

Nanostructures in Thin Films of Block Copolymers

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To meet the increasing demand for smaller, faster microfabricated devices, a continued decrease in the feature size of device components is required. The semiconductor industry, however, is rapidly approaching a hard-stop in the continued drive to meet Moore's Law as lithographic processes reach technological and cost limitations. The inherent limitation of the wavelength of light used to pattern features on surfaces and the cost of production lithographic tools are daunting obstacles. Even still, the semiconductor industry has made incredible advances in achieving feature less than 90 nm in size. For traditional optical systems, decreasing the size scale of features further may not be possible. X-ray and electron beam lithographic processes do not face wavelength limitations, both processes have proven to be impractical in a production setting. Other processes, like nano-imprint lithography, where one mechanically patterns a surface with a master can lead to features on the tens of nanometer size scale and holds promise, but, are still in the research stage. An alternative approach is the use of self-assembly to produce regular patterns of nanoscopic features and combine this with standard photolithographic processes to produce nanoscopic elements. This combination of a "bottom up" self-assembly strategy with traditional "top down" microelectronic approaches is a grand challenge with many unanswered questions.

Block copolymers are comprised of two chemically dissimilar polymer chains that are covalently linked together at one end. Owing to the low entropy of mixing, polymer blends are, in general, immiscible and macroscopically phase separate. However, with block copolymers, due to the connectivity of the two chains, phase separation is limited to the dimensions of the copolymer chain, ~ 5-20 nanometers in size. By heating amorphous block copolymers, comprised of polymers like polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(ethylene-alt-propylene) (PEP), or poly(vinylpyridine) (PVP), the block copolymer will self-assemble into arrays of nanoscopic domains, historically called microdomains. Numerous laboratories have investigated the phase behavior of block copolymers in the bulk. The volume fraction of the components, the rigidity of the segments in each block, the strength of the interactions between the segments, and the molecular weight contribute to the size, shape and ordering of the microdomains. Morphologies ranging from spherical to cylindrical to bicontinuous gyroid to lamellar, as shown in Figure 1, can be obtained by varying these parameters. In addition to the simple linear diblock copolymers, there are multi-block copolymers and block copolymers having different architectures of the chains, as for example with comb-type and star block copolymers, where chain configuration, packing constraints and interfacial curvature, influence the type of morphology formed. The versatility of block copolymers can be appreciated when one considers that the chemistry of the individual blocks can be tailored to

perform a specific function, for example, chemical reactivity, biological activity, conductivity or degradability. The diversity in synthetic strategies in preparing block copolymers opens a plethora of applications where block copolymers can be used. In thin films, if the orientation and lateral ordering of the microdomains can be controlled and methods developed to bias the lattices of the arrays of microdomains, then block copolymers have the potential to become a standard tool in the fabrication of nanostructured devices.

The parameters that underpin the morphology in thin films of block copolymers include the segmental interactions between the components, the rigidity of each block, the surface energies of the components, and the interactions of the blocks with the underlying substrate. In general, preferential interactions of one block with the substrate or a lower surface energy of one component will force a segregation of one block to either the surface or the substrate. Due to the connectivity of the blocks, this forces an orientation of the microdomains parallel to the substrate. While this is desirable for some applications, other applications require that the microdomains be oriented normal to the surface. In the absence of any surface modification, an external field will normally be required to overcome these preferential interactions. Electric fields, that operate on the differences in the dielectric constants of the microdomains, or solvent, where the dilution of each component mediates interfacial interactions, have been used to with great success in orienting the microdomains normal to the film surface. Alternatively, as will be discussed later, surfaces can be chemically modified to control the interfacial interactions of the blocks with the interfaces, removing any preferential affinity of the blocks. Balanced interfacial interactions, while necessary, are not sufficient, since both orientations satisfy this boundary constraint. In the case where the film thickness is not commensurate with the natural period of the copolymer, a difficult task to achieve under normal spin-coating conditions, then only an orientation of the microdomains normal to the film surface will minimize the energy of the copolymer. The segmental interactions, surface energies and rigidity of the segments are dictated by the chemical nature of the chain and, as such, are not subject to change. However, by slightly modifying one of the blocks by the random placement of a second unit along the chain, small changes in the surface energies, segmental interactions and rigidity can be made without sacrificing the overall microphase separated characteristic of the block copolymer.

For essentially all synthetic polymer systems, one inevitably faces the issue of polydispersity, i.e. the distribution of molecular weight obtained in the synthesis. In the case of a block copolymer, the polydispersities of the two blocks can, also, lead to a distribution in the volume fraction of the components from one chain to the next. This may have deleterious consequences in the definition of the microphase separated morphology, since the volume fraction of the components will influence the curvature required to pack chains at the interface between the microdomains. Until recently, achieving narrow molecular weight distributions required the use of anionic procedures, that are time consuming, expensive and not tolerant to many functional groups. This precludes the use of block copolymers in an industrial process. Recently, this has changed with the advent of living free and atom transfer radical polymerization processes where narrow molecular weight distribution homopolymers, random and block copolymers can be prepared inexpensively and in large quantities. These developments have greatly enabled the use of block copolymers in an industrial setting.