## Nanolithography applications of siloxane block copolymers: systematic pattern tunability and pattern-transfer

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Monolayer patterns of block copolymer (BCP) microdomains have been pursued for applications in sub-30 nm nanolithography. BCP self-assembly processing is scalable and low cost, and is well-suited for integration with existing semiconductor fabrication techniques. The two critical issues are how to obtain reliable long-range ordering of features with minimum defect densities and how to successfully transfer the patterns into other functional materials.

We demonstrate the formation of exceptionally well-ordered and robust nanoscale patterns from poly(styrene-b-dimethylsiloxane) (PS-PDMS) BCPs, which have a very large interaction parameter between the blocks compared to other commonly used BCPs.<sup>1</sup> Cylinder- or sphere-forming BCP films were spin-coated over silicon substrates patterned with shallow steps using optical lithography, and solvent-annealed to induce ordering. This generates patterns with a correlation length of at least several micrometers (Fig 1a). The annealed film was treated both with CF<sub>4</sub> plasma and then O<sub>2</sub> plasma to obtain oxidized PDMS patterns with a lateral dimension of 14 - 18 nm. These can be used as an etch mask or an easily removable template for patterning functional materials.

We also report on the solvent vapor induced tunability of pattern dimension and morphology.<sup>2</sup> Different degrees of solvent uptake in BCP films during solvent-annealing can manipulate the interfacial interaction between the two blocks, and a mixed solvent vapor can change the effective volume fraction of each block. Thus, control of the microdomain size, periodicity, and morphology are possible by changing the vapor pressure and the mixing ratio of a selective (heptane) and a partially selective (toluene) solvent (Fig 1b). This allows a range of different pattern geometry and period to be made simply by changing the processing conditions of a given block copolymer.

Methods to transfer the generated patterns into various kinds of materials are described as well. For example, arrays of parallel lines were used as a mask to pattern poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) conducting polymer thin films (Fig 2a). The resulting PEDOT:PSS nanowire array was used as an chemiresistive ethanol sensing device. Metallic films were structured using a pattern-reversal process. Examples of Ti, Pt, Ta, W, and magnetic Co and Ni nanowire, antidot, and ring arrays are presented (Fig 2b-d). These functional nanostructures can be utilized for a variety of devices. The magnetic properties of ferromagnetic dots, antidots, and rings will be discussed.<sup>3,4</sup>

<sup>&</sup>lt;sup>1</sup> Y. S. Jung and C. A. Ross, Nano Letters 7, 2046 (2007).

<sup>&</sup>lt;sup>2</sup> Y. S. Jung and C. A. Ross, Advanced Materials (in press).

<sup>&</sup>lt;sup>3</sup> Y. S. Jung, W. Jung, H. L. Tuller, et al., Nano Letters 8, 3776 (2008).

<sup>&</sup>lt;sup>4</sup> Y. S. Jung, W. Jung, and C. A. Ross, Nano Lett. 8, 2975 (2008).



*Fig 1:* SEM images of self-assembled (a) linear patterns and (b) perforated lamellar morphology induced by a mixed solvent vapor treatment. Both of the samples were obtained using the same cylinder-forming block copolymer.



*Fig 2:* SEM images of various nanostructures after pattern-transfer processes. (a) Conducting polymer (PEDOT:PSS) nanowires, (b) Co double ring arrays, (c) W nanowires, and (d) antidots in a Pt film.