

Molecular orientation of pentacene on polyimide film with rubbed surface of PMDA-ODA studied by NEXAFS

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Abstract

We have performed the near edge x-ray absorption fine structure measurements on pentacene thin films on polyimide films of PMDA-ODA with rubbed surface. Independent on the film thickness, pentacene molecules are aligned vertically. With increasing the film thickness, their tilt angle becomes slightly larger. A mechanism of pentacene molecular orientation on polyimide films is discussed.

1. Introduction

Pentacene ($C_{22}H_{14}$) has attracted much attention because of its possible application to organic electronic devices. A vertical alignment (*c*-axis alignment) of pentacene molecules is necessary for the transistor performance. This molecular alignment depends on the surface condition of the substrates. Hence determination of molecular orientation in organic films is very important. Near edge x-ray absorption fine structure (NEXAFS) is a promising tool for such a structural study. We have found by NEXAFS measurements that the pentacene molecules are aligned vertically on the polyimide film of 2,3,5-tricarboxycyclopentyl acetic dianhydride - diamino diphenyl methane (TCA-DDM) with a zig-zag shape [1] while they are aligned horizontally on the highly ordered pyrolytic graphite (HOPG) with benzene-like rings (π -electron) and a flat surface [2]. In this experiment, in order to see the effect of the π -electron interaction on the molecular alignment, pyromellitic dianhydride - oxydianiline (PMDA-ODA) film is chosen as a substrate since PMDA-ODA has the planer aromatic rings as shown in the inset of Fig. 1. Moreover, PMDA-ODA films rubbed by pile impression make the main chains of the polymer molecules aligned in the rubbing direction. So, we have performed the NEXAFS measurements on pentacene films on PMDA-ODA with rubbed surface to investigate the surface condition effect of the molecular orientation. We discuss a mechanism of pentacene molecular orientation on three kinds of the substrates of PMDA-PDA, TCA-DDM and HOPG.

2. Experimental

First, the polymers were dissolved in an organic solvent and spin-coated onto indium-tin-oxide-coated glass plates. After heating to 80 °C to evaporate the solvent, the polymers were baked at 230 °C for 20 min. The polyimide films were rubbed using a rayon-cloth rubbing machine at 400 rpm rotation speed, 30 mm/sec plate speed, and the 0.4 mm depth of the pile impression. Then, the pentacene films were deposited on the polyimide substrates at room temperature using a thermal evaporation system. The total film thickness was varied with the deposition time.

NEXAFS measurements were performed at the BL-8 of SR Center at Ritsumeikan University, equipped with a grazing incidence monochromator with a varied-line-spacing plane grating [3]. Carbon K-edge NEXAFS spectra of the samples were measured in partial electron yield by a micro-channel plate detector with retarding grids. The retarding voltage was set to -150 V. The incident angle of SR with respect to the surface normal was varied and the electric vector of SR was changed in either parallel or perpendicular to the rubbing direction.

3. Results and Discussion

Figure 1 shows C K-edge NEXAFS spectra of the samples for the parallel geometry. These peaks are attributed to the $C 1s \rightarrow \pi^*$ transitions. With depositing the pentacene, the intensities around 283.5 eV and 286 eV grow. The intensity of these peaks decreased with incident angle, indicating that the pentacene molecules are aligned vertically on the polyimide substrate.

In order to see the effect of the rubbed surface of PMDA-ODA, incident angle dependent NEXAFS spectra are compared for the parallel and the perpendicular geometries, as shown in Figs. 2-4. As for the very thin films of pentacene [Fig. 2(a)], the signals from pentacene around 283.5 eV decreases with incident angle for both the parallel and perpendicular geometries, though the signals are very weak. In order to compare the intensity changes with the incident angles in detail, the signals only from the pentacene between 282.7 eV and 283.8 eV are evaluated [Fig. 2(b)]. The angle dependent intensity ratios are not different each other, indicating that the molecular orientation of the pentacene is independent on the rubbed direction.

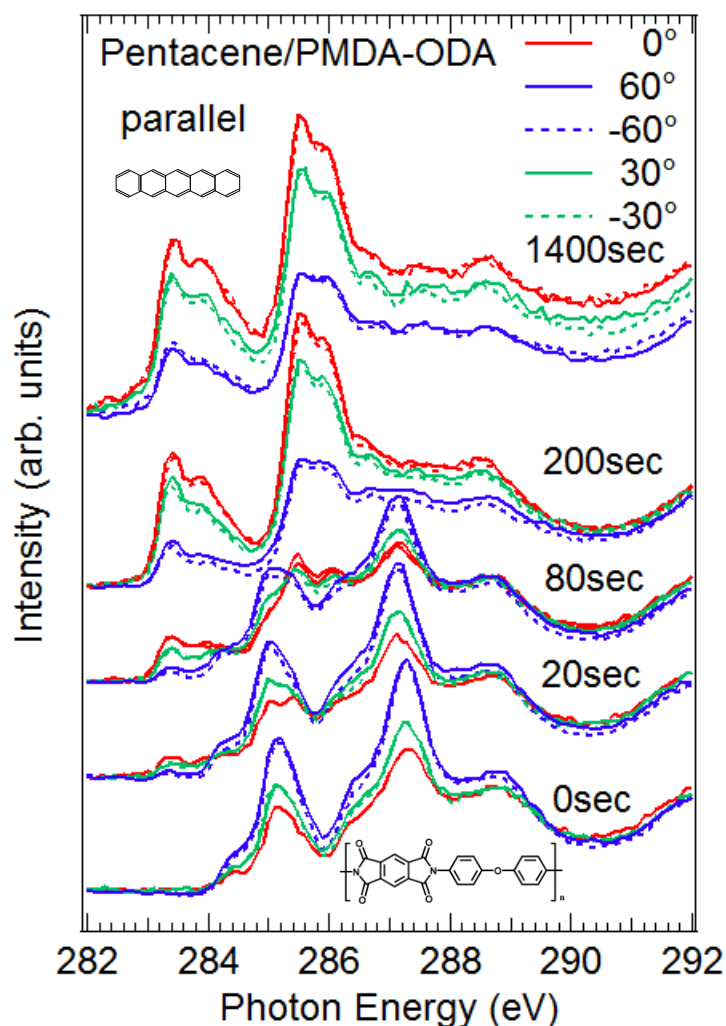


Fig. 1 Incident angle dependent NEXAFS spectra of the pentacene films on PMDA-ODA for the parallel geometry.

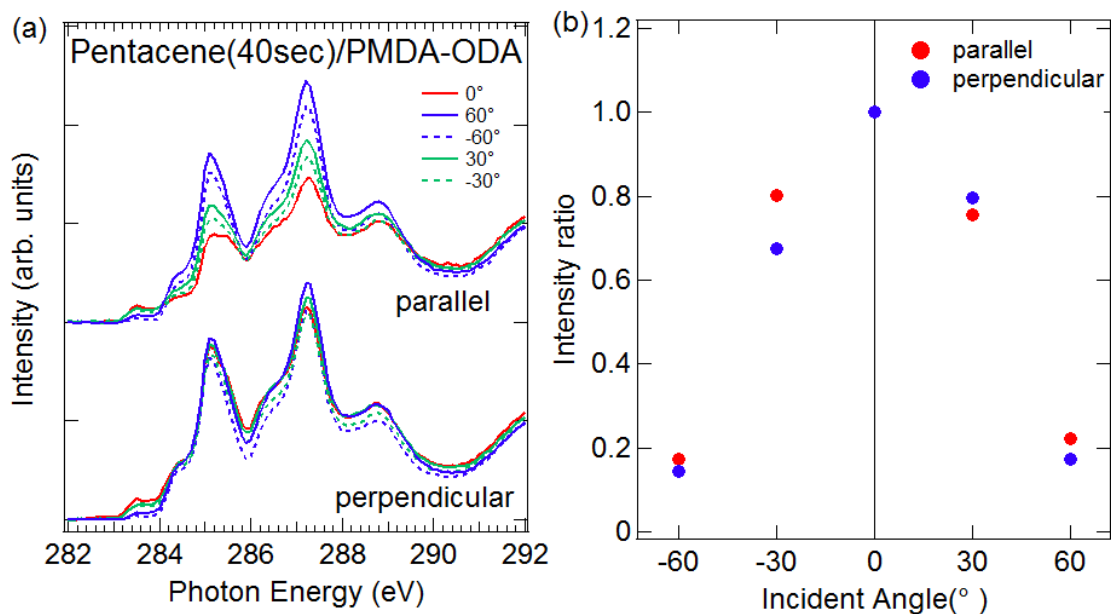


Fig. 2 Incident angle dependent NEXAFS spectra of the very thin pentacene films on PMDA-ODA for the parallel and the perpendicular geometries (a) and their intensity ratios (b).

With further deposition of pentacene, the NEXAFS spectra become more complex, as shown in Fig. 3(a). Similarly, the intensity changes with the incident angles are evaluated for the parallel and the perpendicular geometries [Fig. 3(b)]. For this pentacene film thickness, the angle dependent intensity ratios are not different each other, indicating that the molecular orientation of the pentacene is isotropic.

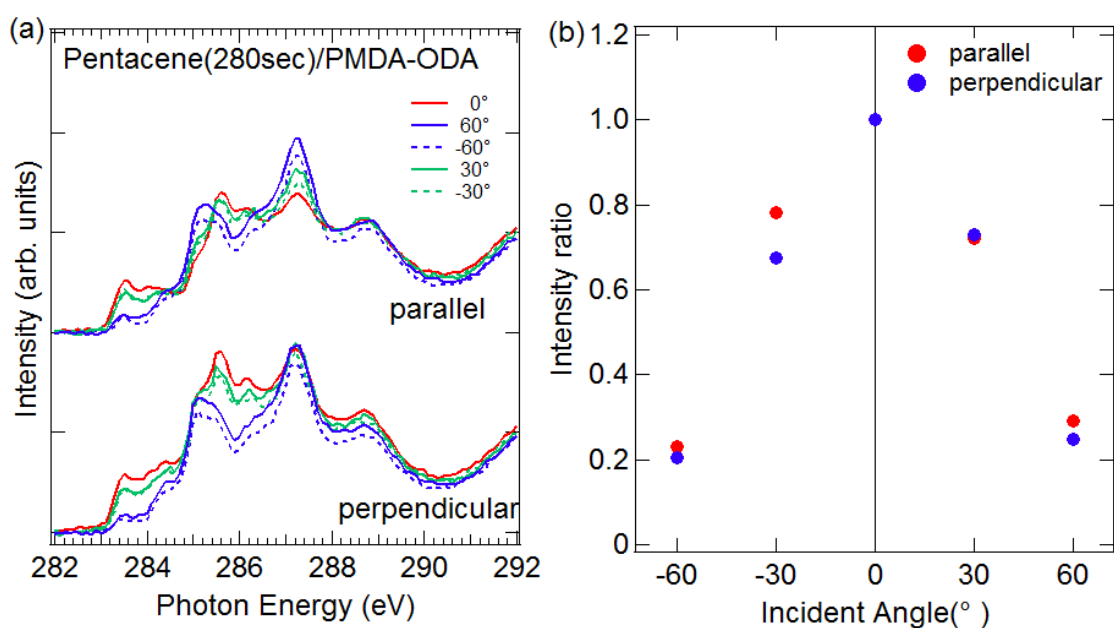


Fig. 3 Incident angle dependent NEXAFS spectra of the thin pentacene films on PMDA-ODA for the parallel and the perpendicular geometries (a) and their intensity ratios (b).

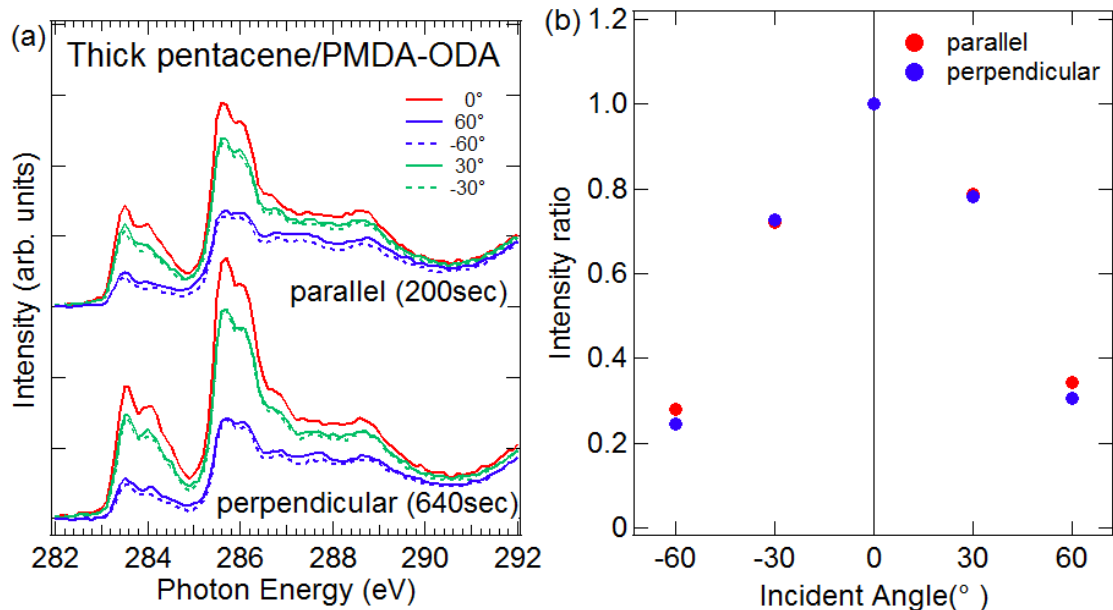


Fig. 4 Incident angle dependent NEXAFS spectra of the thick pentacene films on PMDA-ODA for the parallel and the perpendicular geometries (a) and their intensity ratios (b).

For the very thick pentacene film, the NEXAFS spectra come from only pentacene [Fig. 4(a)]. Therefore, we can compare the angle dependent intensity ratios for the parallel and the perpendicular geometries, though the deposition time was different for each other. For the very thick pentacene film, the angle dependent intensity ratios are not different each other, indicating that the molecular orientation of the pentacene is isotropic.

Finally, the angle dependent intensity ratios are compared with each film thickness for the parallel geometry (Fig. 5). Although the difference is a little, the changes of the angle dependent intensity ratios with increasing thickness indicate that the tilt angle of the pentacene molecules become large.

Considering this result and our previous results [1, 2], we suspect that the π - π interaction alone does not control the molecular orientation of the pentacene and that the surface flatness is also a key parameter.

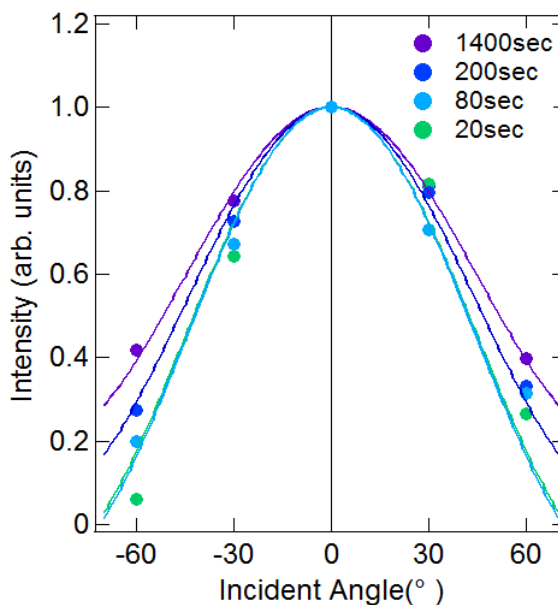


Fig. 5 Polarization dependence of the absorption peaks of the pentacene films on PMDA-ODA.

5. Conclusions

We have performed the near edge x-ray absorption fine structure measurements on pentacene thin films on polyimide films with rubbed surface in order to investigate the molecular orientation of pentacene. Independent on the film thickness, pentacene molecules are aligned vertically. With increasing the film thickness, their tilt angle becomes slightly larger.

References

- [1] Y. Kanekiyo, M. Takizawa, H. Namba, and T. Tominaga, MEMOIRS OF THE SR CENTER RITSUMEIKAN UNIVERSITY No. 15, *to be published*.
- [2] Y. Kanekiyo, M. Takizawa, and H. Namba, MEMOIRS OF THE SR CENTER RITSUMEIKAN UNIVERSITY No. 15, *to be published*.
- [3] H. Namba *et al.*, J. Synchrotron Rad. **5**, 557 (1998).