Electron Beam Lithography by Using Self-Assembled Block Copolymer Thin Films as Positive/Negative Tone Combined Resist

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This paper describes electron beam lithography by using both positive and negative tone mixed films as resist. By this method, we fabricated nanoporous structures only in selective areas whose minimum size was about 100 nm×100 nm.

We used polystyrene-block-poly (methyl methacrylate) (PS-b-PMMA, PS 46.1 kg/mol, PMMA 21 kg/mol) as a resist for electron beam lithography to fabricate nanoporous structures. Figure 1 illustrates lithography processes in this study. A 1.0 wt% solution PS-b-PMMA in toluene was spin coated onto a random copolymer modified Si substrate (PS-r-PMMA, 5.3 kg/mol) to yield 20-25 nm thick films. After annealing at 190 ˚C for 24 h, perpendicular PMMA cylinder structures were fabricated in a PS matrix. The thin films were irradiated by electron beam to pattern the structures. PMMA is widely known as a positive tone resist and PS is used as a negative tone resist[1]. Therefore, cylindrical nanopores of PS remain only in the exposed areas.

Electron beam lithography was operated at 50 kV, 1 nA, PS-b-PMMA thin films were developed by xylene, which dissolves both PS and PMMA, rinsed by hexane and isopropyl alcohol (as shown in Figure 2). We fabricated square patterns (length: 10-1000 nm) and spot patterns by electron beam lithography, and observed structures after development.

Dose curves are shown in Figure 3. When the length of draw pattern is decreased, the adequate electron dose in order to fabricate nanoporous structures is increased. We found the following relationships between normalized thickness and nanoporous structures.

- Normalized thickness > 0.5: Nanopores of PS were clearly observed.
- 0.3 < Normalized thickness < 0.5: Nanoporous structures were unclearly observed and it is difficult to focus SEM images.
- Normalized thickness < 0.3: Void lithography pattern was observed and nanoporous structures were not observed.

A part of our fabricated nanoporous structures is shown in Figure 4. The length of the patterned area was generally 10-20 % longer than draw pattern depending on electron dose. We could fabricate nanoporous structures over 2 dots at selective areas in adjusting draw pattern and electron dose.

In conclusion, we demonstrated new electron beam lithography for fabrication of nanoporous structures in selective areas.

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[1] S. Manako, J. Fujita, Y. Ochiai, E. Nomura, and S. Matsui, Jpn. J. Appl. Phys. 36, 7773 (1997).

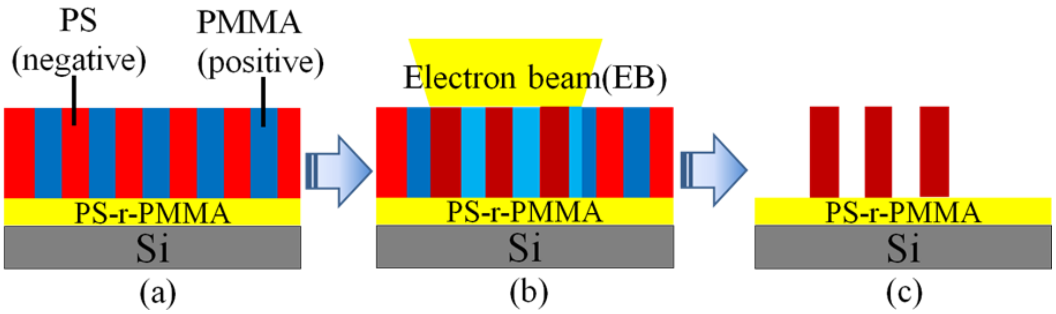

Figure 1: Schematic illustration of electron beam lithography by using PS-b-PMMA thin films as positive/negative tone combined resist: (a) Thin films of perpendicularly oriented PMMA cylinders were fabricated onto PS-r-PMMA modified substrate. (b) When these thin films were irradiated by electron beam, PS gets crosslinked and PMMA degraded in the exposed areas. (c) After development by xylene and rinse by hexane and isopropyl alcohol, nanoporous structures of PS remain only in the exposed areas.

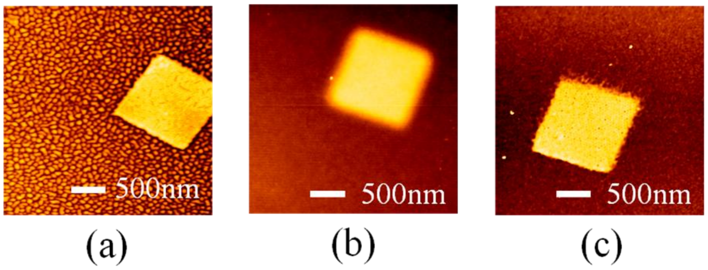

Figure 2: AFM image (height) at difference of rinse condition: Lithography:length is 1 μm, dose: 3.5 mC/cm^2. (a) isopropyl alcohol, (b) hexane, (c) hexane, followed by rinsing by isopropyl alcohol. In (a), residues remained at non irradiation areas. In (b), nanoporous structures were not observed in exposed areas. (c) is a better condition.

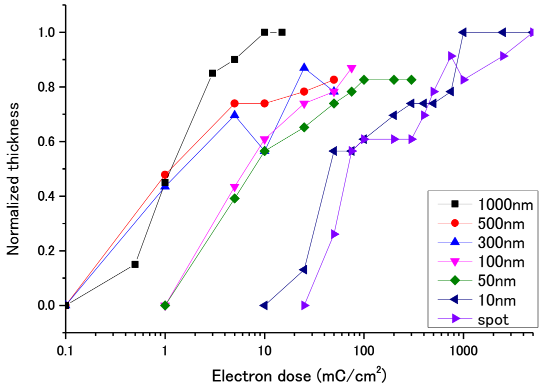

Figure 3: Dose curves for various draw pattern: Normalized thickness = resist height (after development) / resist height (initial)

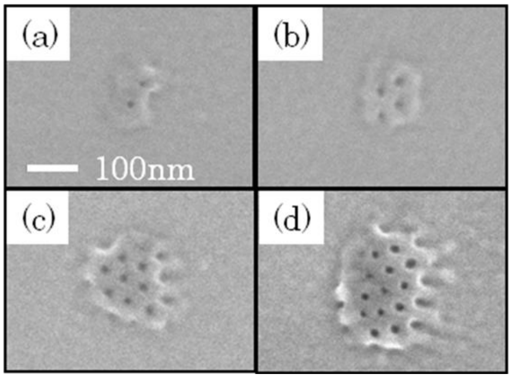

Figure 4: SEM image after development: a) spot, 200 mC/cm^2, b) 10 nm, 75 mC/cm^2, c) 50 nm, 50 mC/cm^2, d) 100 nm, 25 mC/cm^2