Coordination-Driven, Room-Temperature Formation of Inorganic Hard Masks for Block Copolymer Pattern Transfer

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Block copolymer (BCP) self-assembly offers a scalable route to nanoscale pattern generation; however, pattern transfer remains one of the most significant challenges limiting its adoption in semiconductor manufacturing. While self-assembled polymer morphologies can be readily formed[1], translating these patterns into functional materials typically requires additional steps such as selective polymer removal and metal deposition to generate etch-resistant inorganic features[2]. These approaches often involve elevated temperatures, highly reactive precursors, or multi-step processing, which constrain materials compatibility and process flexibility[3, 4]. Here, we demonstrate a coordination-driven vapor infiltration approach that directly forms inorganic hard masks at room temperature and atmospheric pressure. Poly(4-vinylpyridine) (P4VP) selectively reacts with volatile Group-14 precursors, including chlorosilanes and chlorogermanes, through N→Si coordination, producing polymer–inorganic hybrids without thermal activation or vacuum cycling. Solid-state ^{29}Si NMR, FTIR, and Raman spectroscopy confirm the formation of hypercoordinate silicon species confined within the polymer matrix. This chemistry is applied to PS-b-P4VP block copolymer thin films (Figure 1), where infiltration occurs exclusively within the P4VP microdomains. Selective reinforcement of these domains enables the formation of metalloid-based inorganic hard masks that preserve the native morphology after removal of the organic template. Because the inorganic mask is generated during infiltration, the process simplifies pattern transfer and avoids the thermal budgets and precursor limitations associated with conventional ALD-based infiltration methods.

References:

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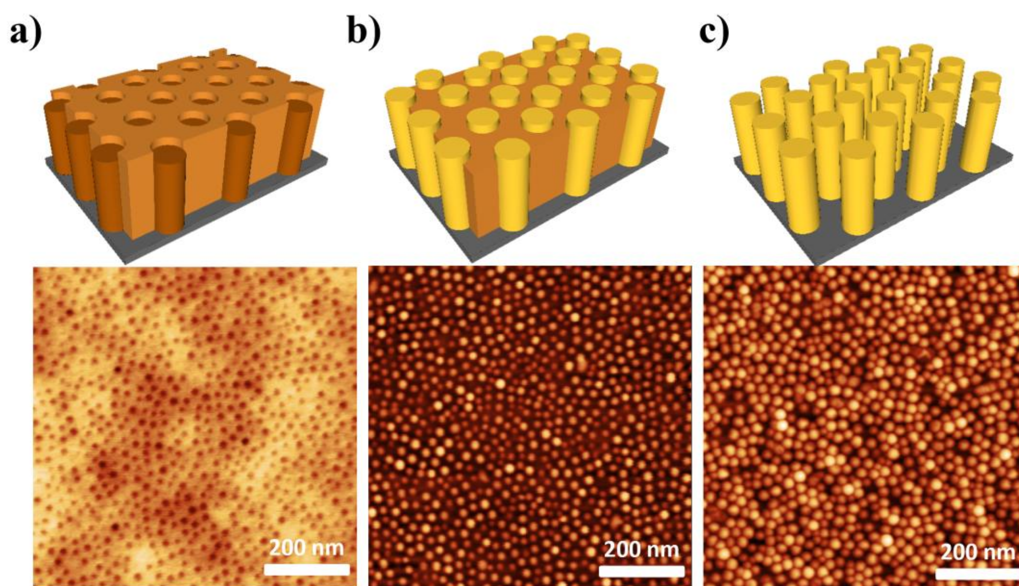

Figure 1. *Schematic illustrations (top row) and corresponding AFM images (bottom row) depicting the processing steps used to create an inorganic hard mask from PS-b-P4VP thin films via selective silane infiltration.* ***(a)*** *P-Sb-P4VP Film after solvent vapor annealing (SVA),* ***(b)*** *film after selective infiltration of trichlorosilane into the P4VP domains, and* ***(c)*** *formation of an inorganic hard mask following removal of the polymer template by UV-ozone etching. Scale bars: 200 nm.*