

Block Copolymers as Nanolithographic Templates

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The area of nanostructure fabrication has experienced a rapid growth in both commercial and academic interest in recent years. Commercially, the most obvious interest has been in reducing the size of integrated circuit devices to produce faster and more powerful computer chips. Also of great promise are the novel properties that many materials and systems exhibit when their dimensions are reduced to the nanometer scale. Current techniques for fabricating microstructures, based on photolithography, are not suitable for sub 100 nm resolution.¹ Although electron beam lithography can create structures as small as 50 nm rather routinely, it is a serial process and hence very cumbersome.

In many applications, including quantum dots² and high density magnetic recording media³, only simple periodic arrays of nanostructures are needed. The ordered domains of block copolymer thin films have dimensions on the order of 10-100 nm and are ideal candidates in producing lithographic templates for such periodic patterning.

Block copolymers consist of 2 or more chemically distinct polymer chains joined by covalent bonds. Living and pseudo-living polymerization techniques⁴ are the principal means of synthesis because of the critical importance of compositional control and narrow polydispersity. With the use of different living polymerization methods, a wide variety of well defined and chemically diverse block copolymers are possible.

The observed phase in a block copolymer system results from a combination of enthalpic and entropic factors.⁵ Unlike mixtures of homopolymers, block copolymers are covalently attached and therefore cannot macroscopically segregate. Enthalpy, as quantified in the Flory-Huggins interaction parameter, χ , is typically reduced by decreasing contact between segments on the different blocks. However, a loss in entropy occurs with segregation from chain stretching and the localization of block-block joints at interfaces. In addition, longer chains have reduced configurational entropy, and therefore the degree of polymerization, N , is inversely proportional to entropy. The magnitude of the product, χN , determines whether enthalpic or entropic factors dominate the system's free energy. When the product is much smaller than 10, a spatially homogenous phase is observed because entropic factors dominate. At values much larger than 10, enthalpic factors dominate leading to sharply segregated microstructures. The morphology of the nanodomains is dependent on the identity of the block constituents and the ratios of the blocks. An illustration of some common morphologies is shown in Figure 1.⁶

The dimensions of these domains can range from 100 nm to less than 10 nm, dependent on the chain size and value of χ . Lithographic strategies involving block copolymers have utilized micellar, hexagonally packed cylindrical and body centered cubic spherical morphologies.



Figure 1

Thin block copolymer films having hexagonally packed cylindrical or lamellae nanodomains would be ideal as lithographic templates. However, when a film is spun cast onto a substrate and annealed, if one block has a lower interfacial energy it will preferably orient at the interphase. The thinness of the film coupled with the block covalent bond cause the cylinders or lamellae to orient parallel with respect to the substrate.⁷ Two methods have been developed to orient the domains in the more favorable perpendicular orientation. Mansky and workers⁷ covalently attached random copolymers consisting of the same monomers as the block copolymer to a silicon wafer. By tuning the composition, an effectively neutral surface can be engineered. A perpendicular orientation is then expected since there is no preferential wetting, and this has been verified recently.⁸ The other method involves subjecting the film to an electric field during orientation.^{9,10} This occurs because a system of 2 dielectrics has its lowest energy when the interface is oriented parallel to the field. The latter method is more promising because the former works only for thin films less than 100 nm in thickness.⁸ Neither technique has yet to result in perfectly aligned domains however.

At this time, there have been no reports in the literature of successful patterning of a substrate from the oriented films described above. Park and workers have patterned hexagonal arrays of dots and holes of 20 nm diameter that are 40 nm apart using body centered cubic spherical domains of polybutadiene(PB) in a polystyrene(PS) matrix as a template.¹¹ They used ozonolysis and OsO₄ staining to create voids or more etch resistant PB domains, and then transferred the pattern to SiN wafers using reactive ion etching techniques. The lab of Vancso have made block copolymers with one block having Si and Fe in the chain and thus resulting in a reduced number of steps in pattern transfer.¹²

Moller and workers have formed ultrathin films of PS-*block*-poly(2-vinylpyridine) on mica substrates¹³. They have been able to produce regular arrays of polystyrene clusters due to the differing wetting properties of the 2 blocks on the highly polar mica. Titanium was found to selectively grow on the PS clusters and they used this to pattern features on mica.

Lithography with block copolymer templates still faces many substantial barriers. Notably, costly synthesis, complex and multiple processing steps, and the lack of a method for perfect domain alignment. However, it has been shown to work in principle, and further research will undoubtedly lead to refinements and possible commercial applications.

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