Fabrication of chemical patterns from negative resist for directed self-assembly at resolution limits of lithography

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Chemically and geometrically well-defined patterns play a crucial role in the directed self-assembly (DSA) of block copolymers (BCPs), offering precise control over domain orientation and lateral order of BCPs. These chemical patterns are carefully designed with geometries matching the natural structure and period (L_0) of BCPs, along with sufficient wetting contrast between the defined region and backgrounds. DSA achieved with chemical patterns with a pitch (L_s) equal to L_0 provides potential in rectifying lithographic imperfections, while density multiplication achieved through patterns with L_s=nL_0 enables higher resolution and throughput imaging for dense arrays of lines or spots compared to original lithographic patterns.

The fabrication of chemical patterns primarily employs "top-down" lithographic techniques with positive tone resists. The processes begin with a topographic resist pattern on a thin film preferential to one block of BCPs, such as a polymer brush or self-assembled monolayer. Subsequently, the geometry of the resist pattern is transferred into the underlayer using a dry-etch followed by stripping resist, with careful control over the chemical contrast between etched and unetched regions by modifying the etched surface. The use of positive tone resists, easily removable without changing the wetting characteristics of the underlayer, facilitates precise engineering of surface chemistry throughout the process. The Liu-Nealey (LiNe) flow significantly refined this process by utilizing a crosslinked polystyrene (PS) mat as an underlayer.

The increasing demand for smaller features in semiconductor manufacturing necessitates the adoption of negative tone resists, such as HSQ and Inpria, to generate chemical patterns for the highest resolution in DSA. However, their usage requires a new fabrication strategy due to challenges in removal while retaining underlayer wetting properties during the conventional process. In this study, we demonstrate a fabrication method for chemical patterns leveraging HSQ patterns from e-beam lithography (Figure 1a). Starting with HSQ patterns on a Cr underlayer, striped Cr patterns were created through reactive ion etching. Subsequently, the Cr patterns were successfully transformed into a chemical pattern by grafting a polyethylene oxide (PEO) brush, removing Cr with a wet etchant, and finally, modifying the Cr-etched region with a PS brush. This strategy yielded chemical patterns with a resolution down to a 24 nm full-pitch, approaching the dimensional limits of top-down lithography techniques (Figure 1b).

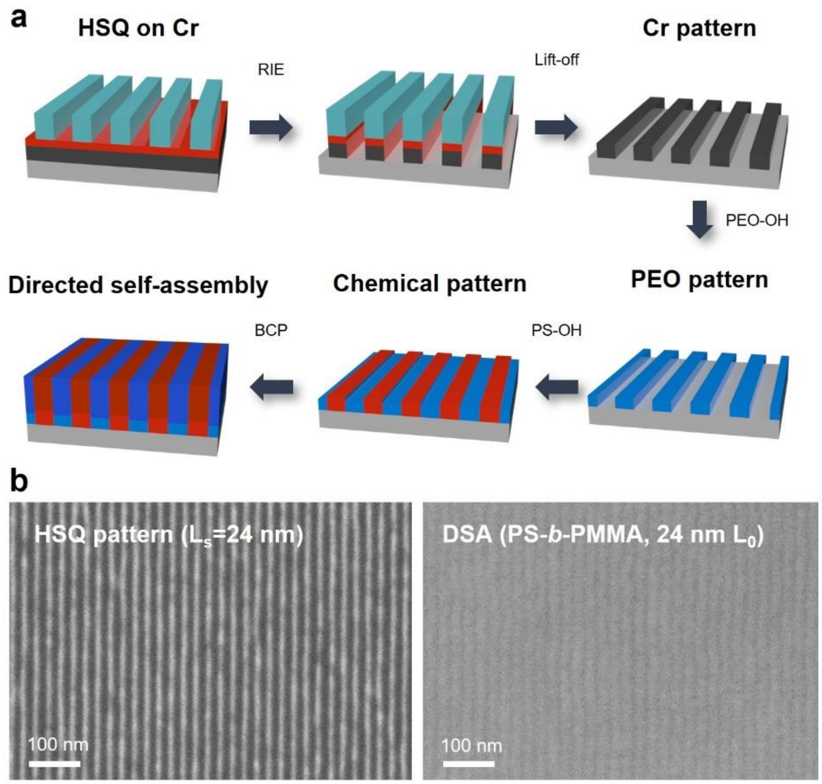

Figure 1. Fabrication of chemical patterns from a negative tone HSQ resist pattern: (a) schematic representation of the process; (b) SEM images of HSQ pattern and PS-*b*-PMMA DSA film at 24 nm full-pitch.