Crystallization Behavior of Polyethylene on Silicon Wafers in Solution Casting Processes Traced by Time-resolved Measurements of Synchrotron Grazing-Incidence Small-angle and Wide-angle X-ray Scattering

S. Sasaki1*, H. Masunaga1, K. Itou2, K. Tashiro3, H. Okuda4, A. Takahara5, M. Takata1, 2, 6
1Japan Synchrotron Radiation Research Institute (JASRI) / SPring-8, Hyogo 679-5198, Japan; 2The RIKEN Harima Institute / SPring-8, Hyogo 679-5198, Japan; 3Graduate School of Engineering, Toyota Technological Institute, Nagoya 468-8511, Japan; 4Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan; 5Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 819-0395, Japan; 6Graduate School of Frontier Science, The University of Tokyo, Chiba 277-8561, Japan.

Corresponding author's E-mail: sono@spring8.or.jp

Abstract. Crystallization behavior of polyethylene (PE) on silicon wafers in solution casting processes has been successfully traced by time-resolved grazing-incidence small-angle and wide-angle X-ray scattering (GISWAXS) measurements utilizing synchrotron radiation. A p-xylene solution of PE kept at ca. 343 K was dropped on a silicon wafer at ca. 298 K. While the p-xylene evaporated naturally from the dropped solution sample, PE chains crystallized to be a thin film. Raman spectral measurements were performed simultaneously with the GISWAXS measurements to evaluate quantitatively the p-xylene the dropped solution contained. Grazing-incidence wide-angle X-ray scattering (GIWAXS) patterns indicated nucleation and crystal growth in the dropped solution and the following as-cast film. GIWAXS and Raman spectral data revealed that crystallization of PE was enhanced after complete evaporation of the p-xylene from the dropped solution. Grazing-incidence small-angle X-ray scattering (GISAXS) patterns implied formation of isolated lamellae in the dropped solution. The lamellae and amorphous might alternatively be stacked in the preferred direction perpendicular to the wafer surface. The synchrotron GISWAXS experimental method could be applied for kinetic study on hierarchical structure of polymer thin films.

1. Introduction
Polymer films have widely been utilized as materials and parts of components in the industrial field. The solution casting method is one of the common film molding methods for polymers. However, hierarchical structure development of polymers during the solution casting hasn’t been revealed on the
meso-to-nano scale. In the case of solution casting with crystalline polymers, polymer chains crystallize as the concentration of polymers increases in the solution due to evaporation of the solvent from it. Therefore, the try-and-error method is necessary to find the best casting condition for control of thickness and morphology of the as-cast films. Crystallization kinetics of polymers and the role of the solvent in the solution casting process have to be clarified to understand relationship between the hierarchical structure and physical property of polymers in the as-cast films.

The grazing-incidence small-angle X-ray scattering (GISAXS) measurements using synchrotron radiation was powerful for hierarchical structure analyses of polymer thin films. Ultra-bright and highly directional X-ray beams generated in the top-up mode in SPring-8 are of great advantage to kinetic study of organic compounds and polymeric materials. We have established a simultaneous measurement system of the grazing-incidence small-angle and wide-angle X-ray scattering (GISWAXS) with two-dimensional (2D) detectors for polymer thin films at the BL40B2 (JASRI Structural Biology II, Bending Magnet) in SPring-8. A time-resolved experimental system of GISWAXS had been expected as a new tool for the most advanced research and development of polymer thin films.

The purpose of this study is to clarify crystallization behavior of polyethylene (PE) on silicon wafers in the solution casting processes by time-resolved synchrotron GISWAXS measurements. A simultaneous experimental method of GISWAXS and Raman spectra has been established to investigate the effect of natural evaporation of the p-xylene solvent on hierarchical structure development of PE.

2. Experimental Section

A sample used in this study was commercially available polyethylene (PE)(P1979-E, Polymer Source Inc., Mn=12500, Mw/Mn=1.05) as a typical example of crystalline polymers. A ca. 1.0 wt % PE was dissolved in the p-xylene at ca. 403 K under N₂ atmosphere. The obtained solution was kept at ca. 343 K at which PE chains still dissolved in the p-xylene. As a sample for GISWAXS and Raman spectral measurements, a small amount of the solution was dropped on the native oxide covered surface of a silicon wafer (dimension / mm³: ca. 2.0 (l) × 5.0 (w) × 0.7 (t)) at 298 K. The p-xylene was evaporated naturally from the dropped solution under atmospheric condition. Instead, PE chains were gradually crystallized there. After a short time, a dry thin film of PE was formed on the wafer. In the solution casting process, t was defined the time passed after a small amount of the p-xylene solution of PE was dropped on a silicon wafer.

Crystallization behavior of PE in the above-mentioned solution casting process was traced by time-resolved measurements of GISWAXS and Raman spectra. To utilize the high brilliance and highly parallel synchrotron X-rays as the incident beams is effective in detecting scattering from a small sample. GISWAXS measurements were carried out at RIKEN Structural Biology Beamline 1 (BL45XU, Undulator) in SPring-8 (Hyogo, Japan) to investigate hierarchical structure of PE thin films on the nano and meso scales. Figure 1 shows experimental geometry of GISWAXS and Raman spectral measurements. The components of the scattering vector, \( \mathbf{q} \), parallel and perpendicular to the sample surface were defined as \( q_y = (2\pi/\lambda) \sin(2\theta) \cos(\alpha_i) \) and \( q_z = (2\pi/\lambda) (\sin(\alpha_i) + \sin(\alpha_f)) \), respectively, for reflected scattering. Here, \( \alpha_i \) is the incident angle of X-ray beams, \( \alpha_f \) is the exit angle, \( \lambda \) is the wavelength of incident X-ray beams and \( 2\theta \) is the angle between the scattered beam and the plane of incidence. The subscript s and w indicate the grazing-incidence small-angle X-ray scattering (GISAXS) and the grazing-incidence wide-angle X-ray scattering (GIWAXS) geometries, respectively. A charge coupled device (CCD) detector (C4880-10-14A, Hamamatsu Photonics K.K.) combined with an imaging intensifier (V5445P, Hamamatsu Photonics K. K.) was used for GISAXS measurements, and a flat panel (FP) detector (C9728DK, Hamamatsu Photonics K. K.) for GIWAXS. Meso-scale structural features of the sample on the wafer, such as lamellar stacking distance and lamellar orientation, can be evaluated on the basis of 2D GISAXS patterns. On the other hand, nano-scale structural information on crystal structure and orientation can be obtained by analyzing 2D GIWAXS patterns. The \( \lambda \) of incident X-rays was 0.09 nm and the sample-to-detector distances were ca. 2290
mm for GISAXS and ca. 70 mm for GIWAXS. A 2100 mm-length vacuum path was utilized between a sample cell and the detector for GISAXS measurements. Scattering patterns from the sample were measured at the $q_\parallel$ of 0.10 deg., which were lower than the critical angle of total external reflection at silicon surface. Therefore, the incident X-rays go through the dropped solution or the as-cast PE film and reflect on the silicon wafer surface. The data collection time per scattering pattern was 0.5 s and the interval time between the two sequent patterns was 1.5 s. The dry chicken collagen fibers and the powder CeO$_2$ (National Institute of Standards and Technology, U.S.A.) were used for the standard samples for GISAXS and GIWAXS measurements, respectively. The detectable $q$-range of GISAXS was ca. 0.09 nm$^{-1}$ ~ 2.1 nm$^{-1}$ and that of GIWAXS was ca. 10 nm$^{-1}$ ~ 32 nm$^{-1}$. Raman spectral measurements were carried out with a mobile Raman spectrum unit (Spectra View 2000, Rambda Vision Inc.) to evaluate quantitatively the $p$-xylene the dropped solution contained. The wavelength of the built-in laser of the unit was 785 nm.

3. Results and Discussion

Crystallization behavior of PE in the solution casting process was traced by time-resolved simultaneous measurements of GISAXS, GIWAXS and Raman spectrum. The time ($t$) passed after dropping the $p$-xylene solution of PE on a silicon wafer was recorded. Figure 2 shows time-resolved 2D GISWAXS patterns of the $p$-xylene solution of PE dropped on a silicon wafer measured at $t$ = 20, 120, 126, 128, 130, 132, 134 and 180 s. The 2D GIWAXS patterns indicated that typical isotropic
scattering from the dropped solution changed gradually to the (110) and (200) reflections from the oriented orthorhombic PE crystals by way of the Debye-Sherrer ring from unoriented those. On the other hand, the 2D GISAXS patterns showed that isotropic scattering from the solution changed gradually to anisotropic one. A broad peak appeared in the out-of plane direction on the \(q_z\) axis around 120 s and shifted to the higher \(q_z\) range increasing in intensity until 134 s.

Figure 3 shows time dependence of in-plane GIWAXS patterns in the solution casting process shown in Figure 2. The in-plane line in the GIWAXS patterns in Figure 2 was parallel to and a few pixels-upper from the \(q_y\) axis. The (110) and (200) reflections from the orthorhombic PE crystals were detected in the \(q_y\) range of 14 ~ 18 nm\(^{-1}\) from the begging of the measurements. These reflections increased in intensity with time. And then, broad scattering from the solution and the amorphous PE measured in the \(q_y\) range of 8 ~ 20 nm\(^{-1}\) decreased in intensity instead. The profiles didn’t change in intensity after 132 s, which suggested that the solvent evaporation and nano-scale crystallization was almost finished around 132 s.

Figure 4 shows Raman spectral profiles in Raman shifts of 750 ~ 1100 cm\(^{-1}\) measured in the solution casting process in Figure 2. Strong peaks at ca. 1000 cm\(^{-1}\) characteristic of the \(p\)-xylene decreased gradually in intensity with time. Those spectral peaks completely disappeared around 100 s. Figure 5 shows comparison of peak intensity of the (110) reflection in Figure 3 with that of the Raman spectra at ca. 1000 cm\(^{-1}\) in Figure 4. It clearly indicates that the \(p\)-xylene evaporated completely from the dropped solution around 100 s. Instead, the (110) reflection increased drastically in intensity. It should be mentioned that crystallization of PE was enhanced after complete evaporation of the \(p\)-xylene. Due to the latent heat of vaporization of the \(p\)-xylene, the sample might be cooled from ca. 343 K to ca. 298 K during the GISWAXS measurements. Therefore, it was considered that PE chains in the amorphous state could crystallize in such cooled sample after complete evaporation of the \(p\)-xylene.

Figure 6a and 6b show time dependence of the azimuthal intensity profiles of the (110) and (200) reflections in Figure 3. The azimuthal angles on the in-plane line parallel to the \(q_y\) axis and on the \(q_z\) axis were defined as 0 deg. and 90 deg., respectively. The intensity of these azimuthal profiles near 0 deg. increased gradually with time. As time passed, broad peaks around 0 deg. in these figures increased in intensity. This means that the [110] and [200] directions of the orthorhombic PE crystal became relatively parallel to the wafer surface. In other words, it was found that the \(a\) and \(b\) axes of the orthorhombic PE crystal gradually oriented parallel to the wafer surface with time. At the same time, the \(c\) axis (// the chain axis) became perpendicular to the wafer surface. The flat-on lamellae with respect to the wafer surface might mainly be formed in the end of the solution casting process. Figure 7 shows time dependence of the out-of-plane GISAXS profiles at \(q_y = \) ca. 0.11 nm\(^{-1}\) (along the broken line parallel to the \(q_y\) axis) in Figure 2. At the beginning before 128 s, a board peak was observed near \(q_y = 0\), which indicated formation of isolated lamellae in the dropped solution. From 128 s to 132 s, a shoulder peak appeared, shifted to the higher \(q_y\) of ca. 0.5 nm\(^{-1}\), and increased in intensity. After 132 s, the profile showed little change in intensity. This indicated that the flat-on lamellae and amorphous might alternatively be stacked preferentially in the perpendicular direction to the wafer surface after complete evaporation of the \(p\)-xylene. The long
period of this lamellar stacking structure estimated from the peak position was ca. 12 nm for the as-cast film.

The GISWAXS and Raman spectral data suggested that the crystallization behavior of PE chains in the solution casting process could be explained as the following. (1) Nucleation of the orthorhombic PE crystals occurred in the dropped solution during evaporation of the p-xylene from it. (2) The nucleuses grew to be isolated lamellar crystals. (3) After complete evaporation of the p-xylene from the dropped solution, PE chains in the amorphous state crystallized rapidly. (4) The lamellae oriented gradually flat-on with respect to the wafer surface. (5) Alternative stacking of the flat-on lamellae and amorphous occurs preferentially in the perpendicular direction to the wafer surface. (6) Lamellar stacking structure with the long period of ca. 12 nm was established in the as-cast film.

4. Conclusion

In this study, the time-resolved and simultaneous experimental method of synchrotron GISWAXS and Raman spectra has been established with 2D detectors at the BL45XU in SPring-8. On the basis of this method, nucleation, formation, alignment and orientation of PE crystals on silicon wafer substrates could successfully be traced in the solution casting processes on the molecular and lamellar scales. It was found that the p-xylene might play a very important role especially in crystal nucleation. After complete evaporation of the p-xylene from the dropped solution, crystallization of PE chains in the amorphous state and formation of lamellar stacking structure was enhanced. Time-resolved synchrotron GISWAXS experimental method can be applied to a various kinds of kinetic researches in the thin-film, surface, and interface science of polymeric materials from the academic and industrial viewpoints.

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