Epitaxial Self-Assembly of Block Copolymer Thin Film for Nanofabrication

*Sang Ouk Kim**

Department of Materials Science & Engineering, Korea Advanced
Institute of Science & Technology (KAIST), Daejeon, Korea
sangouk.kim@kaist.ac.kr

Introduction

Self-assembled nanostructures of block copolymer thin films have gathered significant attention due to their potential applications as templates for the fabrication of photonic bandgap materials [1], ultrahigh density nanodots [2,3] or nanowire arrays [4,5], memory and capacitor devices [6] and nanopatterned substrates for biosensors. Despite its advantages such as parallel processing, molecular level resolution, and the capability to generate three dimensional structures, the practical application of block copolymer thin films has been limited. The lack of a robust strategy to control the structure formation in thin film geometries has been considered a major obstacle. Various methods such as graphoepitaxy [7], neutral treatment of surface [8], application of external fields [4], directional solidification, solvent aging, etc. have been developed to control the nanostructures of block copolymer. A new hybrid technique to control the self-assembled nanostructure of block copolymer has been developed and will be presented. Chemically patterned surface prepared by advanced lithography successfully registered nanodomains in block copolymer thin film without any single defect [9,10].

Experimental

Phenethyltrichlorosilane (PETS) self-assembled monolayer (SAM) or hydroxyl-terminated polystyrene was deposited on the native oxide layer of silicon wafer as an imaging layer for chemical patterning. A thin layer (50 ~ 80 nm) of photoresist (PMMA) was spin coated on the imaging layer deposited surface and patterned by advanced lithographic techniques such as EUV interferometric lithography or E-beam lithography. The topographic pattern in the photoresist was replicated into a chemical pattern in the imaging layer by high flux X-ray radiation or oxygen plasma treatment. The imaging layer not protected by the photoresist was selectively oxidized to form a polar region of pattern, whereas the protected part does not undergo any chemical change. After removing the photoresist by solvent washing, the thin film (thickness: 40 ~ 60 nm) of symmetric block copolymer (PS block: 50 kg/mol, PMMA block: 54 kg/mol, lamellar period: 48 nm) or its blends with PS and PMMA was spin-coated on the patterned surfaces and annealed at a high temperature for a sufficiently long time. The finally obtained self-assembled nanostructures of block copolymer in thin films were characterized by Scanning electron microscopy (LEO 1550 VP field emission SEM).

Results and discussion

Figure 1 illustrates the procedure to prepare well-defined block copolymer nanopattern. The topographic pattern of photoresist was transferred into the chemical pattern of imaging layer by selective oxidation using X-ray radiation or oxygen plasma treatment. Comparing the finally obtained block copolymer pattern with photoresist pattern revealed that block copolymer forms well-aligned defect-free structure when the surface pattern was well-prepared.
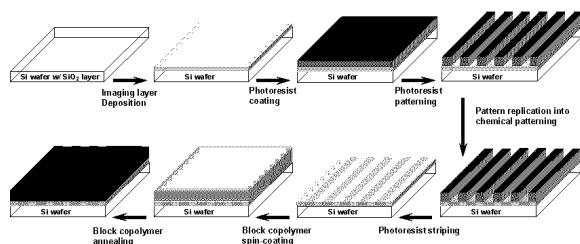

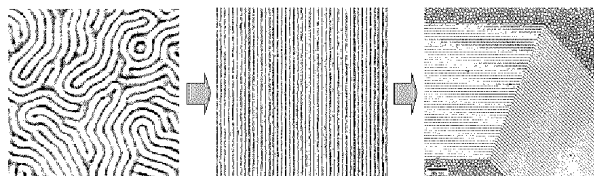Figure 1. Schematic representation of the procedure for 'epitaxial self-assembly'

Figure 2. SEM images of the spontaneously self-assembled lamellar structure with disordered arrangement of lamellae (left), the epitaxially self-assembled defect-free lamellae (middle) and epitaxially directed nested array of lamellae (right) in block copolymer thin films.

Figure 2 compares spontaneously formed and epitaxially directed lamellar structures of block copolymer thin films. The spontaneously assembled structure (Fig. 2 left) showed the disordered arrangement of lamellae with a high density of defects. Predominantly low energy defects such as edge dislocations and $\pm 1/2$ disclinations appeared as well as a small number of +1 disclinations. In contrasts, lamellae formed well-aligned defect-free structure on the chemically patterned surfaces provided that the surface pattern period was commensurate to the natural lamellar period of the block copolymer (Fig. 2 middle). Lamellae were perfectly registered due to the preferential wetting of each block to a particular part of surface pattern. When the surface pattern and lamellar periodicities were incommensurate, however, various new structures were found (not shown here). When the surface pattern was slightly narrower than the lamellar period, a defect structure of dislocation dipole appeared. Several curved layers were enclosed by a pair of oppositely directed edge dislocations, maintaining a minimized layer distortion outside of the dipole. If the surface pattern was slightly wider than the lamellar period, lamellae were tilted away from the surface normal direction to form an undulated morphology at the free boundary of the top side of film [11].

In order to maximize the opportunity for the practical application of block copolymer lithography to device fabrication, self-assembly of block copolymer was tested on device-oriented nonregular shaped surface patterns. Arbitrary shaped surface patterns were fabricated by e-beam lithography followed by oxygen plasma treatment. Lamellar structure of block copolymer was successfully adapted to various nonregular shaped patterns including nested arrays of lines with sharp bends (Fig. 2 right).

Conclusions

Epitaxial self-assembly of lamellar structure in PS-b-PMMA thin film was achieved by a hybrid approach combining bottom-up approach of block copolymer self-assembly with top-down approach of advanced lithographic techniques. The nanostructures having ~25 nm periodicity could be prepared without any defects over an arbitrarily large area. Moreover, nonregular device oriented structures could be prepared, which opened up new opportunities for nanofabrication.

References

[1] V. Z.-H. Chan, et al., *Science* **1999**, 286, 1716.
[2] M. Park, C. Harrison, P. M. Chaikin, R. A. Register, D. H. Adamson, *Science* **1997**, 276, 1401.
[3] J. Y. Cheng, C. A. Ross, Z.-H. Chan, E. L. Thomas, R. G. H. Lammertink, G. J. Vansco, *Adv. Mater.* **2001**, 13, 1174.
[4] T. Thurn-Albrecht, et al., *Science* **2000**, 290, 2126.
[5] W. A. Lopes, H. M. Jaeger, *Nature* **2001**, 414, 735.
[6] C. T. Black et al., *Appl. Phys. Lett.* **2001**, 79, 409.
[7] R. A. Segalman, H. Yokoyama, E. J. Kramer, *Adv. Mater.* **2001**, 13, 1152.
[8] P. Mansky, Y. Liu, E. Huang, T. P. Russell, C. J. Hawker, *Science* **1997**, 275, 1458.
[9] S. O. Kim, H. H. Solak, M. P. Stoykovich, N. J. Ferrier, J. J. de Pablo, P. F. Nealey, *Nature* **2003**, 424, 411.
[10] M. P. Stoykovich, et al., *Science* **2005**, 308, 1442.
[11] S. O. Kim, et al., *Macromolecules* under revision.