Hexagonal Dot Pattern Fabrication by Self-assembled Colloidal Silica Grafted with a Concentrated Polymer Brush

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Directed self-assembly (DSA) has been attracting much interest for bottom-up lithography using diblock copolymer (BCP) or colloidal particles [1, 2]. DSA provides a simple process for making large-area periodic nanostructures, which are expected to be suitable for pattern-templates for photonic devices, patterned media, nonvolatile memories, and logic devices. DSA using BCP has an advantage for the fine pattern such as below 20 nm due to controllability of polymer-chain length by chemical synthesis. However, it is difficult to realize the pattern size of over 50 nm with BCP because of the difficulty of phase separation, and also BCP has issues concerning durability as an etching mask. In contrast, inorganic colloidal particles have strong durability for the etching mask, and can realize the diameter of over 50 nm. We have formed well-ordered single layer non-close-packed hexagonal dots pattern on Si substrate using polymer grafted Au particles (diameter of 10 nm) by the dip coating method [3].

In the present work, we investigated the fabrication of non-close-packed hexagonal dot pattern by self-assembly of polymer grafted silica particles. The silica particles with a diameter of about 130 nm were surface-modified with polymethyl methacrylate (PMMA) by reversible addition–fragmentation chain transfer polymerization. The two kinds of PMMA were grafted to silica particles, and their molecular weights are 59 kg/mol and 120 kg/mol respectively. Figure 1 shows SEM top-view images of assembled particles with non-close packed hexagonal pattern before and after PMMA etching. The ordered pitches of silica particles grafted with 59 kg/mol and 120 kg/mol are about 220 nm and 275 nm respectively. And their standard deviations are 7.1 nm (C.V. value of 3.2%) and 22.0 nm (C.V. value of 8.0%) respectively. The non-close packed hexagonal assembly was achieved by the polymer-grafted silica particles in large area of over 1 μm^2, and the pitch of the assembled particles was controlled by the molecular weight of the grafted polymer. We also discuss results of solvent annealing for better ordering and the pattern transfer onto the substrate.

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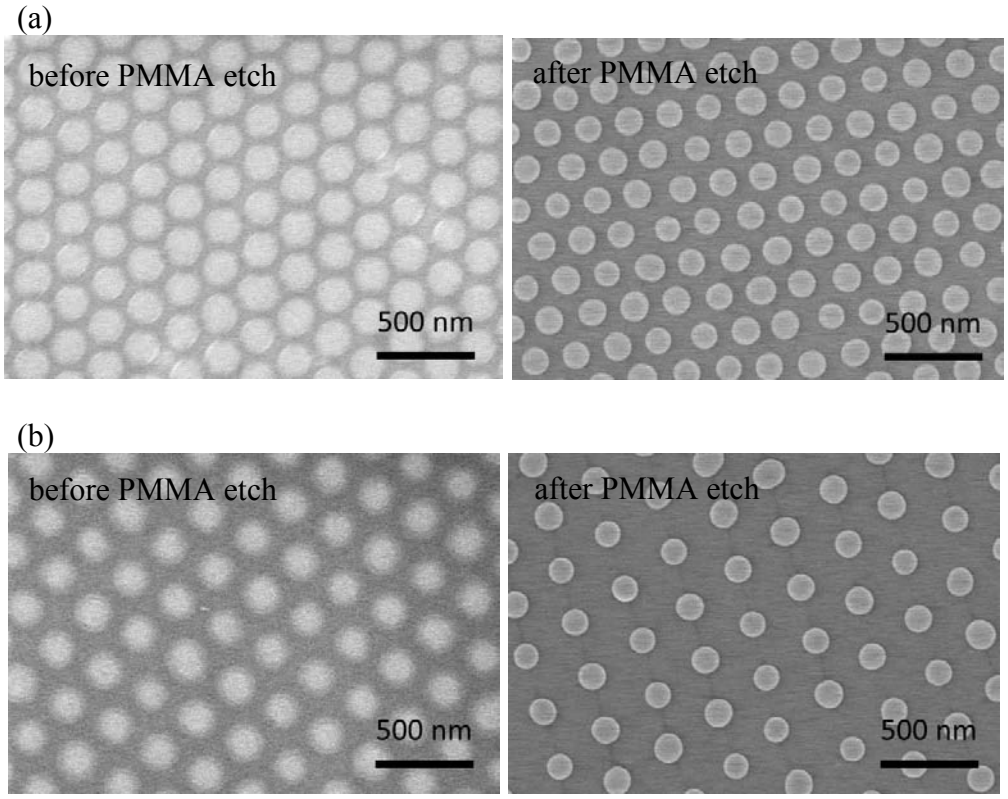

Fig.1 SEM top-view of a monolayer film of silica particles grafted with (a) Mn=59 kg/mol and (b) Mn=120 kg/mol PMMA respectively. The left and right images correspond to before and after PMMA removal by O_2 dry etching respectively. The ordering pitch of silica particles is about 220 nm and 275 nm respectively depending on the molecular weight of grafted PMMA.