Creation of Chemical Pre-patterns from Graphoepitaxially Assembled Block Copolymer Films by Molecular Transfer Printing

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Directed assembly and graphoepitaxy are two predominant approaches to assemble block copolymer films. Directed assembly of block copolymers on chemical pre-patterns has been demonstrated with high degrees of registration, increased feature density, and improved critical dimension control.[1] Directed assembly was listed as one of potential lithography solutions for sub-22 nm patterning in the 2007 International Technology Roadmap for Semiconductors.[2] However, fabrication of chemical pre-patterns by eBeam lithography or extreme ultraviolet interference lithography at such small feature dimension is either low-throughput or prohibitively expensive to practice. Graphoepitaxial assembly of block copolymers on topographic substrates has also been demonstrated with increased feature density than the original topographic pattern and improved orientation and registration of block copolymer domains in films.[3] However, the topographic nature of the underlying substrate may limit the pattern transfer operation.

Here we demonstrate a new strategy that combines the advantages of both approaches to direct the assembly of block copolymers. In this new strategy, we assemble a block copolymer film on a topographic HSQ substrate to increase the feature density,[3] replicate the surface domain pattern using the molecular transfer printing (MTP) technique to create 1:1 chemical pre-pattern,[4] and then direct the assembly of block copolymers on the pre-pattern to realize high-aspect ratio nanostructures (Fig 1a).[1] In one demonstration, graphoepitaxial assembly of a thin film of a cylinder-forming ternary blend C45 (L_B=45.6nm) on a PS-modified topographic HSQ substrate (pattern period L_s=90 nm) resulted in the formation of interpolated parallel cylinders, multiplying the feature density by a factor of 2 (Fig. 1b).[1c,5] The parallel cylinders and the topographic features may cause difficulties for pattern transfer into substrates. MTP was performed using the assembled parallel cylinders as masters to create a chemical pre-pattern that was then subsequently used to direct the assembly of a lamellae-forming PS-*b*-PMMA (37-37kg/mol, L_o=42.5 nm) film. The lamellar domains were faithfully registered on the replica, expanding in period to match the pattern period (Fig. 1c). The high-aspect-ratio structure has a better pattern transfer property than the parallel cylinders.

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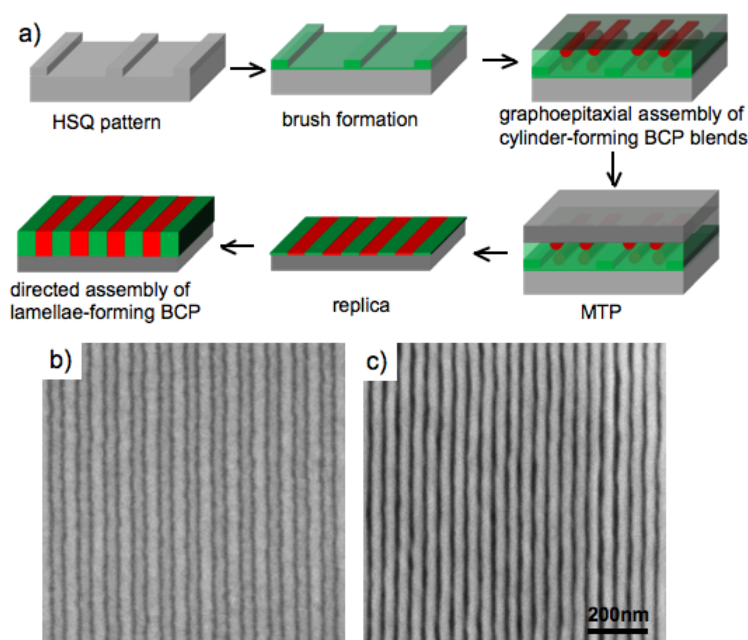

Figure 1. a) Schematic of the combination of graphoepitaxial assembly of a cylinder-forming block copolymer blend film on a topographic HSQ pattern and molecular transfer printing to create chemical pre-patterns for directed assembly of block copolymers.; **b)** SEM image of a 40-nm-thick film of blend C45 [L_B=45.6 nm, consisting of 90 wt% PS-*b*-PMMA (50-21 kg/mol), 7 wt% PS-OH (6 kg/mol), and 3 wt% PMMA-OH (6 kg/mol)] assembled on a topographic PS-modified HSQ pattern with L_s=90 nm. The height and width of HSQ stripes are ~ 15 and 20 nm, respectively.; **c)** SEM image of a 50-nm-thick PS-*b*-PMMA (37-37 kg/mol) film assembled on the MTP replica.