Evaluation of Block Copolymer Structure using Soft X-Ray Scattering

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In DSA pattern observation of hp 5 nm and below, the pattern observation method for physical and chemical structures is necessary. Scattering measurement of hard X-rays is one method which can quantitatively evaluate the physical structure of materials. However, when many components such as polymer materials are mixed, it can observe the averaged physical structure, and it is difficult to evaluate the structure of the individual chemical components. Thus, we developed a scattering measurement method using soft X-rays near the carbon absorption edge. Since the absorption spectrum varies in the near carbon absorption edge for each polymer molecule, the individual physical structures can be observed from the scattering profile with different photon energy. In this study, both the physical and chemical structures of the triblock terpolymers such as poly[isoprene-block-styrene-block-(2-vinylpyridine)] which consists of polyisoprene, polystyrene, and poly(2-vinylpyridine) were observed. The physical structure of the triblock polymer observed two types of the packed cylinder structures such as the tetragonal and hexagonal packed structures. The film thickness of this triblock polymer was 400 nm. By varying the photon energy of the scattering measurement, the scattering light intensity changed greatly, and the signal from each polymer could be evaluated. The soft X-ray scattering measurement at the near absorption edge can be measured the molecular structure of a composite material such as a blended polymer individually and can be utilized in material development.

Keywords: Soft X-ray scattering, DSA, Block copolymer, Synchrotron radiation, NEXAFS

1. Introduction

The directed-self-assembly (DSA) is one of the candidates for the advanced lithography of half pitch (hp) 5 nm and below to fabricate semiconductor devices. To achieve the pattern size of hp 5 nm and below, guide pattern which is replicated by EUV lithography is necessary. In DSA pattern observation of hp 5 nm and below, the pattern observation method is necessary.

In general, the X-ray absorption spectroscopy (XAS) is very powerful tool to evaluate the electronic state of each element of the chemical compound. We have developed this method for characterizing extreme-ultraviolet (EUV) resist materials at NewSUBARU BL-10 beamline [1-7]. Under EUV exposure, from the absorption peak value and the chemical shift in the X-ray absorption spectra, the chemical bonding changes can be estimated at the C_C region. As the result, it can be understood the EUV chemical reaction for advanced EUV resist materials by XAS measurement. Recently, evaluation of stochastic process in resist such as acid diffusion and its distribution, and distribution of functional groups become significant issue to achieve low line-edge-roughness. Thus, it is required to evaluate the chemical state and functional groups distribution in nanometer scale. If
the spatial resolution of XAS realize in nanometer scale, the stochastic which is own to the electron state of each element in the resist material can be captured by this high-spatial-resolution XAS. However, the X-ray beam size on sample was 0.1 mm in vertical and 0.8 mm in horizontal at the XAS measurement of BL-10 beamline. This beam size was very large to obtain the chemical density mapping of the resist polymer.

Recently, the scanning transmission soft X-ray microscope (STXM) has developed to observe images of the chemical mapping with 30 nm spatial resolution [8]. The soft X-ray beam is focused on a sample using a Fresnel zoneplate in small spot size, and transmission beam through the sample is detected to obtain the chemical mapping. STXM is very useful to image chemical state distribution.

Otherwise, the scattering measurement is benefit for observation of the physical structure. In X-ray region, small angle X-ray scattering (SAXS) is widely used for the physical structure analysis using the X-ray energy of 8 keV in usual.

In this study, soft X-ray scattering employed as a probe light with varied photon energy was employed to study the physical and chemical structures of a tri-block polymer. The scattering signal from the sample includes not only the information of the physical structure but also the information of the chemical structure. And the scattering signal intensity depends on the chemical state near the absorption edge. Wang et al. reported this scattering method of resonant soft X-ray scattering (RSoXS) for the measurement of the triblock terpolymers such as poly[1,4-isoprene-block-styrene-block-(2-vinylpyridine)]. The RSoXS is used for the measurement of spatial composition correlations in organic sample [9].

In this study, we have analyzed the physical structure of poly[isoprene-block-styrene-block-(2-vinylpyridine)] (ISP) triblock terpolymer blends. In this paper, isoprene, styrene, and 2-vinylpyridine polymers are represented as I, S, and P polymers, respectively. This terpolymer has cylinder structure of I and P polymers in S polymer. These samples were also measured by the transmission electron microscopy (TEM). The block copolymer consists of two or more covalently bonded polymer chains and self-assembles by microphase separation into a regular microstructure [10-12]. The 3-component block terpolymer is widely used for controlling morphology with a complicated microphase separated structure [13-24].

2. Materials and Methods

2.1. Measured sample

Figure 1 shows the triblock polymer samples with (a) hexagonal packed cylinders and (b) tetragonal packed cylinders, respectively. These sample were prepared by same method for the physical structure observation using TEM. The triblock polymer was packed by surrounding with epoxy resin. Thin packed sample were sliced to a thickness of 400 nm using a microtome. The ultrathin sections were floated on a water and transferred onto a Cu grid with having a center hole of 1.5-mm-diameter.

![Fig. 1. Photograph of the optical-microscope sample images of ISP triblock copolymers; (a) the hexagonal packed copolymer, and (b) the tetragonal packed copolymer.](image_url)
approximately 2500. The scattering measurement chamber using in this study is installed at 2.1 m downstream from the vertical and horizontal focal points in the beamline. The stage and the CCD camera which we have been used for a EUV microscope described in the paper [25].

Figure 2 shows a schematic diagram of the scattering measurement system which is installed at the BL-10 beamline.

A \( \Phi 100\mu m \) pinhole was used as an aperture for the soft-X-ray incident beam. The distance from the pinhole to the sample is 30 mm, and the distance from the sample to the CCD camera is 33 mm. The maximum acceptance angle is 24°, which corresponded to \( q_{\text{max}} \) of 0.59 nm\(^{-1}\) at 280 eV.

The scattering light from the sample is recorded by the CCD camera in vacuum. To cut off the direct light with strong intensity, a 1-mm-wide center-stop plate was set in front of the CCD camera.

The scattering angle and pitch of the sample structure are described by the following diffraction equation eq. (1).

\[
d \sin \theta = m \lambda \quad (1)
\]

Where \( d \) is the pitch of the cylinder structure, \( \theta \) is the scattering angle, \( m \) is the diffraction order, and \( \lambda \) is the wavelength of the incident soft X-ray.

3. Results and Discussion

3.1. Hexagonal packed cylinder

Figures 3(a)-(e) show scattering images of the hexagonal packed ISP triblock terpolymer at five photon energies of 280.0, 284.0, 285.6, 288.6, and 300.0 eV, respectively. And in each figure, the contour plots of the light intensity distribution is shown in logarithmic scale.

Figure 3(f) shows a TEM image of this terpolymer. The black circle, the grey circle, and the back white region indicate the I, P, and S polymers, respectively.

In the scattering images, the bright center region indicates scattering light from the incident pinhole. The outer region of this scattered light was blocked with the Cu grid hole. The black rectangle at the center region indicates shadow of the center block plate, which blocked the bright direct beam.

Two scattering signals with the ring-shape were recorded, with ellipse shape, not circle shape. The radius of horizontal direction was smaller than the vertical direction. This ellipse indicates that the sample is stretched along the horizontal direction. In addition, the ring-shape indicates that the domain size of the terpolymer is sufficiently smaller than the beam diameter of 100 \( \mu m \). This scatter signal is an averaged signal obtained from a small cylinder having a random direction.

The scattering intensity of scattered ring strongly depends on the incident photon energy. The outer ring signals were observed as shown in Fig. 3 (a), (b), and (c), the inner signals were observed as
shown in Fig. 3 (c), and (d). At the absorption energy of 285.6 eV which can be assigned as \( \pi^* \)
bonding of benzyl group, the scattering intensity of the two rings was strongest. The d-spacing of the outer ring was estimated to be 49 nm along the horizontal direction, and 39 nm along the vertical direction. The inner ring had \( \sqrt{3} \) times larger pitches. The d-spacing ratio and TEM image indicates that the outer and inner rings corresponded to the scattering from the P-P and I-P physical structures, and I-I physical structure. These structures are shown in Fig. 3(f).

Since scattering efficiency depends on not only the absorption but also the refractive index, it is hard to discuss the scattering signal only with the TEY result. However, the refractive index is closely related to the absorption, and the scattering intensity was strongly dependent on the absorption. At the RSoXS measurement, it is possible to obtain scattering signals distinguishing the polymer types by changing the probe photon energy.

This triblock polymer usually measured by the SAXS. However, the scattering signal includes only the I polymer physical structure in the S and P polymers. For the SAXS measurement, the photon energy is usually 8 keV. The S and P polymer has the same contrast. Thus, it is hard to achieve the P polymer physical structure information.

Figures 5 shows the scattering profiles of the hexagonal packed cylinders observed by seven photon energy conditions. The horizontal axis shows the scattering vector \( (q) \), which is shown in eq. (2).

\[
q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (2)
\]

The vertical axis shows the scattering intensity at the radial position. Since it is an ellipse rather than a circle, scattering intensity in vertical direction is shown in Fig. 5.

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As results, at the seven photon energy from 250.0 eV to 300.0 eV in Fig. 5, there are two peaks of inner and outer ring as shown in Fig. 3(a)-(e) around $q = 0.093 \text{ nm}^{-1}$ and 0.16 nm$^{-1}$, where these d-spacing of its physical structure width were 68 and 39 nm, respectively. The ratio of these peaks is exactly $\sqrt{3}$. The scattering intensity strongly depends on the photon energy. The scattering intensity ratio of the outer peak to the inner peak was also changed with varying the photon energy. For example, at the photon energy of 285.6 eV, the ratio was approximately 1, where the scattering signals were due to the P-P, I-P, and I-I polymer physical structures. At the photon energy of 288.6 eV, the scattering signal was mainly due to the I-I polymer physical structures because the intensity ratio was 0.4. The scattering contrast of the P polymer to the base S polymer was small. At the photon energies of 280.0 and 284.0 eV, the ratio was 6. The scattering signal was due to the P-P polymer physical structure. The scattering contrast of the I polymers to the base S polymer was very small. Thus, the RSoXS measurement resolved the I and the P polymer physical structures.

3.2. Tetragonal packed cylinder

Figures 6(a)-(e) show the scattering image of the tetragonal packed ISP triblock terpolymer. In each figure, the contour plots of the light intensity distribution is shown in logarithmic scale. Figure 6(f) shows the TEM image. Figure 7 shows the scattering profiles of the tetragonal packed cylinders observed by seven photon energy conditions.

In the scattering image of Figs. 6(a)-(e), there was no ring-shaped scattering like the hexagonal packed cylinders. Four scattering signals were recorded at each inner and outer region. This non-ring scattering indicates the domain size of this terpolymer was larger than the illumination size of 100 μm. The azimuth angle of the inner scatterings has 45°-difference from that of the outer scatterings. The scattering angle of the outer scatterings was approximately $\sqrt{2}$ times larger than that of the inner scatterings. The d-spacing of the inner scatterings was estimated to be 59 nm. The d-spacing of the outer scatterings was estimated to be 42 nm, which corresponded to that of the I-I and P-P physical structures.

Since the scattering angle ratio of the horizontal to vertical directions was approximately one, this terpolymer was not stretched. The scattering intensities of the inner four scatterings were symmetric, and asymmetric at the outer side. According to the previous hexagonal packed case, the P-P physical structure was observed without the information of the I-I and I-P structures at the photon energies of 280.0 and 284.0 eV. The outer
asymmetric scattering signal was due to nearest neighbor the P-P physical structure shown in Fig. 6(f). As a result, microdomain structure of the P polymer would have the lamellar structure, which caused this asymmetric scattering. This structure was not observed in the TEM image.

4. Conclusion

In the RSoXS, soft X-rays irradiate on a thin film sample, and a scattering signal corresponding to the structure of the sample material and the absorption/refractive index contrast is obtained. By changing the energy of incident light near the absorption edge, the contrast images of the constituent atoms, molecular structure, and chemical state can be obtained. Therefore, it is possible to distinguish each component of blend polymer having close density, and it is a method that can evaluate the structure of each molecule. Especially, it is possible to obtain very strong intensity with repetitive pattern and it is suitable for physical structure analysis of the triblock terpolymer.

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