Etching Process for Patten Transfer from Sphere-type PMMA-*b*-PMAPOSS Block Copolymer

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Directed self-assembly of block copolymer (BCP) is known as a technology for forming a well-aligned high-density pattern. If the BCP pattern can be transferred to a silicon substrate accurately, the substrate can be used as an imprint mold. A directed self-assembled dot pattern with a 4.6 Tdot/in² density was demonstrated using PMMA-*b*-PMAPOSS¹, and the BCP is applicable to the fabrication process² of high-density bit patterned media. However, an increase in the dot size distribution during the pattern transfer process is a concern because PMMA has spherical structure in the PMAPOSS matrix. In this study, we developed an etching process for the pattern transfer from PMMA-*b*-PMAPOSS that has PMMA spheres.

The PMMA-*b*-PMAPOSS and hard-mask films were coated on a Si substrate. The PMMA spheres align at 18.1-nm-pitch hexagonal close-packed position. Figure 1 shows the scanning electron microscope (SEM) image of the BCP. The average dot diameter and standard deviation (sigma) were 10.0 and 1.8 nm, respectively. A selective etching of the BCP, a hard-mask etching with a PMAPOSS mask, and Si substrate etching with a hard-mask were carried out for the pattern transfer.

High selectivity etching is profitable for the BCP because the BCP layer is very thin at less than 20 nm. However, low selectivity etching is also required to remove the PMAPOSS layers because these layers exist at the top and bottom of the PMMA sphere. We call this process the multi-step method. On the other hand, if positions of the PMMA spheres have variations in vertical direction to the film surface, it will probably generate a dot size distribution. Therefore, we suggest a single-step method with a proper etching selectivity. According to a calculation of the dot size distribution, if the sphere position sigma is more than 5% of the BCP thickness, using a single-step method with a selectivity of three has an advantage over the multi-step method. Figures 1 (a) and (b) show the SEM images of the transferred pattern. Figure 2 shows a histogram of the dot size distribution. Table 1 lists the average dot diameter, sigma, and defect ratio. As a result, we found that the pattern could be transferred while maintaining the dot size dispersion by using a single-step method for the BCP etching, even if there was a large dispersion of the PMMA sphere position.

¹ H. Yoshida *et al.*, 37th International Conference on Micro and Nano Engineering (2011). Tada *et al.*, Macromolecules, in press, DOI: 10.1021/ma201822a.

² T. Hirai *et al.*, Advanced Materials (2009), **21**(43), 4334-4338.



Figure 1: SEM micrograph of (a) initial PMMA-b-PMAPOSS, (b) transferred pattern on hard mask via multi-step method, and (c) transferred pattern on silicon via single-step method.



Figure 2: Dot size distribution of initial BCP and transferred patterns.

		Initial PMMA-b- PMAPOSS	Multi-step method	Single-step method
Dot diameter	Average	10.0 nm	12.2 nm	12.3 nm
	Standard deviation	1.8 nm	4.1 nm	1.9 nm
Defect ratio		-	38%	2%

Table 1: Average dot diameter, standard deviation, and defect ratio of initial BCP and transferred patterns

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