbf{a}_m}{\sin \pi \mathbf{g}_i \cdot \mathbf{a}_m} \cdot \frac{\sin(2N+1)\pi \mathbf{g}_i \cdot \mathbf{b}_m}{\sin \pi \mathbf{g}_i \cdot \mathbf{b}_m}.$$

M and N are the numbers of unit cells in the 2D molecular layer along two independent directions from the center of a domain. This equation can be rewritten as the following with $s = \boldsymbol{g}_1 \cdot \boldsymbol{a}_m$, $t = \boldsymbol{g}_2 \cdot \boldsymbol{a}_m$, $u = \boldsymbol{g}_1 \cdot \boldsymbol{b}_m$ and $v = \boldsymbol{g}_2 \cdot \boldsymbol{b}_m$ from Eq. (1) in the case of HOPG surface.

$$E = -(2M+1)(2N+1)A_0$$
$$- A_1 \cdot \frac{\sin(2M+1)\pi s}{\sin \pi s} \cdot \frac{\sin(2N+1)\pi u}{\sin \pi u}$$
$$- A_2 \cdot \frac{\sin(2M+1)\pi t}{\sin \pi t} \cdot \frac{\sin(2N+1)\pi v}{\sin \pi v} \qquad (4)$$
$$- A_3 \cdot \frac{\sin(2M+1)\pi(-s-t)}{\sin \pi(-s-t)} \cdot \frac{\sin(2N+1)\pi(-u-v)}{\sin \pi(-u-v)}$$

In the case of a vacuum deposited layer, M and N are large because the domain size is usually very large. Consequently, the Laue functions in Eq. (4) have sharp peaks around integer values of coefficients (Fig. 6(a)). When all s, t, u and v are integers, the interaction energy displays the large minimum, which means that the commensurate epitaxy is the most stable interface as expected. When a pair of (s,u) or (t,v) are integers, one of A_1 and A_2 terms in the Eq. (4) exhibits a minimum, so that the secondary stable point-on-line epitaxy is realized. Although the point-on-line epitaxy

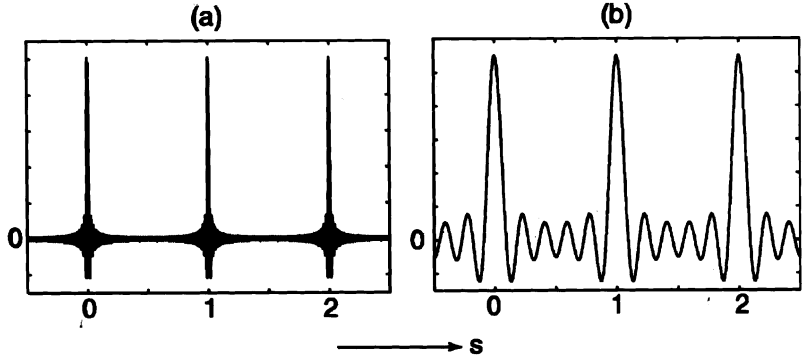

FIGURE 6 Laue functions at M = 50 (a) and M = 5 (b). Broadening of the function is clear in the case of M = 5 (2M+1 = 11; about 11 nm in diameter of domain).

is secondary stable, the deformation of molecular unit cell from a stable unit cell, if any, is smaller than that in commensurate epitaxy.

The above discussion is, however, valid in the case of large N and M. When the M and N become relatively smaller, for example, in the case of small domains formed at liquid-solid interface as the present study, the Laue function turns broader around integer values of coefficients (Fig. 5(b)). The s, t, u and v can, therefore, fluctuate around the integers, so that various values of s, t, u and v can contribute to the lattice-lattice interaction though the stabilization energy, if the coefficients are not so different from integers. Thus, the pseudo-commensurate can be observed when the domain size is small and the epitaxy coefficients s, t, u and v are values near integers.

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