

## Molecular orientation of regioregular poly(3-hexylthiophene) film

Hiromi Ikeura-SEKIGUCHI\*<sup>1</sup>, Tetsuhiro SEKIGUCHI<sup>2</sup>

<sup>1</sup>National Institute of Advanced Industrial Science and Technology (AIST),  
Tsukuba, Ibaraki 305-8568, Japan

<sup>2</sup>Japan Atomic Energy Agency (JAEA), Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan

### Introduction

Intermolecular  $\pi$ -stacking interactions through its aromatic rings play a dominant role in the performance of organic semiconductor devices. Regioregular (RR)-P3HT has been used as the active material in OFETs in which the preferential  $\pi$ -stacking of the polymer chains perpendicular to the substrate produces charge transport between the source and the drain occurs parallel to the substrate. On the contrary, in bulk heterojunction (BHJ) solar cells, the charges have to be transported perpendicular to the substrate to reach each electrode. The  $\pi$ -stacking oriented perpendicular to the substrate takes advantage of high mobility pathways to the electrodes. The degree of regioregularity of P3HT backbone strongly influence on structural order which is related to solar cell performance.

### Experimental

Experiments were performed at beamline BL-27A with energy resolution of 0.9 eV around the S  $K$ -edge using X-ray absorption spectroscopy (XAS). The XAS spectra were measured using monitoring sample drain current near the S  $K$ -edge (2465–2500 eV). Such energies were chosen to excite the S  $1s$  core electron to unoccupied orbitals of regioregular poly(3-hexylthiophene) RR-P3HT. Angle dependent XAS data were obtained by changing the angle between the incoming x-ray beam and the sample surface.

### Results and discussion

Figure 1 shows the S  $K$ -edge XAS spectra of RR-P3HT film at various angles of X-ray incidence  $\theta$ , between the direction of propagation of incident synchrotron light X-ray and the surface plane. The XAS of RR-P3HT film changes in intensity at Peak 1 and Peak 2, which indicates that a well-ordered morphology is produced. In contrast, the XAS of polycrystalline RR-P3HT powder shows no polarization dependence and is reasonably similar to that of the film at  $\theta = 55^\circ$  (magic angle). Peak 1 can be assigned to S  $1s \rightarrow \pi^*$  (C=C) and  $\pi^*$ (S-C) unoccupied states on the previous XAS studies of thiophene[1] and polythiophene[2]. The S  $1s \rightarrow \pi^*$  (C=C) excitation is lower in energy by  $\sim 1$  eV than the S  $1s \rightarrow \pi^*$ (S-C). On the analogy of polythiophene spectra[3] as probed by XAS combined with Resonant Auger Spectroscopy[3], Peak 1 is suggested to be dominated by S  $1s \rightarrow \pi^*$ (S-C) excitation. Peak 1 is enhanced at normal incidence of X-ray, while peak 2 is enhanced at grazing incidence and almost absent at normal incidence. Peak 1 and peak 2 clearly show opposite polarization dependence

with changing incidence angles. Thus, peak 2 can be assigned to S  $1s \rightarrow \pi^*$  excitation. It is therefore considered that most RR-P3HT chains are well-aligned and oriented *face-on* with respect to the Si substrate.

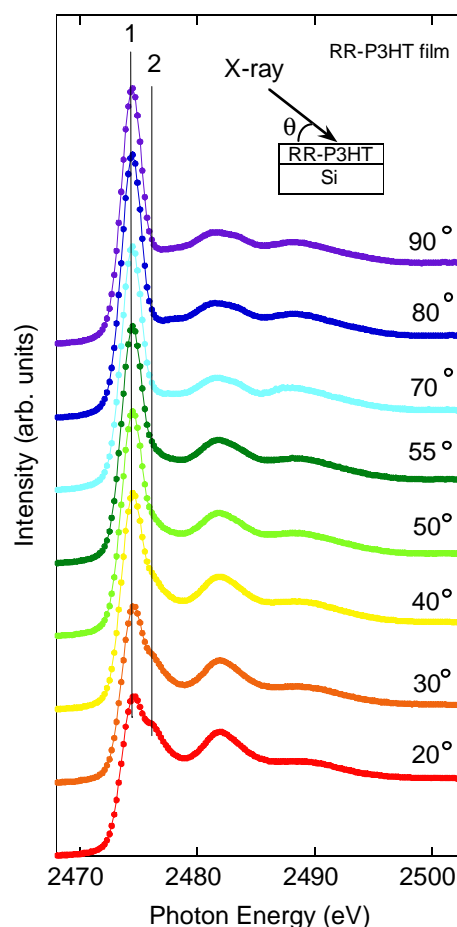


Fig.1 XAS spectra of RR-P3HT  $\pi$ -stacking film as a function of angle of X-ray incidence near the S  $K$ -edge together with RR-P3HT polycrystalline powder.

### References

- [1] A.P. Hitchcock, J.A. Horsley, J. Stöhr, *J. Chem. Phys.* **85**, 4835 (1986).
- [2] H. Ikeura-Sekiguchi, T. Sekiguchi, *Surf. Int. Anal.* **40**, 673 (2008).
- [3] H. Ikeura-Sekiguchi, T. Sekiguchi, *Phys. Rev. Lett.* **99**, 228102 (2007).

\*ikeura-sekiguchi@aist.go.jp