In situ Investigation of Annealing Effect on Higher-order Structure of Polyethylene Thin Films by Synchrotron Grazing-incidence Small-angle and Wide-angle X-ray Scattering

Polymer thin films have been used for parts of components of displays, as the insulation layer of semiconductors and as materials to coat papers for printing. To satisfy the physical properties of the thin films as materials, it is important to control their higher-order structures at nano-to-meso scales. In general, crystalline polymers form a higher-order structure consisting of crystalline and amorphous regions. The surface and local morphologies of thin films are generally investigated by microscopic observation. However, the essential structural property of the thin films is still under discussion. The grazing-incidence small-angle X-ray scattering (GISAXS) method has recently attracted considerable attention as a powerful tool for the meso-scale structural analysis of the thin films of polymers, for example, microphase-separated block copolymers and nanoporous polymers [1,2]. In this study, the annealing effect on the lamellar stacking structure of polyethylene thin films prepared on Si wafers has been investigated at molecular and lamellar scales by synchrotron GISWAXS measurements [3].

The sample used in this study was additive free high-density polyethylene (HDPE, melt index = 14) supplied from Mitsui Chemicals, Inc., as a typical example of crystalline polymers. Thin films with a thickness of ca. 400 nm were prepared onto the native oxide covered Si (110) surface of wafers with a 0.1 wt% *p*-xylene solution of HDPE under a N_2 atmosphere by a dip-coating method [4]. The obtained films were isothermally crystallized from the melt at 373 K for 24 h under a N_2 atmosphere.

In general, scattering from an organic thin film is relatively weak in intensity. Therefore, utilizing high brilliance and highly parallel synchrotron X-rays as incident beams is effective in detecting GISWAXS from HDPE thin films. To investigate the molecular and meso-scale order structure of the films, synchrotron GISWAXS measurements were carried out using an imaging intensifier (II), a charge coupled device (CCD) detector and imaging plate (IP) detectors at beamline **BL40B2**. Figure 1 shows the experimental geometry of the GISWAXS measurements. The components of the scattering vector, **q**, parallel and perpendicular to the sample surface were defined as $\mathbf{q}_y = (2\pi/\lambda)\sin(2\theta_f)\cos(\alpha_f)$ and $\mathbf{q}_z = (2\pi/\lambda)(\sin(\alpha_i) + \sin(\alpha_f))$, respectively, for reflected scattering. Here, α_i is the incident angle of the X-ray beams, α_f is the exit angle, λ is the wavelength of the incident X-ray beams and $2\theta_f$ is the angle between the scattered beam and the plane of incidence. The subscripts s and w in Fig. 1 indicate the GISAXS and the grazing-incidence wide-angle X-ray scattering (GIWAXS) geometries, respectively. The nano-scale order structure such as the chain-packing distance and chain orientation in the crystal region can be evaluated for the films by two-dimensional GIWAXS measurements. On the other hand, the meso-scale order structure such as lamellar stacking distance and lamellar orientation can be investigated for the films on the basis of the two-dimensional GISAXS data. The λ of the incident X-rays was 0.15 nm and the sample-to-detector distances were *ca.* 100 mm for GIWAXS and *ca.* 2177 mm for GISAXS. A 2000 mm-long vacuum path was utilized between the sample cell and the detector for GISAXS measurements. The data collection time was 10 s per GISAXS pattern with the II + CCD detector and 300 s per GIWAXS or GISAXS pattern with the IP detector.

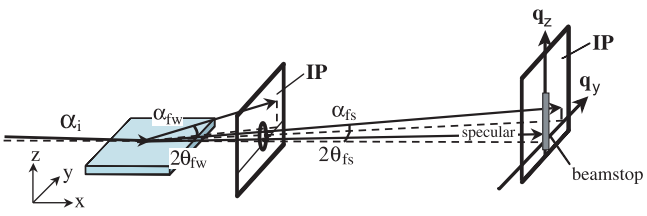

Fig. 1. Schematic geometry of GISWAXS measurements.

In situ GISWAXS measurements were carried out for the films at the annealing temperatures, *Ta*, of 378 K, 383 K, 388 K and 393 K in a stepwise annealing process from 300 K to 453 K. The film on the silicon wafer was placed on the heater stage of a low-vacuum sample cell, and the sample temperature was accurately monitored and controlled with ultra-thin and wide K-type thermocouples and a program temperature controller. At each *Ta*, GISWAXS from the film was measured for 300 s after annealing for 600 s. The heating rate was *ca.* 10 deg/min and the temperature fluctuation of the film at each *Ta* was ± 0.5 deg. The detectable **q**-ranges of GIWAXS and GISAXS in these experiments were *ca.* 21 nm^{-1} ~ 4.2 nm^{-1} and 1.3 nm^{-1} ~ 4.2 × 10^{-2} nm^{-1}, respectively.

Figures 2(a) ~ 2(f) show GISWAXS patterns measured at α_i = 0.13 deg for a melt-crystallized HDPE thin film in the initial state at 300 K, in the stepwise annealed state at 378 K, 383 K, 388 K and 393 K, and in the melt state at 453 K, respectively. As shown in the GIWAXS pattern in Fig. 2(a), the (110) and (200) reflections of oriented HDPE orthorhombic

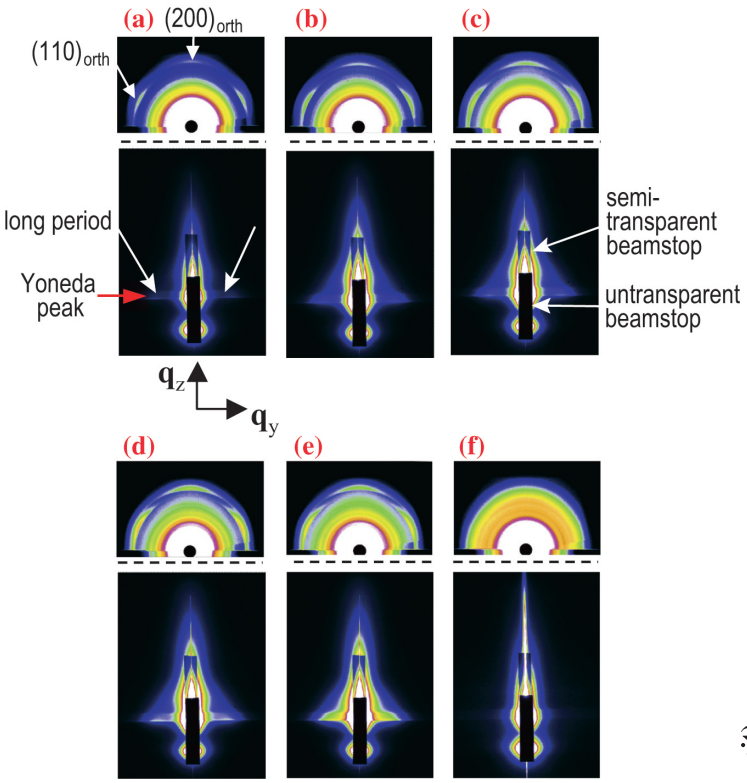

Fig. 2. GISWAXS patterns measured at α_i = 0.13 deg for a melt-crystallized HDPE thin film in the initial state at 300 K **(a)**, in the stepwise annealed state at 378 K **(b)**, 383 K **(c)**, 388 K **(d)** and 393 K **(e)**, and in the melt state at 453 K **(f)**. The upper and lower images at each temperature are the GIWAXS and GISAXS patterns, resp1ectively.

crystals were measured in the out-of-plane direction for the initial thin film. These reflections were azimuthally broad peaks and the maximum intensity of the (200) reflection was on the $\mathbf{q}_z$ axis. It was revealed that the a axis of the orthorhombic unit cell was oriented in the perpendicular direction to the film surface. In other words, the chain axis (the *c* axis) was oriented parallel to the film surface. The reflection peaks for the annealed thin films were almost the same in $\mathbf{q}_y$ and $\mathbf{q}_z$ as those for the initial thin film. The relative intensity of these reflections increased with an increase in annealing temperature, as shown in the GIWAXS patterns of Figs. 2(b) - 2(e). This implied that the degree of crystallinity was increased by annealing.

On the other hand, scattering peaks were detected only in the in-plane direction near a Yoneda peak in the GISAXS pattern in Fig. 2(a), which means that crystalline lamellae were stacked parallel to the film surface. The $\mathbf{q}_y$ of these peaks relates to the long period, the average distance between stacked crystalline lamellae. The Yoneda peak arises in the in-plane direction due to the interference of the incident and scattered waves [5]. By stepwise annealing, these scattering peaks slightly shifted to a lower $\mathbf{q}_y$ range in the in-plane direction and increased in relative intensity with an increase in *Ta*. Figure 3 shows the in-plane intensity profiles of the *in situ* GISAXS patterns at α_{fs} = 0.13 nm^{-1} along the Yoneda peak in Figs. 2(a) - 2(e). It clearly indicated that the shoulder peak gradually shifted from $\mathbf{q}_y$ = *ca.* 0.25 nm^{-1} to *ca.* 0.20 nm^{-1} with increasing sample temperatures from 300 K to 393 K. The GISAXS data suggested that crystalline lamellae were stacked with large disordering parallel to the film surface, and the long period became longer from *ca.* 25 nm to *ca.* 32 nm by annealing. These results suggest that the synchrotron GISWAXS experimental technique can be applied to the kinetic study of the higher-order structure of polymer thin films.

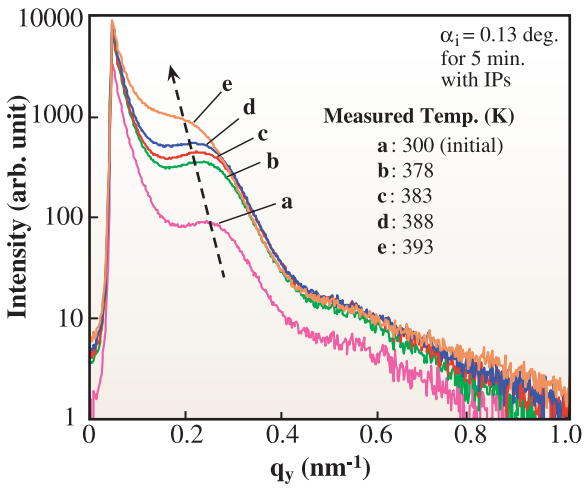

Fig. 3. In-plane intensity profiles of the *in situ* GISAXS patterns in Figs. 2**(a)** – 2**(e)** measured for the HDPE thin film in a stepwise annealing process from 300 K.

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