Si-containing block copolymers for self-assembled nanolithography applications

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The ability of block copolymers to self-assemble into periodic nanoscale structures makes them attractive for the patterning of nanoscale features. Moreover, the processing requirements for block copolymers (spin coating, annealing, reactive ion etching) are compatible with standard semiconductor processing techniques. The geometry of the self-assembled structures (e.g. arrays of spheres, cylinders or lamellae) and their length scales can be controlled via the molecular weights of the blocks from which the polymer is composed. The long range ordering and the registration of the features can be controlled by using chemical or topographical patterns on the substrates, and placement to within 2-3 nm of a reference feature has been demonstrated. These characteristics make block copolymer lithography a potentially cost-effective method for the formation of dense arrays of nanoscale features.

The majority of block copolymer patterning work has been based on polystyrene-polymethylmethacrylate (PS-PMMA) diblock copolymers. In this system the PMMA is easily removed, leaving the PS features on the substrate. However, PS is a poor etch mask, which limits subsequent pattern transfer processes. By using a Si-containing material as one block of the polymer, a more robust etch mask is formed, which enables the formation of high aspect ratio features.

In this presentation we describe pattern formation and pattern transfer from two Si-containing diblock copolymers, polystyrene-polyferrocenyldimethylsilane (PS-PFS) and polystyrene-polydimethylsiloxane (PS-PDMS). In both cases, after annealing to promote microphase separation of the blocks, the PS is removed with oxygen reactive ion etching, leaving oxidized PFS or PDMS features that can serve as masks for pattern transfer. The PS-PFS, which contains ~20vol% PFS, is spin-coated then annealed at 140 – 180˚C to form a monolayer of close-packed PFS spheres within a PS matrix. The array row spacing is 25 – 50 nm depending on the molecular weight of the block copolymer. We show how these spheres can be templated using shallow substrate topography made in silica to form arrays in 2D and 3D with good long range order. Significantly, well-ordered arrays form even if the template spacing is incommensurate with the period of the block copolymer array: the array can distort elastically to conform to the template dimensions and to accommodate template edge roughness. For very narrow templates, a single row of PFS spheres can form within the template, and the spheres distort into ellipsoids if the template width is unequal to the array spacing.

The PS-PDMS block copolymer contained 27 vol%PDMS, and formed an array of parallel PDMS cylinders in a PS matrix. PS-PDMS has a higher chi-parameter than PS-PMMA or PS-PFS, and therefore a stronger tendency for microphase separation, which could be accomplished by solvent annealing at room temperature in a toluene vapor. In thin films the cylinders could be oriented either parallel or perpendicular to the edges of a topographical template depending on the annealing conditions and substrate geometry, while in circular pits, the cylinders curved to form concentric ring patterns with spacing governed by the pit diameter.

Block copolymer patterns were transferred into various materials, including magnetic and

nonmagnetic metals, silica, silicon and antireflective coatings, using etching or liftoff processing. A method has been developed to make the topographic templates from a polymer that can be removed after the block copolymer anneal to leave a smooth substrate. We will describe the pattern transfer processes and the properties of the resulting structures. We will also discuss the use of triblock copolymers to enable a wider range of self-assembled geometries.

References: Y. S. Jung and C. A. Ross, Nano Letters **7** (7), 2046 (2007); V.P. Chuang, J.Y. Cheng, T.A. Savas, C.A. Ross, Nano Letts. 6 (10), 2332 -2337, (2006); J.Y. Cheng, V. Chuang, F. Zhang, A. Mayes, C.A. Ross, Nano Letts. 6 2099-2103 (2006)

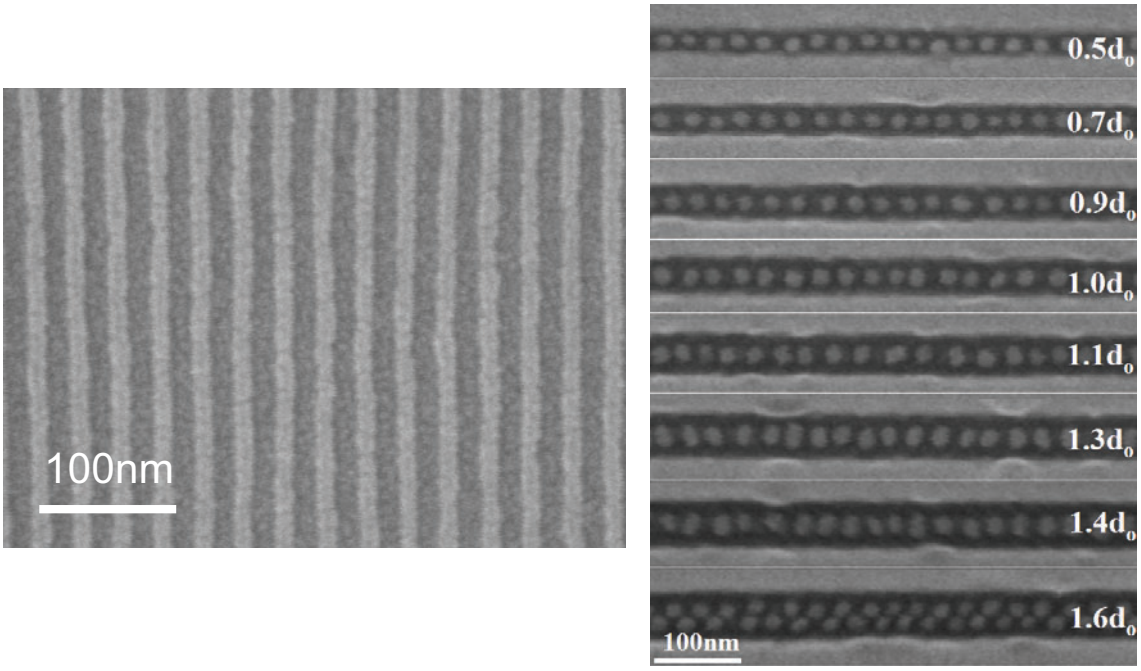

Figure 1. Left: Section of a 32 nm period PDMS line array ordered within a 875nm wide shallow silica groove (groove edges are not shown). Right: Composite image of one dimensional arrays of PFS spheres within narrow silica grooves. The shapes of the spheres are ellipsoidally distorted when the groove width deviates from d_o, the equilibrium row spacing.

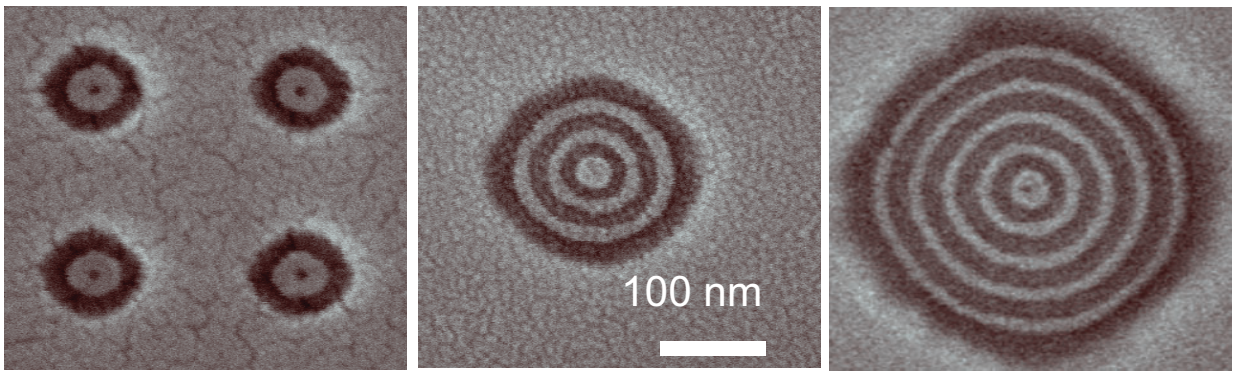

Figure 2: PDMS cylinders confined within circular pits curve to follow the pit edges. The number of concentric rings is governed by the template diameter. The central feature can be a PS 'dot' (dark) or a PDMS 'dot' (white, middle image).