In-situ measurement of molecular orientation of the pentacene ultrathin films grown on SiO$_2$ substrates

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Abstract

Molecular orientations of pentacene ultrathin films grown on SiO_2 substrates were studied without the influence of the atmosphere by vacuum atomic force microscopy (V-AFM) and near edge X-ray absorption fine structure (NEXAFS). The experimental processes from deposition of pentacene to characterization of films were performed under vacuum condition without exposure to the atmosphere. V-AFM and NEXAFS measurements showed that pentacene molecules tend to grow on SiO_2 surface with their molecular long axes perpendicular to the substrate surfaces (Standing-mode) irrespective of preparation procedure of SiO_2 substrate.

Keywords

Pentacene; In-situ characterization; Atomic force microscopy; Near edge extended X-ray absorption fine structure (NEXAFS); Surface structure, morphology, roughness, and topography; Silicon oxides; Aromatics; Thin film structures

1. Introduction

Pentacene has been receiving an increasing amount of attention in recent years. The interest can be attributed to its promising potential for flexible and low-cost electronic devices, especially for organic field effect transistors (OFET). Among all channel materials for organic thin film transistors studied so far, pentacene shows the highest carrier mobility [1]. Thereby, there have been numerous reports investigating electrical and morphological properties of pentacene thin films grown on gate insulator materials, mostly SiO_2 substrates [1,2]. Recently, our group revealed that an accumulation layer in the bottom-contact FET structure is limited within the first several pentacene layers from the pentacene-SiO_2 interface [3]. This result teaches us that the molecular orientation at the initial stage of growth strongly affects the FET performance. Thus, its characterization would provide useful information on improvement of FET performance, which is still poor as compared with inorganic semiconductors. In order to clarify the orientation of the molecules in the first few layers, a surface sensitive tool is necessary. In the commonly used bottom-contact FET structure, however, electron beam could not be used as the probe because the insulating nature of substrate causes a charge build-up problem. Thereby, conventionally used surface sensitive techniques such as electron diffraction, scanning tunneling microscope, etc. don't work well for that purpose.

Recently, some studies, in which electron was not used as the probe, have been reported on the first monolayer of the pentacene film grown on a SiO_2 substrate [4-6]. Using grazing incidence X-ray diffraction (GIXD) and atomic force microscopy (AFM), they showed that the pentacene molecules grew with their molecular long axes perpendicular to the surface. Diffraction measurement such as GIXD, however, can probe only the molecules in order, so that the degree of ordering of the whole film can not be known only by the diffraction method. AFM, on the other hand, is a powerful tool to obtain the whole structure of the ultrathin film

from a morphological viewpoint, although the molecular orientation could not be usually determined.

Another problem relates with the effect of atmosphere. In most of the past works, the pentacene films were characterized after putting them out from the vacuum chamber. Organic materials, especially in an ultrathin film state, are susceptible to H_2O, O_2, and other environmental elements present in the atmosphere. No one could exclude the possibility that the structure of a pentacene film would have changed by exposure to air, because there is no strong interaction such as chemical bond between a pentacene molecule and an inert SiO_2 substrate of amorphous structure. Actually, many studies have been reported about the influence of these gases on OFET properties [7-9], suggesting the occurrence of any structural change. Qiu et al. have reported that the pentacene FET was significantly degraded by H_2O and the morphology of the film changed after the transistor had been kept in the atmosphere [10]. Accordingly, with respect to the molecular orientation of pentacene ultrathin films on SiO_2, it has not been recognized yet whether the observed structure is truly as-grown one or changed by the influence of the atmosphere. Therefore, the elucidation of the molecular orientation of a pentacene ultrathin film without the influence of the atmosphere is important not only for the fundamental research but also for the application.

In the present study, we present the experimental results on the molecular orientation in a monolayer pentacene film, which was characterized without exposure to air. We constructed a vacuum AFM (V-AFM) system, in which all procedures, from deposition on SiO_2 substrates to the AFM measurement, can be done under vacuum condition. Hence, the V-AFM can measure the film morphology at the initial stage of growth without the influence of the atmosphere. In addition, we connected the deposition chamber directly to the synchrotron radiation (SR) facility and measured the near edge X-ray absorption fine structure

(NEXAFS) of an as-grown pentacene film, probing the molecular orientation of all the pentacene molecules in the film.

2. Experimental Details

The experiments were performed in a custom-designed UHV system with a base pressure of 10^{-7} Pa. In order to confirm the influence of charge build-up or the preparing condition of the substrates, three types of SiO_2 substrates were used; prepared by oxidation of a Si wafer with Shiraki method [11], Shiraki method and following anneal in dry O_2, and a commercially obtained Si wafer with thermally oxidized amorphous SiO_2 layer. The thickness of SiO_2 layer of these substrates is 1.5 nm, 10 nm, and 300 nm. All the substrates were rinsed in acetone and ultra pure water before loading into vacuum chamber without succeeding annealing in the growth chamber. Pentacene molecules were evaporated from a Knudsen-cell onto the substrates maintained at 298 K. Growth rate and the mean film thickness were monitored using a quartz crystal oscillator, and the rate was on the order of 0.1 nm/min. Grown films were transferred to the directly connected AFM chamber without exposure to the atmosphere. V-AFM images were recorded in the tapping mode with JEOL JSPM-5200V. C K-edge NEXAFS measurement was carried out at the BL-7A of the Photon Factory in the Institute of Materials Structure Science [12]. The sample grown in the deposition chamber was transferred to the manipulator at the BL-7A station without breaking vacuum. C K-edge NEXAFS spectra were then obtained in-situ by the partial electron yield method with a micro-channel plate. The degree of the beam polarization was estimated to be 0.92.

3. Results and Discussion

Figure 1 shows the V-AFM image and its height profile of a pentacene film deposited on a commercially obtained amorphous SiO_2 substrate. The mean film thickness was about 0.2 nm. Pentacene films deposited on the SiO_2 substrates prepared by Shiraki-method showed similar

V-AFM images. The height of pentacene islands is uniquely determined to be 1.6 nm in close agreement with the molecular long axis of a pentacene molecule (1.65 nm). Therefore, it is not unreasonable to consider that pentacene molecules were grown with Standing-mode (cf. Fig. 2). This result is consistent with the previous result measured by GIXD [4]. There were several reports investigating the monolayer pentacene film by AFM in the atmosphere. They also indicated the Standing-mode similar as shown in Fig. 2. The significance of the present result is that we have clarified the morphology of the whole pentacene film excluding the influence of the atmosphere completely.

In order to probe the molecular orientation from a viewpoint of the direction of an electron orbital, we measured the NEXAFS of pentacene films. Figure 3 shows the C K-edge NEXAFS spectra of pentacene films deposited on the SiO_2 substrate prepared by Shiraki-method. Pentacene films deposited on SiO_2 substrates prepared by other methods showed similar NEXAFS spectra. Intense peaks observed around 283-288 eV can be assigned to the transitions from C 1s to π^* orbital (perpendicular to the pentacene molecular plane; π^*-peak) [13,14]. Splitting of the π^*-peak could be attributed to the transitions from C 1s to LUMO and LUMO+1, while the fine structures in each peaks could be attributed to the chemical shifts of the excited carbon atoms within pentacene molecule [14]. Although the peaks observed above 290 eV would be attributed to the transitions from C 1s to σ^* orbital, it is difficult to distinguish from other elements such as multi-electron resonance. Accordingly, we concentrate on π^*-peak to determine the molecular orientation. Clear polarization dependence was observed in all films with different thickness, that is, π^*-peak was most enhanced at normal X-ray incidence (90°), while almost no peak was observed at grazing incidence (15°), similar to the former report [15]. The results in Fig. 3 indicate that pentacene molecules grew with their molecular plane perpendicular to the substrate surfaces. Detailed curve fitting analysis of π^*-peaks revealed that the inclination angle of π^* orbital to the

substrates was almost 0° in the sub-monolayer film, and less than 10° ± 5° even in the film with 10 nm thick (shown as 'multi layer' in Fig. 3), indicating some randomly oriented molecules were grown in the multi layer film. Two types of structure can be expected from these results of NEXAFS. One is "Standing-mode", in which the molecular long axis of pentacene directs perpendicular to the substrate surface, and the other is "Buddha-lying-mode", in which the molecular long axis directs parallel to the surface. Note that molecular plane of pentacene is perpendicular to the surface in the both structures (cf. Fig. 2). Combined with the result of V-AFM, it turns out that pentacene should grow with the former structure because islands or steps with about 0.7 nm height corresponding to the short edge of the molecular plane (0.73 nm) would have been observed in the V-AFM image if pentacene grows with latter structure. Accordingly, we can reveal that almost all of the pentacene molecules grow in Standing-mode from the initial stage of the growth. The results of V-AFM and NEXAFS, both methods probe the whole film and its surface morphology of pentacene sub-monolayer films, revealed that pentacene grows in Standing-mode from the initial stage of the growth in vacuum condition irrespective of the type of SiO_2 substrates prepared by different procedures. Thus, our study elucidated that the pentacene islands with standing molecules were not formed by the effect of exposure to the atmosphere but by the nature of the pentacene on SiO_2.

Finally, we discuss the growth mechanism of pentacene molecules on the SiO_2 substrate. π-conjugated molecules such as pentacene or sexithienyl (6T) tend to grow in Lying-mode on relatively active surface such as metals [16-18]. There are some electronic interactions between the molecules and active surfaces. SiO_2 substrate, on the other hand, has a relatively inert surface, so that there would be little interaction between the molecules and the surface. Thereby, pentacene molecules tend to grow in the Standing-mode as well as the 6T molecules grown on the inert surface such as SiO_2 or KBr [19,20]. Another reason for the difference in

the growth mode would be attributed to the lattice incommensurability or roughness of the substrates. In fact, 6T molecules tend to grow in Standing-mode on poly-crystalline metal surfaces [21], while they grow in flat-lying-mode on single-crystalline metal surfaces [17,22], and copper phthalocyanine (CuPc) molecules also grow in Standing-mode on rough hydrogen-terminated Si(111) surface, while in lying-mode on the flat surface [23]. SiO_2 surfaces used in the present study have an amorphous structure with some roughness (root mean square (rms) values of these surfaces were about 0.2 nm), thus there is no commensurability and little interaction between pentacene molecules and the surface, resulting in the Standing-mode as well as the 6T or CuPc molecules.

The above mentioned discussion could explain the tendency of standing growth of pentacene molecules, while it could not explain the reason why the pentacene grows not in Buddha-lying-mode but in Standing-mode. In order to elucidate the mechanism, we have to consider the thermodynamic behavior of long-chain molecules such as pentacene. Kubono *et al.* simulated time-dependent changes in the number of standing and lying long-chain molecules during the film growth [24]. According to their simulation, standing molecules increase faster than lying molecules when the substrate temperature is high, and it shows the opposite tendency with decreasing substrate temperature. This behavior is explained as follows. The lying molecule on the surface has larger surface-area/volume ratio than the standing molecule, so that the velocity of re-evaporation of lying molecules from the surface should increase at high substrate temperature, resulting in the saturation of the number of lying molecules. As a consequence, the standing molecules come to have large majority with increase of the substrate temperature. In the case of fatty acids (C_{16} – C_{22}) on KCl or paraffin (C_{40}) on glass substrates, standing molecules become majority with increase of the substrate temperature [25,26]. It should be noted that, in any case, the tendencies of the temperature dependence of the molecular orientation are similar, irrespective of the chain length or the

8

type of substrate, and the critical temperature is about 270 - 300 K, which is close to the result of the simulation performed by Kubono *et al*. In the present study, the SiO_2 substrates were kept at 298 K during deposition, which would be comparatively high, so that the pentacene molecules grew in Standing-mode on the SiO_2 substrate. In addition, the Standing-mode growth of pentacene on the condition used in the present study, that is, higher substrate temperature and lower deposition rate, could also be explained by the classical nucleation model which considers the anisotropy of the surface energy [27].

4. Conclusion

Molecular orientations in the pentacene ultrathin films grown on SiO_2 substrates were studied by V-AFM and NEXAFS without exposing the specimen to the atmosphere. All results were consistent and revealed that pentacene grows with their molecular long axes perpendicular to the SiO_2 surface (Standing-mode) from the initial stage of the growth irrespective of the type of SiO_2 substrates prepared by different procedures. The growth mechanism could be explained by the interaction between the molecules and the substrates, and the thermodynamic behavior of growing molecules.

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Figure captions

Fig. 1

(a) V-AFM image of a pentacene film deposited on a commercially obtained SiO_2 substrate, and (b) its height profile of the area indicated by an arrow in the image. The mean film thickness was about 0.2 nm.

Fig. 2

Schematic illustrations of the possible configurations of pentacene molecules on a substrate with each π^* orbitals. The incident directions of X-ray with its electric vector are also shown.

Fig. 3

C K-edge NEXAFS spectra of pentacene films grown on SiO_2 prepared by Shiraki-method. Peaks observed around 283-288 eV correspond to the transition from C 1s to π^* orbital of pentacene.

Figure1
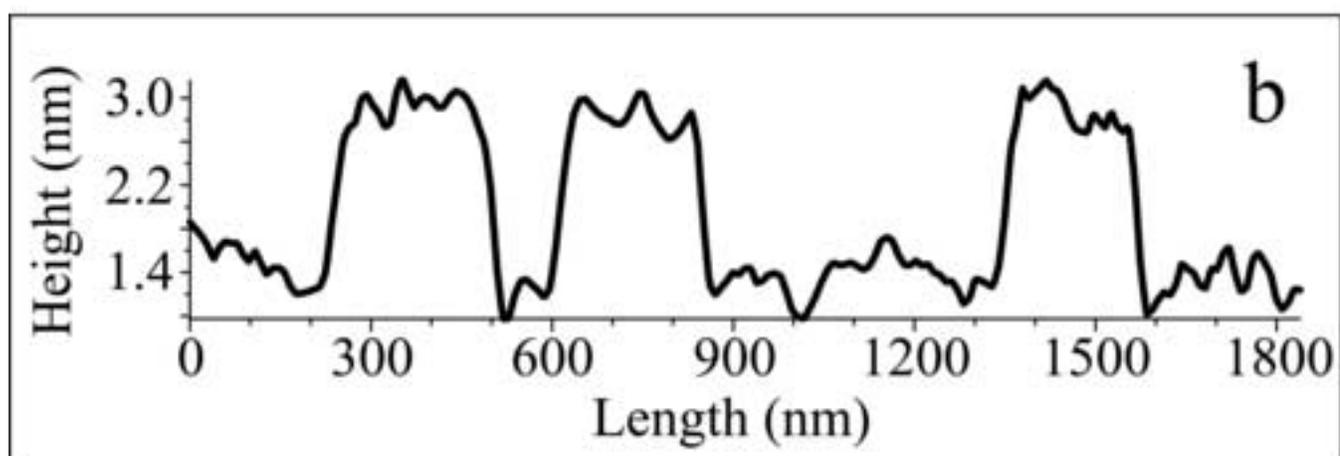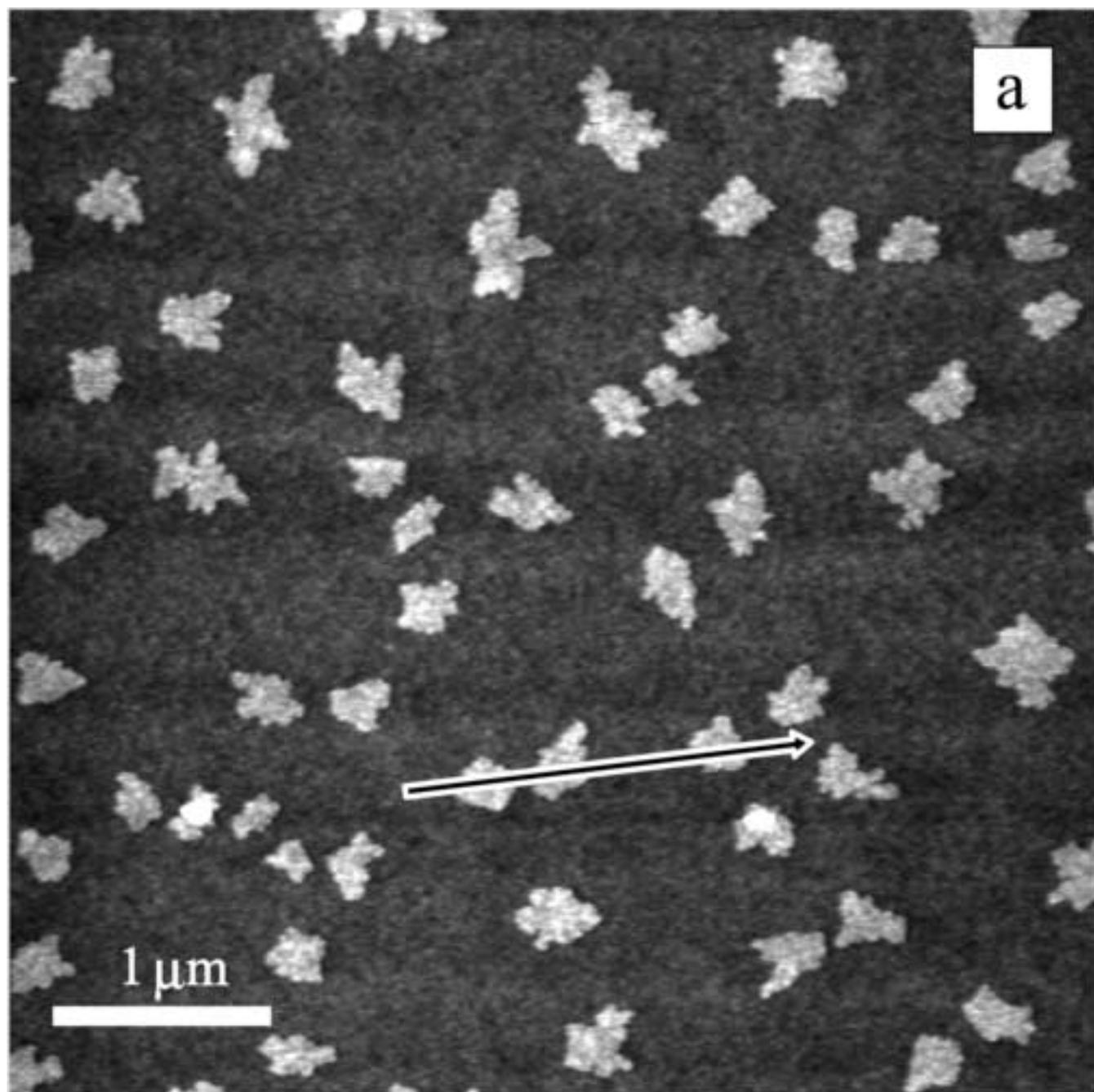**Click here to download high resolution image**
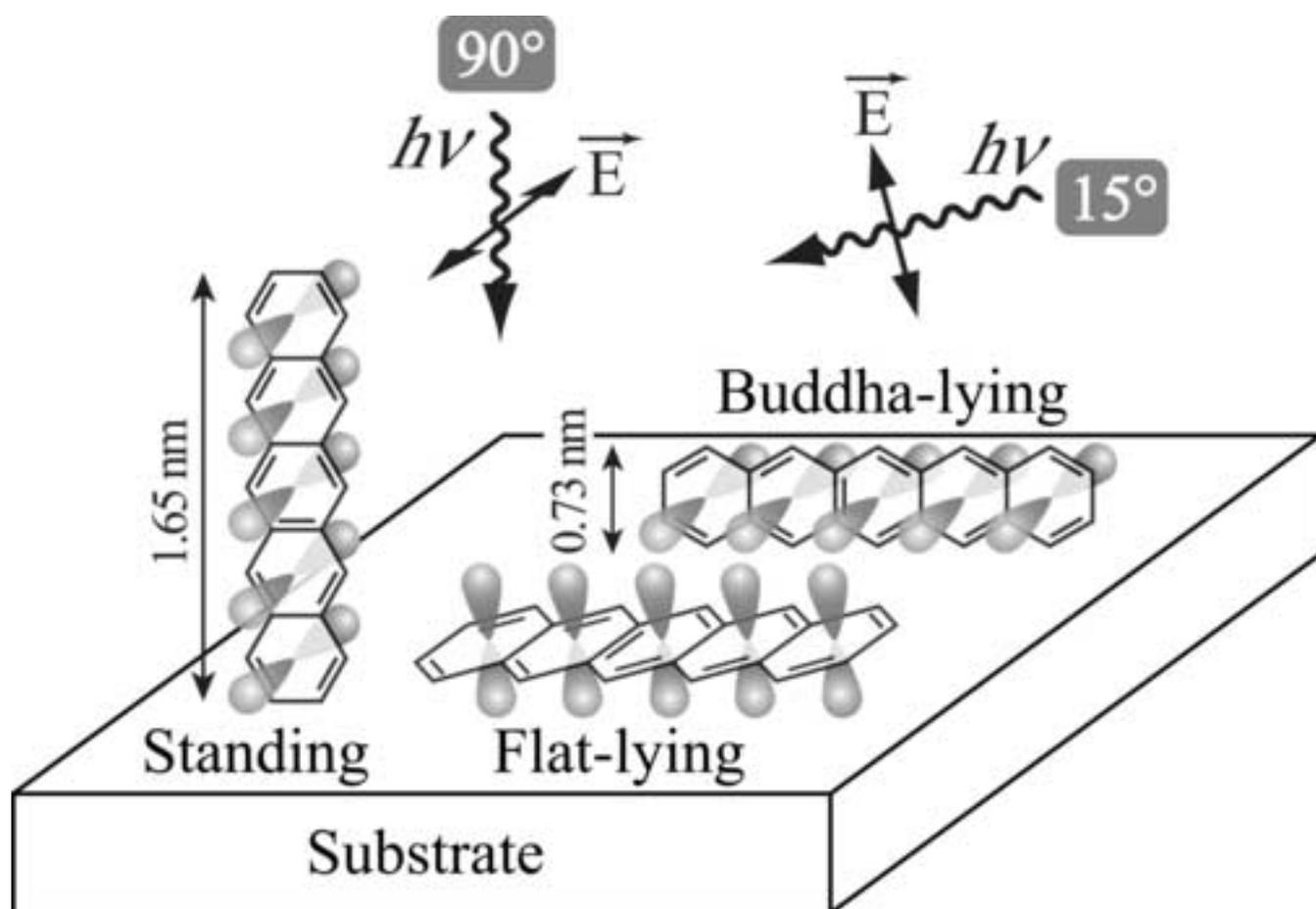
Figure2
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