The morphological change in block copolymer thin films analyzed by SCF simulation.

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薄膜におけるブロック共重合体のミクロ相分離構造は、膜厚や表面自由エネルギーにより通常バルク状態とは異なる多様な構造を示す。例えば，バルク状態にてシリンダー構造を呈するブロック共重合体が、膜厚によっては球構造を呈する場合がある。この実験では、構造形成初期にみられるシリンダードメインの格子歪みが構造変化を誘起していると予測されている。本研究では、self-consistent field (SCF) theory に基づいたシミュレーションによりシリンダー構造と球構造の Helmholz 自由エネルギーを格子歪みの関数として計算し、薄膜中の構造の安定性に関する検討を行った。

1 Introduction

The microphase-separated structures in a block copolymer thin film depend on the confinement of the film thickness and the surface energy unlike those of bulk state [1]. Although a considerable number of studies have been carried out on a such thin films of block copolymer, less is known about the process of self-assembly in block copolymer thin films. Recently, we reported that a process of three-dimensional (3D) structural formation in a block copolymer thin film which forms lamella microdomains in the bulk state was studied by transmission electron microtomography (TEMT)[2]. The TEMT is an effective tool to characterize 3D structures so that it could obtain structural information not only lateral but also depth directions of the thin film. In this study, the evolution of the microphase-separated structure in a block copolymer thin film which exhibits cylindrical microdomains in the bulk state was explored by TEMT. In addition, we investigated the free energy of the system using simulations based on self-consistent field (SCF) theory.

2 Experiments

The sample was poly(styrene-*block*-isoprene) (SI) [M_n=5.1×10^4, M_w/M_n=1.06] which forms cylindrical structure in the bulk state. A mica substrate was cleaved and then coated with carbon by vacuum deposition in advance. SI thin films were prepared by spin-coating from 2 wt % toluene solution of the SI copolymer onto the mica substrate. The copolymer film (ca. 100 nm) on the substrate was further annealed at 120 °C for 48, 96 and 150 hours under vacuum.

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Annealed thin films were floated off the mica substrate and picked up onto Cu mesh grid. Thin films were stained with OsO_4 vapor for 30 min to enhance the contrast under transmission electron microscopy (TEM) and TEMT. Prior to the TEMT and TEM experiments, gold particles of 10 nm diameter were deposited from aqueous suspension. Series of TEM images were acquired at tilt angles ranging from -60° to 60° in 1° increments and aligned by fiducial marker method and then reconstructed on the basis of the filtered-back projection method. The SCF simulation was carried out with OCTA to calculate free energy of the system [3]. The simulation condition is shown that the scheme of cylindrical or spherical lattice at Figure 1. Modifying inter-layer distance and inter-domain distance, we evaluated the stability of cylindrical and spherical structures in this system.

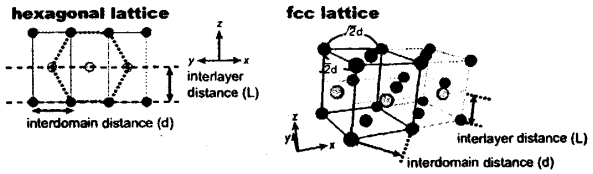

Figure 1: The schematic illustration for SCF calculation condition of cylindrical or spherical lattice.

3 Results and discussion

3D structures of the thin film formed bicontinuous-like structures right after the spin-casting. Upon annealing, the initial structure transformed into cylindrical microdomains of the lateral direction of the thin film (see Figure 2 (a)), and further to spherical microdomains. Final equilibrated morphology was FCC sphere (see Figure 2 (b)). Clarifying those structures with TEMT, we expected that the distortion of hexagonal lattice of PI cylinders just before morphological change drove cylindrical structures of PI in thin films and transformed to spherical structures. Figure 2 (c) shows that the phase diagram of the equilibrium state obtained by SCF simulations under the condition of the distortion of hexagonal lattice. Simulation results approximately agreed with experimental results and suggested that the morphological change was caused by the distortion of hexagonal lattice which was attributed to the confinement of the film thickness.

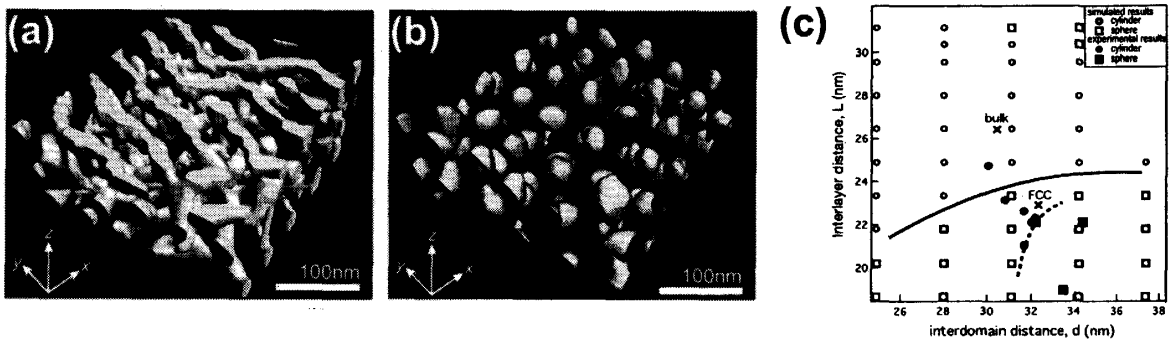

Figure 2: 3D reconstructed images of the thin films after annealing at 120°C for (a) 48 hours, (b) 150 hours. White phase corresponds to PI phase. Z direction corresponds to depth direction of the thin film. (c) The phase diagram of the equilibrium state by SCF calculation.

References

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[3] Using OCTA http://octa.jp