Quantitative Synchrotron Grazing Incidence X-ray Scattering Analysis of Cylindrical Nanostructures in Supported Thin Films

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ABSTRACT

Nondestructive nanostructural analysis is indispensable in the development of nano-materials and nano-fabrication processes for use in nanotechnology applications. In this paper, we demonstrate a quantitative, nondestructive analysis of nanostructured thin films supported on substrates and their templated nanopores by using grazing incidence X-ray scattering and data analysis with a derived scattering theory. Our analysis disclosed that vertically oriented nanodomain cylinders had formed in 20–100 nm thick films supported on substrates, which were consisting of a mixture of poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) and PMMA homopolymer, and that the PMMA nanodomain cylinders were selectively etched out by ultraviolet light exposure and a subsequent rinse with acetic acid, resulting in a well-ordered nanostructure consisting of hexagonally packed cylindrical nanopores.

Keywords: grazing Incidence X-ray scattering, quantitative scattering data analysis, nanostructure template, porous nanocylinder

1 INTRODUCTION

Block copolymer thin films with well defined nanostructures have recently received considerable attention for their potential nano-fabrication applications [1,2]. In these applications, controlling the morphology of the block copolymer thin film, particularly the orientation and ordering of the phase-separated microdomain, is essential. For characterizing the structures and orientation, microscopy tools such as transmission electron microscopy, scanning electron microscopy and atomic force microscopy are commonly used [3]. With these tools, images such as those that show local structures near the surface have been obtained, thus enabling discussion of the underlying physics. From the viewpoint of fabrication, this approach is often sufficient, but from the scientific point of view, X-ray scattering measurements are required because only they provide information on a larger scale at high resolution. In particular, grazing incidence X-ray scattering (GIXS) has emerged as a powerful technique for characterizing internal structure of thin film [4]. The X-ray beam impinges at a grazing angle onto the sample slightly above the critical angle, so that the film is still fully penetrated by X-ray. Analytical solutions of GIXS patterns based on the distorted wave Born approximation have been developed to describe the complicated reflection and refraction effects [4], which are not found in conventional transmission X-ray scattering. Recently we derived a GIXS formula under the DWBA for analysis of the structures in thin films deposited on substrates [4,5]. Using the derived GIXS formula, the GIXS patterns obtained for polystyrene-*b*-polyisoprene diblock copolymer thin films with various morphologies (hexagonal, hexagonal perforated layer, and gyroid structure) deposited on silicon substrate were characterized quantitatively [5].

In this study, we fabricated cylindrical nanostructures in thin films by using a poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) mixed with a small amount of PMMA homopolymer, and investigated the nanostructures before and after selective etching of the phase-separated PMMA microdomains with the aid of ultraviolet (UV) light irradiation and a subsequent rinse with acetic acid (namely, UV-etching) by using GIXS with synchrotron X-ray radiation sources.

2 EXPERIMENTAL

In this study, three polymers were used. One is asymmetric PS-*b*-PMMA (f_{PMMA} = 0.25, volume fraction of the PMMA block) with a weight-average molecular weight ($\overline{M}_w$) of 73,000 and a polydispersity index (PDI) of 1.06 and the second one a random copolymer, PS-*r*-PMMA (f_{PMMA} = 0.60) with $\overline{M}_w$ = 9,600 and PDI = 1.80. The third

polymer is an atactic PMMA homopolymer with $\overline{M_w}$ = 31,800 and PDI = 1.08. A neutral brush layer was deposited on precleaned silicon substrates with a native oxide layer by spin-coating PS-*r*-PMMA solution and drying. The mixture of PS-*b*-PMMA/PMMA was then deposited on the substrates by spin-coating and drying in a vacuum oven at 170 °C for 2 days. For some films, the PMMA phase (PMMA microdomains plus PMMA homopolymer) was etched out as follows. The film was exposed to the UV light (λ=253.7 nm) of a UV lamp for 90 min in a vacuum chamber, developed by immersion in acetic acid for 1 h at room temperature, and then finally rinsed several times with deionized water. The patterned films were dried in vacuum for 12 h at room temperature. GIXS measurements were carried out at the 4C1 and 4C2 beamlines of the Pohang Accelerator Laboratory. An incidence angle of X-ray beam was 0.20°, which is between the critical angles of the films and the silicon substrates.

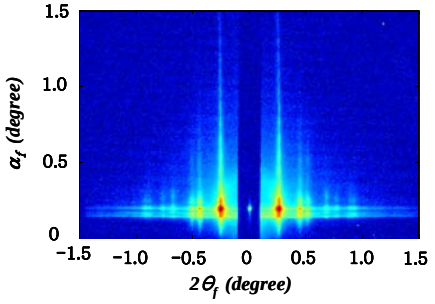

Figure 1: 2D GIXS patterns measured for a UV-etched film of PS-*b*-PMMA block copolymer.

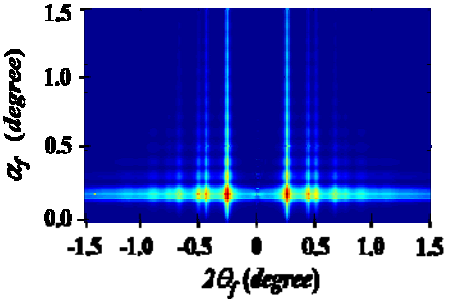

Figure 2: Calculated 2D GIXS patterns for a UV-etched film of PS-*b*-PMMA block copolymer using developed GIXS equation.

3 RESULTS AND DISCUSSION

A representative 2D GIXS pattern is shown in Figure 1, which was measured for a UV-etched film. All the measured scattering patterns can be satisfactorily fitted with a GIXS formula derived for hexagonal packed structures with orientation in thin films supported on substrates. From the quantitative analysis of the scattering data, the important structural parameters—cylinder shape, radius and radius distribution, length, center-to-center distance, orientation, degree of packing order, position distortion factor, electron density, and porosity—were precisely determined. The structural details provide important information about the microdomains formed in the thin PS-*b*-PMMA/PMMA films and the templated pores as follows.

First, the lengths of the cylindrical PMMA microdomains formed in the film are equivalent to the film thickness. For films of 28.5–78.8 nm thickness, the PMMA cylinders have radii in the range 11.0–11.4 nm with a radius distribution of 3.00–3.01 nm. These results confirm that the cylindrical PMMA microdomains are preferentially formed perpendicular to the film plane, i.e., they occupy the whole film thickness, and that the formation of these PMMA cylinders in the films occurs for film thicknesses in the range 28.5–78.8 nm.

Second, the lengths of the cylindrical nanopores templated in the UV-etched films are equivalent to the film thickness. The radii (11.7–11.8 nm) of the templated cylindrical nanopores in the etched films are comparable to those (11.0–11.4 nm) of the PMMA cylinders in the unetched films. The radius distribution (2.90–2.95 nm) of the templated cylindrical nanopores is also comparable to that (3.00–3.01 nm) of the PMMA cylinders in the unetched films. These results indicate that the UV-etching process effectively and selectively etched the cylindrical PMMA microdomains through the whole film thickness, resulting in cylindrical nanopores in the film.

Third, both the vertically oriented PMMA cylinders in the film, and their templated cylindrical nanopores, were found to laterally assemble to form a hexagonal paracrystal lattice with paracrystals that are rather randomly packed in the film plane. In addition, it was found that the cylindrical air-filled nanopores have a very sharp interface with the PS matrix.

Fourth, the critical angle of each thin film ($\alpha_{c,f}$) was determined from the analysis of its out-of-plane scattering profile. $\alpha_{c,f}$ was found to be 0.156° for the unetched films and 0.135–0.136° for the etched films. $\alpha_{c,f}$ is directly related to the electron density of the film ($\rho_{e,f}$). Using this relationship, the electron densities of the thin films were estimated from the $\alpha_{c,f}$ values: $\rho_{e,f}$ is 348 nm^{-3} for the unetched films and 261–265 nm^{-3} for the etched films.

Fifth, the porosities P_e of the UV-etched films can be estimated from the electron densities $\rho_{e,f}$ with respect to those of the unetched films. The obtained P_e values are in the range 25.3–26.6%, which are in good agreement with the volume per cent (26.7%) of the PMMA phase in the films before UV-etching.

Finally, by using these structural parameters, we attempted to calculate the 2D GIXS patterns using the GIXS formula for the model of the hexagonal paracrystal

lattice of cylinders. A representative result is presented in Figure 2.

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REFERENCES

[1] P. Mansky, P. Chaikin, and E. L. Thomas, J. Mater. Sci., 30, 1987, 1995.

[2] a) M. Park, C. K. Harrison, P. M. Chaikin, R. A. Register, and D. H. Adamson, Science, 276, 1401, 1997. b) S. Herrninghaus, K. Jacobs, K. Mecke, J. Bischof, A. Fery, M. Ibn-Elfraj, and S. Schlagowski, Science, 282, 916, 1998.

[3] a) E. Schaffer, T. Thurn-Albrecht, T. P. Russell, and U. Steiner, Nature, 403, 874, 2000.

[4] a) B. Lee, Y.-H. Park, Y.-T. Hwang, W. Oh, J. Yoon, and M. Ree, Nature Mater., 4, 147, 2005. b) B. Lee, W. Oh, Y.-T. Hwang, Y.-H. Park, J. Yoon, K. S. Jin, K. Heo, J. Kim, K.-W. Kim, and M. Ree, Adv. Mater., 17, 696, 2005. c) B. Lee, W. Oh, J. Yoon, Y. Hwang, J. Kim, B.G. Landes, J.P. Quintana, and M. Ree, Macromolecules, 38, 8991, 2005. c) B. Lee, J. Yoon, W. Oh, Y.-T. Hwang, K. Heo, K. S. Jin, J. Kim, K.-W. Kim, and M. Ree, Macromolecules, 38, 3395, 2005.

[5] a) B. Lee, I. Park, J. Yoon, S. Park, J. Kim, K.-W. Kim, T. Chang, and M. Ree, Macromolecules, 38, 4311, 2005. b) I. Park, B. Lee, J. Ryu, K. Im, J. Yoon, M. Ree, and T. Chang, Macromolecules, 38, 10532, 2005.