

## Molecular Orientation of Pentacene on Rutile TiO<sub>2</sub>(110)

Tomoki Sugie, Yuuki Itani, and Masaru Takizawa

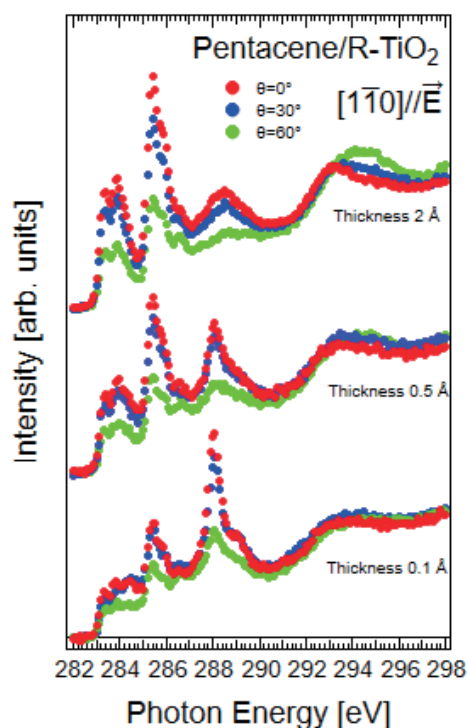
*Department of Physical Sciences, Faculty of Science and Engineering, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan*

An organic semiconductor is expected to be a next generation semiconductor instead of the silicon semiconductor. Molecular orientation control is important for high efficiency of organic thin film device. Pentacene has high hole mobility therefore it is one of organic molecules that is most widely used as an organic electron device. Pentacene molecules stand upright to semiconductor substrates such as SiO<sub>2</sub>. On the other hand, on metallic substrates such as Au, pentacene molecules lie down parallel to the substrate. Rutile TiO<sub>2</sub>(110) is widely used as a substrate because it has atomically flat surface and the surface state can be modified by chemical treatment. Molecular orientation is known to change under the influence of surface state of substrate but interaction between organic molecule and substrate remains unclear. In this work, we have investigated molecular orientation of pentacene thin film by vacuum deposition method on the different surface state substrates. The molecular orientations have been evaluated by using near edge X-ray absorption fine structure spectroscopy (NEXAFS).

The measurements were performed in the BL-8 of SR center. Three types of substrates, reduced TiO<sub>2</sub> (R-TiO<sub>2</sub>), oxygen rich TiO<sub>2</sub> (O-TiO<sub>2</sub>) and sputtered TiO<sub>2</sub> (sputt. TiO<sub>2</sub>), were prepared. The clean TiO<sub>2</sub> surface was prepared with the cycles of Ar<sup>+</sup> sputtering and annealing. Ar<sup>+</sup> sputtering was performed with 0.75 kV and 20 mA for 30 min and annealing was performed at 600 °C for 10 min. Pentacene thin films were evaporated with 0.1 Å/sec rate in ultrahigh vacuum of ~10<sup>-6</sup> Pa. The NEXAFS measurements were performed at room temperature in ultrahigh vacuum of 8 × 10<sup>-8</sup> Pa. The NEXAFS spectra were recorded in the partial electron yield mode. On the different surface state substrates

Figure 1 shows NEXAFS C *K*-edge spectra of pentacene on R-TiO<sub>2</sub>. The peak intensity around 283 - 286 eV depends on incident angles of SR, indicating that pentacene molecules stand upright to the substrate for all thickness. The tilt angle for each film thickness is evaluated to be 70±5° from the intensity change of  $\pi^*$  around 285 eV. (O-TiO<sub>2</sub> and sputt. TiO<sub>2</sub>), polarization dependent NEXAFS spectral intensities were similar (not shown). Focusing around 288 eV, the sharp peak at 288.1 eV appeared for the pentacene thickness of 0.1 Å and 0.5 Å. This peak was assigned to C=O bonding [1]. For the 2 Å thickness, the peak of 288.1 eV disappeared but the new peak appeared at 288.5 eV. This new peak derived from interaction between pentacene

molecules because it was also observed in spectra of pentacene 1.5 nm thickness on SiO<sub>2</sub> (not shown). Interestingly, on the different surface state substrates, C=O peak intensities were different: it reduced on O-TiO<sub>2</sub> and almost disappeared on sputt. TiO<sub>2</sub> (not shown). Because the oxygen vacancy on R-TiO<sub>2</sub> is highly reactive, it is conceivable that this may be the adsorption site for pentacene.



**Fig. 1** Polarization dependent NEXAFS C *K*-edge spectra for various thickness of pentacene thin films (0.1, 0.5, and 2 Å) on R-TiO<sub>2</sub>.

From the NEXAFS measurements, it was found that the pentacene plane was oriented perpendicular to the Rutile TiO<sub>2</sub>(110) substrate surface in any of the R-TiO<sub>2</sub>, O-TiO<sub>2</sub> and sputt. TiO<sub>2</sub> surface states. A peak of 288.1 eV was also observed at pentacene film thicknesses of 0.1 Å and 0.5 Å on R-TiO<sub>2</sub> substrates. Since this is decreased on the O-TiO<sub>2</sub> substrate and not observed on the sputt. TiO<sub>2</sub> substrate, it is considered that oxygen defects of R-TiO<sub>2</sub> interact with pentacene to form growth sites.

### Reference

- [1] G. Yoshikawa *et al.*, Surf. Sci. **2006**, 600, 2518.