Nanoporous Structure Fabrication in Selective Areas by Block Copolymer Self-Assembly and Electron Beam Lithography

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1. Introduction

This paper proposed a facile method to fabricate nanoporous structures in selective areas by block copolymer self-assembly and electron beam lithography. The block copolymer self-assembly is a promising method to fabricate periodic nanostructures such as sphere, cylinder or lamellar in a large area [1]. In particular, perpendicularly oriented cylinder structures to a substrate have been used as templates for a number of applications, including photonic crystals [2-3], nanowires [4], nanodot arrays [5-6], magnetic storage devices [7-8], and nanomembrane filters [9]. Perpendicular orientation of cylinder forming block copolymer is held by means of surface neutralization [10-11], chemical patterning [7-8, 12], solvent annealing [13-14], graphoepitaxy [15], and electric fields [4]. In order to apply many devices, partially control of nanoscopic patterns is important. Methods to selectively control block copolymer nanostructures are partially modified substrate [16-17], nanoimprint [18], photo lithography [19-20], UV irradiation [21-22] and electron beam irradiation [23-24]. In these methods, however, it is still difficult to localize or partially change the morphology of the structures, and less common polymers are used as the case may be. Therefore applications are limited in scope.

Polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) is one of commonly-used block copolymers in block copolymer self-assembly [4-5, 7-13, 15-18]. PMMA is well-known as a positive tone resist [12] and PS is used as a negative tone resist [25-26]. In this paper, we used PS-b-PMMA thin films as a resist for electron beam lithography. We fabricated thin films of perpendicularly oriented PMMA cylinders in a PS matrix onto a substrate [10]. These thin films were irradiated by electron beam to pattern the structures. In exposed areas, PS gets cross-linked, and PMMA degraded. After electron beam irradiation, thin films were developed by solvent, which dissolves both PS and PMMA. Therefore, cylindrical nanopores of PS remained only in the exposed areas after development. Here, we demonstrated the simple method for fabricating periodic nanoporous structures in selective areas.

2. Experimental Methods

2.1 Materials

We used cylinder forming PS-b-PMMA (PS 46.1 kg/mol, PMMA 21 kg/mol) and hydroxyl terminated PS-random-PMMA (PS-r-PMMA, 5.3 kg/mol, PS 61.7 %). Polymers were purchased from Polymer Source, Inc.

2.2 Block copolymer self-assembly

Si wafers were cleaned by UV irradiation (UL0-6Q, USHIO Inc. Peak wavelengths are 184.9 nm and 253.7 nm). Solutions of hydroxyl terminated PS-r-PMMA in toluene (1.5 wt%) were spin-coated at 4000 rpm onto cleaned Si wafers and annealed at 175 °C for 2 days under vacuum. The substrates were sonicated in toluene to remove ungrafted polymer.

On these PS-r-PMMA grafted wafers, solutions of cylinder forming PS-b-PMMA in toluene (1.0 wt%) were spin-coated to produce films with the thickness of 20 ~ 25 nm. These coated thin films were annealed at 190 °C for 1 day under vacuum to
2.3 Electron beam lithography

The electron beam lithography was performed onto PS-b-PMMA thin films. In exposed areas, electron beam irradiation induces the degradation of PMMA cylinders and cross-link of a PS matrix (Figure 1b). After exposure, thin films were developed by O-xylene for 2 min, and rinsed by hexane for 5 s and IPA for 2 min. O-xylene dissolves both PS and PMMA. Therefore, nanoporous structures were fabricated only in exposed areas after development (Figure 1c).

We used ELS7500 electron beam writing system (ELIONIX Inc.). The acceleration voltage, beam current and electron dose were 50 kV, 1 nA, 0.5~25 mC/cm², respectively. Draw patterns were square and line patterns (width: 1 μm, pitch: 2 and 5 μm). The structures were observed by AFM (SPA-400, SII NanoTechnology Inc.).

![Figure 1. Schematic illustration of nanoporous structures fabrication in selective areas:](image)

(a) Spin-coating and annealing PS-b-PMMA onto PS-r-PMMA modified substrate to form vertical PMMA cylinders in a PS matrix. (b) When these thin films were irradiated by electron beam, PS gets cross-linked, and PMMA degraded in exposed areas. (c) After development by O-xylene, nanoporous structures of PS remained only in irradiated areas.

3. Results

3.1 Results of line pattern

AFM height images of line pattern were shown in Figure 2.

(1) Electron dose < 2 mC/cm² (Figure 2a, 2d),

In exposed areas, nothing, void or normal lines were observed, and nanoporous structures were not observed. The measured width of line was 950 ~ 1200 nm, and was increased relative to electron dose. In non exposed areas, subtle surface roughness was measured (1 ~ 3 nm).

(2) 2 mC/cm² ≤ electron dose < (pitch 2 μm) 2.5 mC/cm², (pitch 5 μm) 4 mC/cm² (Figure 2b, 2e).

In exposed areas, nanoporous structures were observed (diameter: 20 nm, pitch: 40 nm). The measured width of line was 1100 ~ 1230 nm. In non exposed areas, surface in (2) was rougher than that in (1). Surface roughness was 2 ~ 5 nm.

(3) Electron dose ≥ (pitch 2 μm) 2.5 mC/cm², (pitch 5 μm) 4 mC/cm² (Figure 2c, 2f).

In exposed areas, nanoporous structures were observed (diameter: 20 nm, pitch: 40 nm). Nanopores of PS in (3) were clearer than those of PS in (2). The measured width of line was 1150 ~ 1300 nm. In non exposed areas, polymer residues remained.

![Figure 2. Results of line pattern (a-c): pitch 2 μm, d-f): pitch 5 μm): a), d): 1.5 mC/cm², b), e): 2 mC/cm², c): 2.5 mC/cm², f): 4 mC/cm²](image)

3.2 Results of square pattern

AFM height images of square pattern were shown in Figure 3.

(1) Electron dose < 3 mC/cm² (Figure 3a, 3d),

In exposed areas, nothing, void or normal squares were observed, and nanopores of PS were not observed. The measured width was 980 ~ 1180 nm, and was proportional to electron dose. In non exposed areas, subtle surface roughness was measured (1 ~ 3 nm).

(2) 3 mC/cm² ≤ electron dose < (pitch 2 μm) 5 mC/cm², (pitch 5 μm) 15 mC/cm² (Figure 3b, 3e).

In exposed areas, nanoporous structures were observed (diameter: 20 nm, pitch: 40 nm). The measured width was 1100 ~ 1300 nm. In non exposed areas, surface roughness was increased relative to electron dose, and was 2 ~ 5 nm.

(3) Electron dose ≥ (pitch 2 μm) 5 mC/cm², (pitch
5 μm) 15 mC/cm² (Figure 3c, 3f).

In exposed areas, nanoporous structures were observed (diameter: 20 nm, pitch: 40 nm). Nanopores of PS in (3) were sharper than those of PS in (2). The measured width was 1140 ~ 1350 nm. In non exposed areas, polymer residues remained. Figure 3. Results of square pattern (a)-c): pitch 2 μm, d)-f): pitch 5 μm): a), d): 2 mC/cm², b): 3 mC/cm², c), e): 5 mC/cm², f): 15 mC/cm²

4. Discussion

First, we will discuss polymer residues. At high electron dose, copolymer residues remained in non exposed areas (Figure 2c, 2f, 3c, 3f). The residues of pitch 2 μm were more than those of pitch 5 μm without relation of draw pattern. The relation between height of structures (pitch 5 μm) and electron dose was shown in Figure 4a. The thickness of sample was 23 nm. In line pattern, the height was increased from 0 to 3.5 mC/cm². Measured maximum thickness was 22 nm. The difference of initial thickness is considered the error of measurement. At over 4 mC/cm², height of nanostructures was less than initial thickness, and was decreased relative to electron dose. At 25 mC/cm², nanoporous structures were observed in non exposed areas (Figure 4b). These results suggest that the electron backscattering cause polymer residues or nanoporous structures in non exposed areas. If you want to lessen the electron backscattering effect, electron beam lithography needs to be performed at the proper electron dose.

Second, we would like to examine the difference of draw pattern. When the electron dose was insufficient, nanopores of PS were not observed (Figure 2a, 2d, 3a, 3d). If you look at Figure 4a, the adequate electron dose of line pattern was lower than that of square pattern. It is likely to be due to the area of lithography pattern. When areas of draw pattern are large, the proximity effect of electron beam lithography enlarges, and the adequate electron dose lessens.

![Graph showing relationship between electron dose and structure height]

Finally, we will discuss the width of nanoporous structures. The measured width after lithography was 10 ~ 30 % longer than the width of lithography pattern (1 μm). The magnified figures are shown in Figure 5. At proper electron dose, at which the electron backscattering effect was low, nanoporous structures were not observed at the edge of structures (Figure 5a). The measured width of nanoporous structures was 1000 ~ 1080 nm. These values were close to the width of lithography pattern (1 μm). However, at high electron dose, at which the electron backscattering was high, the width of nanoporous structures was equal to the whole width of structures (Figure 5b). The possible causes are the proximity effect, the electron beam backscattering and the tail of electron beam. We are sure that these effects enlarge the whole width of structures. These results suggest that the width of nanoporous structures is controllable.

5. Conclusion

In this paper, we demonstrated nanoporous structure fabrication in selective areas by block copolymer self-assembly and electron beam lithography. We examined the relationship between the height and the electron dose, and found the proper electron dose in this process. If you operate the electron beam lithography at the proper electron dose.
dose, you can control the width of nanoporous structures. In conclusion, this novel method is a promising tool to fabricate selective nanoporous structures.

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References