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Polarization dependent sulfur K-edge XAFS measurements of P3HT thin films for determination of film orientations with the improved sensitivity

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1. Introduction

X-ray absorption fine structure (XAFS) measurements in the soft X-ray region are widely conducted with a total electron yield (TEY) method under the vacuum owing to the difficulties in preparing samples of appropriate optical thickness for the transmission method, and the X-ray fluorescence yield (XFY) method is supplementary employed for other cases. We have been employing a conversion electron yield (CEY) method that utilizes the ionization of surrounding He gas molecule by the energetic Auger electrons from a sample. The CEY is advantageous in the sense of S/N compared to the XFY. However, the use of an electrode that prevents created electron-ion pairs from recombination has generally made the geometrical restrictions for angular dependent measurements. We have developed a new device that can make the angular dependent XAFS measurements using CEY method. And we report the results of determination of the orientation for P3HT thin films using the developed device.

2. Experimental

2.1 A CEY device

A principle of the CEY measurements is similar to that of X-rays with an ionization chamber except for the source of the gas ionization. Therefore, a planer electrode has been adopted in the experimental setup at BL11 [1]. To realize the angular dependent measurements we have developed a new device shown in Fig.1. The device is equipped with a rod-shaped electrode. The diameter of the electrode in the new device was 6 mm, and the relatively wide diameter of the anode has maintained the strength of the electric field within the region of the ionization chamber. The cross section of the anode was semicircle, and the electrodes are placed above and below the beam height.

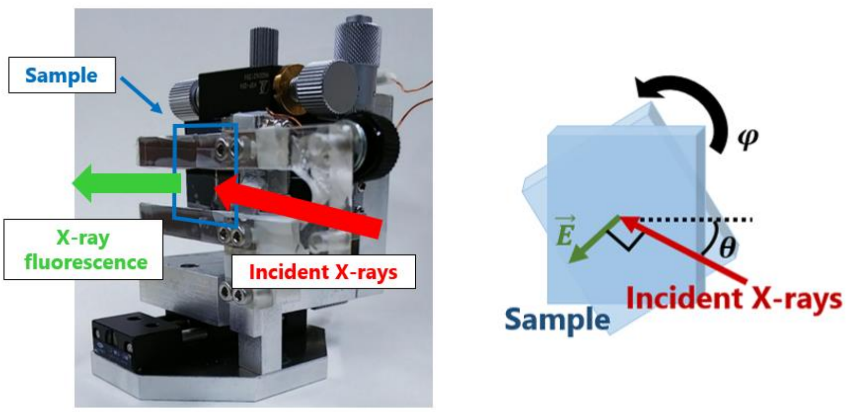

FIGURE 1. A photograph of the new device for the angular dependent CEY measurements (left), and a schematic layout of the sample geometry including glancing angle, θ and the azimuthal angle, φ (right).

2.2 XAFS measurements

XAFS measurements were performed at BL-11 of HiSOR. Incident X-rays were monochromatized with a Si(111) double crystal monochromator. The XFY was detected with a silicon drift detector (SDD) in a He filled chamber. A poly(3-hexylthiophene) (P3HT) film on ITO glass substrate was utilized as a sample having an anisotropy in sulfur K-edge XAFS spectra. A chlorobenzene solution of P3HT(Rieke Metals, Mw=58000) was spin-coated on a special ITO/glass substrate, and the surface of the substrate was previously brushed with a velvet fabric. The majority of backbones of edge-on oriented molecules are expected to be aligned in the brushing direction [2]. The azimuthal angle, φ was defined to be 0 when the electric field of the incident X-rays was normal to the brushing direction.

3. Results and Discussion

FIGURE 2 shows the azimuthal angle, φ dependence of S K-edge XAFS spectra from a P3HT thin film at θ = 80°. The 1s to π* peak (π*) showed strong peak under the condition of φ = 0 °. A plot of the intensities of π* peak is shown as a function of azimuthal angle (FIGURE 3). We consider a three-component system that includes edge-on orientation (uniaxial and random) and face-on as components of orientation. But the almost direct incidence condition suggests that the contribution from the face-on orientation of the molecules is negligible, and the obtained π* data can be attributed to molecules in the uniaxial edge-on direction and those in the random edge-on direction. This anisotropy could be expressed by the $\cos^2\varphi$ function. On the other hand, the azimuthal dependence of the σ*S-C peak (FIGURE 4) should include the contribution of molecules in the face-on orientations. As the anisotropy of the σ*S-C peak was originated from the molecules in the uniaxial orientation, analysis of these two curves enabled us to determine the fractions of three components, and the fraction of the uniaxial orientation (edge-on) was determined to be 35 %.

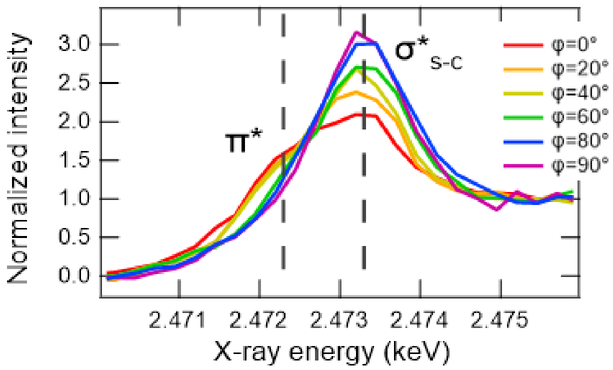

FIGURE 2. Azimuthal angle dependence of S K-edge XAFS spectra (θ=80°) from uniaxial edge-on oriented P3HT thin film.

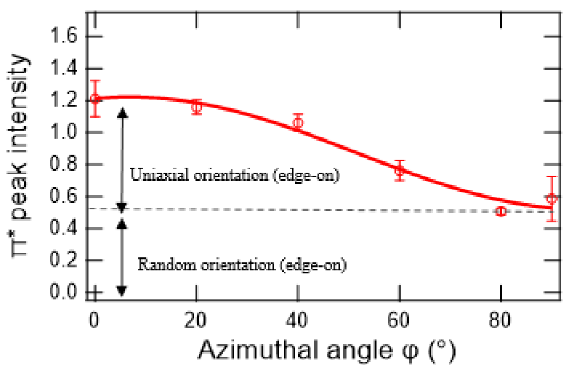

FIGURE 3. A plot of the π* peak intensities as a function of the azimuthal angle.

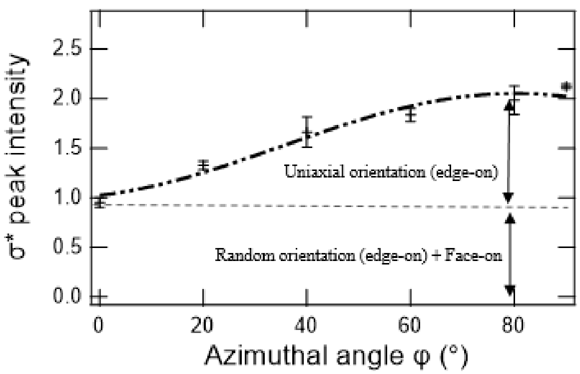

FIGURE 4. A plot of the σ* peak intensities as a function of the azimuthal angle.

References

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[2] M. Imanishi, D. Kajiya, T. Koganezawa, K. Saitow, Sci.Rep.**7,** 5141 (2017)