Analyses of Surface Nano-structure of Organic Semiconductor Thin Films by Grazing Incidence X-ray Diffraction

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Molecular aggregation structure of organic thin films has been received a great attention because of their applications to various electronic devices. One of the factors influencing the performance might be the surface and interfacial molecular aggregation structure of organic thin films. A grazing incidence X-ray diffraction (GIXD) using evanescent X-rays is an excellent method to characterize the surface and interfacial molecular aggregation structure of the organic polymer thin films[1,2]. In this study, the surface nano-structure of poly(3-hexylthiophene) (P3HT) thin films was investigated by GIXD.

P3HT was used as samples in this study. GIXD measurements were carried out at the BL-13XU beamline. The GIXD measurements of P3HT thin films were carried out at an incident angle to the surface of a sample (α_i) smaller than the critical angle (α_c). Bragg diffractions from the crystallographic planes normal to the sample surface were measured in the in-plane direction by a scintillation counter. The scattering vector parallel to the sample surface is defined as q_{xy} (= $2\pi d = 4\pi\sin\theta/\lambda$)) where d, θ, and λ are the d-spacing, the Bragg angle, and the wavelength of incident X-rays, respectively.

P3HT thin films prepared on Si substrates by spin-coating and a P3HT powder sample were annealed at 473 K for 30 min. Figure 1 shows $2\theta/\theta$ symmetric reflection and in-plane GIXD profiles of the annealed P3HT films and a powder diffraction profile of the annealed P3HT. On each profile for the films and the powder sample, annealing effect was observed as sharpening of the diffraction peaks, appearance of higher-order peaks and decrease in intensity of the amorphous scattering. The powder diffraction profile showed the (100) and its higher order reflections corresponding to the side-chain lamellar stacking distance (d_{100}= 1.60 nm) as well as the (010) reflection (d_{010}= 0.38 nm) corresponding to the π–π stacking of the thiophene ring in the main chain. In the symmetric reflection profile, the relative intensity of the (100) and its higher order reflections to the (010) reflection was very strong. This result indicated that the main chains had a tendency to orient parallel to the film surface. On the other hand, the in-plane GIXD profile exhibited the (010) reflection corresponding to the π–π stacking of the thiophene ring as well as the (100) reflection. The comparison between the symmetric reflection and GIXD profiles revealed that the degree of side-chain lamellar orientation was relatively low in the near-surface region. The control of orientation of conjugated lamellae is expected to control the anisotropic carrier mobility.

References
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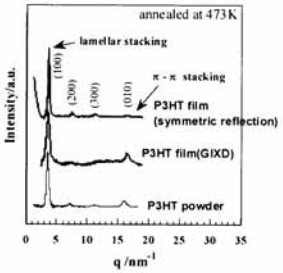

Figure 1 $2\theta/\theta$ symmetric reflection and in-plane GIXD profiles of the annealed P3HT films and a powder diffraction profile of the annealed P3HT.

High-precision structure analysis of metallic one-dimensional chains on the Cu(001)

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In this work, we performed a grazing-incidence surface X-ray diffraction (GI-SXRD) experiment on the Cu(001)-(5x1)-Ga surface, which we have already studied by means of scanning-tunneling microscopy (STM) and angle-resolved photoelectron spectroscopy (ARPES). According to the STM result, the surface appears to be composed of close-packed atomic chains of gallium aligned along the [110] direction. The ARPES shows the surface resonance band induced by gallium, which is fairly well explained within a quasi-one-dimensional, nearly-free-electron model. The purpose of the present SXRD work is to determine the atomic structure of this surface quantitatively, which will then be used for the first-principles full-potential electronic-structure calculation. Thus we will obtain a comprehensive understanding of the quasi-one-dimensional gallium metallic chains.

The surface was prepared in situ in the ultrahigh vacuum chamber set on the (2+2)-type AODOHYO diffractometer at BL-13XU of the Spring-8. After the surface was cleaned by the standard procedure, the (5x1)-Ga was prepared by depositing gallium with the sample at room temperature.

The X-ray diffraction was measured at a wavelength of 60.9 pm. We have measured the more than eighty in-plane diffraction intensities of (h, k, 0.3), including symmetrically equivalent ones, and several crystal-truncation and superstructure rods.

We are currently analyzing the data by using the ANA-ROD software originally developed by E. Vlieg [1] and maintained by ESRF [2]. We started with two structure models: One is an overlayer model which contains three Ga chains separated by 1.5a or 2a, where a denotes surface lattice constant of Cu(001). The other is a surface alloy model in which gallium and copper atoms form a quasi-hexagonal monolayer alloy and, due to the confinement of the substrate lattice, the monolayer is strongly buckled to give rise to a 1D chain-like structure.

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[2] URL: <http://www.esrf.fr/computing/scientific/joint_projects/ANA-ROD/>