Directed Self-assembly with Density Multiplication of POSS-Containing Block Copolymer via Controlled Solvent Annealing

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Directed self-assembly of block copolymers (BCP)[1] on lithographically defined chemical-contrast templates is perceived as a promising route to high density patterns with sub-lithographic resolution. However, multiple challenges still exist in fabricating high-density patterns beyond one tera-dot/in^2 (Tdpsi) with sufficient uniformity and placement accuracy for lithographic applications. Here, we report directed self-assembly in excess of 3 Tdpsi with improved fidelity employing optimized solvent annealing of strongly segregating polyhedral oligomeric silsesquioxane (POSS) containing BCP.

Poly(methyl methacrylate-*b*-methacrylate POSS), PMMA-*b*-PMAPOSS, was synthesized by living anionic polymerization.[2] A sparse chemical contrast template was prepared by electron beam lithography on a polystyrene layer grafted to a Si wafer. The PMMA-*b*-PMAPOSS used in this work self-assembles into a hexagonally closed packed (hcp) array of dots with (10) lattice plane spacing d_o= 13 nm (corresponding to 3.3 Tdpsi). A block copolymer film was spin coated on a sparse chemical contrast pattern with (10) lattice plane spacing, d_{sub}= $3d_o$ = 39 nm. The sample was solvent-annealed under a mixed vapor of CS_2 and acetone in a chamber with N_2 counter flow to control the swelling ratio.

The degree of swelling of PMMA and PMAPOSS depend on the preferential solubility of solvent molecules to each of the polymer chains. Figure 1 shows the influence of solvent composition on swelling behavior for PMMA and PMAPOSS thin films. The result suggest that pure CS_2 is a slightly preferential solvent for PMAPOSS, while a 9/1 v/v mixture of CS_2 and acetone swells PMMA and PMAPOSS almost equally. Figure 2(a) and (b) show SEM images of PMMA-*b*-PMAPOSS self-assembled on the template by annealing under pure CS_2 vapor and under a CS_2/acetone = 9/1 v/v mixture, respectively. Degree of swelling was adjusted at 140%, which is just above the value at which PMMA-*b*-PMAPOSS chains gain mobility to undergo microphase separation. As can be seen from the images, annealing under the mixed solvent induced directed assembly with 9x density multiplication whereas annealing under pure CS_2 resulted in a higher defect density with poor registration. This result suggests that pattern fidelity can be improved by solvent annealing employing a neutral solvent to both polymer blocks.

PMMA-*b*-PMAPOSS can potentially self-assemble into ordered domains with sub 10 nm lattice spacing. Solvent annealed directed self-assembly provides a promising method for extending directed assembling techniques to high densities well beyond 1 Tdpsi with a high degree of registration and pattern uniformity.

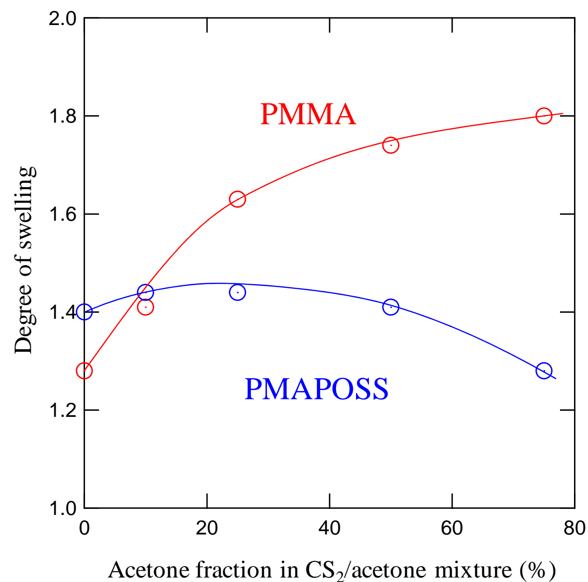

Figure 1. Degree of swelling of PMMA and PMAPOSS thin films under vapor of CS_2 and acetone mixtures.

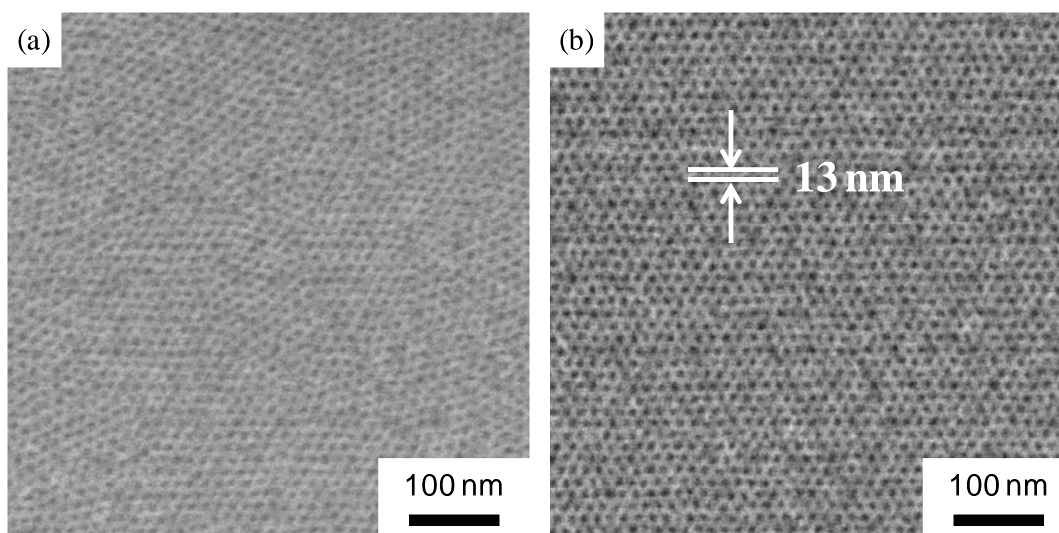

Figure 2. SEM images of PMMA-*b*-PMAPOSS with d_o = 13nm self-assembled on chemically pre-patterned template with d_{sub} = 39 nm. (a) Annealed under pure CS_2 vapor. (b) Annealed under vapor of CS_2/acetone=9/1v/v mixture. M_n of PMMA-*b*-PMAPOSS = 14,900 and $\phi_{PMAPOSS}$ = 0.83.

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[1] R. Ruiz et al., *Science* **321**, 936 (2008).

[2] T. Hirai et al., *Macromolecules* **41**, 4558 (2008).

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