Sulfur *K*-edge analysis of C_8-BTBT thin films

Kennosuke Tanaka, Kei Mitsuhara 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 molecule containing sulfur has attracted much attention as an organic semiconductor material with high carrier mobility. Among them, 2,7-dioctyl [1] benzothieno [3,2-b] benzothiophene (C_8-BTBT) has been extensively investigated [1]. In the previous study, C *K*-edge X-ray absorption fine structure (XAFS) spectra have revealed the surface molecular orientation of the thin films [2]. And we have already performed the S *K*-edge XAFS measurements, revealing that the entire molecules of the C_8-BTBT thin films grown under an external temperature gradient [1] are standing-up on the substrate and aligned along the temperature gradient direction to some extent. Although S *K*-edge spectra showed some sharp peaks, some components of the molecular orbitals were difficult to be resolved. In this study, we have performed S *K*-edge XAFS measurements with high energy-resolution and analyzed the S *K*-edge XAFS spectra.

XAFS measurements were performed at the BL-13 of SR center, Ritsumeikan University. XAFS spectra were collected by total electron yield through a sample drain current. In order to analyze the components of the molecular orbitals, the incidence angle with respect to the substrate normal was varied and the samples were azimuthally rotated around the substrate normal.

The S *K*-edge XAFS spectra showed two sharp peaks around 2473 eV and 2475 eV, whose incident angle dependences showed opposite behavior. The former peak is assigned to the σ* molecular orbital (and weak π*), while the latter can be assigned to another σ* molecular orbital whose transition dipole moment is perpendicular to the molecular long axis [3]. Therefore, the polarization dependences of the peaks were opposite. Figure 1 shows S *K*-edge XAFS spectra with fitting curves of step function (background), π*, $\sigma^*_{//}$, and $\sigma^*_{\perp}$ peaks. With these components, all the incident-angle dependent XAFS spectra were reproduced well (Fig. 1).

As shown in Fig. 2, all the intensity changes of the molecular orbitals are well explained with the molecular tilt angle of 8±2° and the angle between the molecular plane and the growth direction of 48±2°.

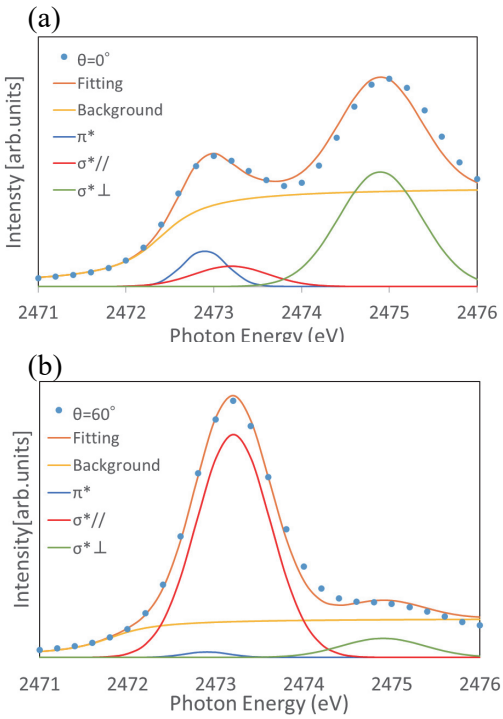

Fig.1: S *K*-edge XAFS spectra of the C_8-BTBT thin film with the fitting curves. The incident angle was varied to be 0° (a) and 60° (b).

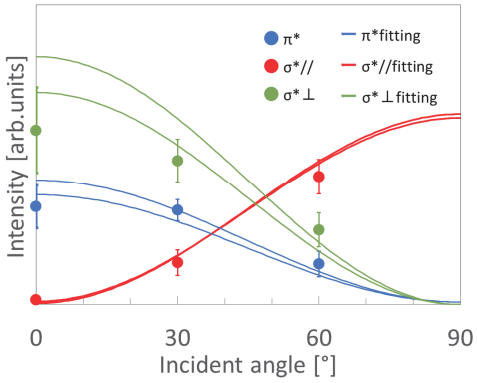

Fig.2: Incident angle dependence of the π*, $\sigma^*_{//}$, and $\sigma^*_{\perp}$ peak intensities for the C_8-BTBT thin films with the theoretical curves.

References

[1] N. Iizuka, T. Zanka, Y. Onishi, and I. Fujieda, Proc. SPIE **9745**, 97451J (2016).
[2] H. Watanuki, K. Mitsuhara, and M.Takizawa, e-J. Surf. Sci. Nanotech. **16**, 79 (2018).
[3] A.B. Fernándeza *et al*., Materials Chemistry and Physics **221**, 295 (2019).