



High- χ Block Copolymers For Perpendicularly Oriented Nanostructures in Thin Films

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As the demand for miniaturized devices and increased on-chip density is constantly increasing in the microelectronics industry, the target critical dimensions for semiconductor devices have shifted to successively smaller and smaller sizes. In the last several decades, a production method that has received growing interest for producing higher levels of pitch subdivision is block copolymer (BCP) lithography in conjunction with directed self-assembly (DSA). BCPs are of great interest for high resolution patterning due to their affordability and high throughput potential. In addition, as the processing of BCPs is compatible with current patterning and exposure technologies, it is possible to combine the most advanced exposure tools and the perpendicular lamellar or parallel cylindrical morphologies of self-assembled BCP materials to expand current manufacturing technologies to fabricate line and space (L/S) structures with domain dimensions of 10 nm and less. In particular, perpendicularly-oriented lamellae are preferred for such applications due to the increased aspect ratio of the structure when compared to parallel cylindrical morphologies.

To obtain BCPs that can self-assemble into domains with sub-10 nm feature sizes, high- χ BCPs with highly thermodynamically incompatible blocks such as hybrid BCPs composed of organic and inorganic Si-containing blocks are required. However, although the large chemical dissimilarities between the organic and inorganic blocks serve to increase χ and enhance the phase separation behavior, it also renders the orientation control of the BCP domains in thin films difficult. To overcome this challenge, we recently developed novel BCPs with an interfacial affinity control unit in the form of the block segment. In this talk, a promising candidate BCP, poly(polyhedral oligomeric silsesquioxane methacrylate-*block*-2,2,2-trifluoroethyl methacrylate) (PMAPOSS-*b*-PTFEMA), that is capable to form perpendicularly oriented nanostructures in the thin films, will be described. Fluorine-containing polymers such as PTFEMA not only display increased segregation strengths when compared to analogous non-fluorinated polymers, but also increased etching contrasts. In addition, the surface free energies (SFE)s of PTFEMA and PMAPOSS are highly similar (PTFEMA: 25.1 mJ/m², PMAPOSS: 28.7 mJ/m²), allowing for the easy control of the lamellar orientation and high resolution patterning with a high aspect ratio on thin films.

Herein, reversible addition-fragmentation chain transfer (RAFT) polymerization was employed to fulfill such requirements. PMAPOSS-*b*-PTFEMA was synthesized via RAFT and morphological studies in the bulk and thin film were conducted to achieve precisely controllable feature sizes of *ca.* 11, 13, 15, and 17 nm. Small-angle X-ray scattering (SAXS) studies revealed that PMAPOSS-*b*-PTFEMA is an extremely high- χ BCP with an effective Flory-Huggins interaction parameter (χ_{eff}) of *ca.* 0.45. In addition, the evolution of the self-assembled morphology on the thin film

was observed directly using transmission electron microscopy (TEM)

In order to find out if the BCP is compatible with the directed self-assembly (DSA) process, a technique used industrially for density multiplication to realize linear sub-10 nm L/S patterns, grapho-epitaxy DSA using an Ar-F immersion fabricated topographically prepatterned substrate was carried out using PMAPOSS₅-*b*-PTFEMA₆₈. A 2.0 wt % solution of PMAPOSS₅-*b*-PTFEMA₆₈ dissolved in PGMEA was spin-casted onto a prepatterned substrate at 1500 rpm for 35 s. Then, the thin film was thermally annealed at 110 °C for 1 min under ambient conditions and successively at 150 °C for 24 h under a nitrogen atmosphere. Subsequently, the PTFEMA block was selectively removed by O₂-RIE for 15 s (power, 300 W; O₂/Ar flow, 25/ 425 sccm; pressure, 3 pa). Furthermore, the thin film was thermally annealed at 150 °C for 24 h to obtain well-defined nanopatterns. As shown in the figure, perpendicularly oriented lamellar domains with a half pitch size of *ca.* 8 nm were well-aligned along the guides. A higher thermal annealing temperature of 150 °C and a longer annealing time of 24 h was used to obtain well-aligned perpendicularly oriented lamellar patterns. These experimental results indicate that PMAPOSS-*b*-PTFEMA can become the most promising candidate for a next-generation BCP lithography material because of its ability to align into sub-10 nm lamellae normal to the substrate surface through simple thermal annealing that does not require any additional surface treatment processes.

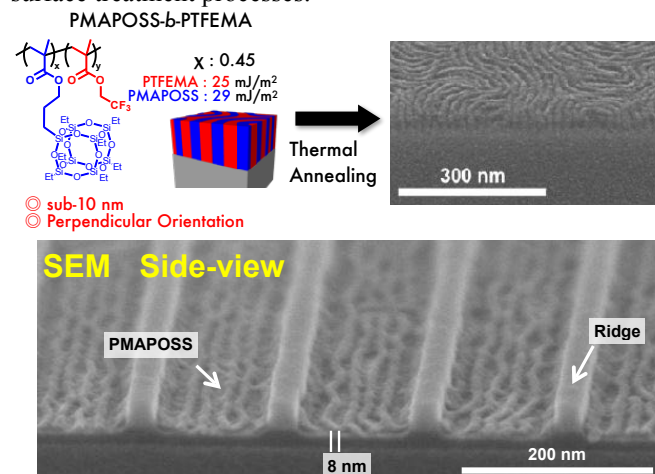


Figure 1 Chemical structure of PMAPOSS-*b*-PTFEMA and SEM image of line patterns created by grapho-epitaxy directed self-assembly.

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