

Directing the Self-Assembly of Nanoscale Polymeric Templates

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ABSTRACT

Ultrathin diblock copolymer films have been offered as promising candidates for bottom-up templates in nanotechnological applications. Their natural tendency to self-organize into laterally alternating domains with a length scale tunable in the range of 10-100 nm is fundamental to their potential in this arena. However, having arbitrary control over the orientation of these domains is equally crucial and, until now, largely unrealized. We will present a novel lithographically assisted self-assembly approach that leads to low defect density domains of mesoscopic dimensions spanning 0.2-2 μm in width, 100 μm in length, and with nanoscopic features down to 20 nm. Potential applications extend from fundamental polymer science to sensor technology, electronics/spintronics, and optics.

INTRODUCTION

Fabrication of periodic nanoscale structures using self-organizing systems has garnered significant attention because of the simplicity and low cost of the method. Ultrathin diblock copolymer films are propitious candidates for bottom-up nanotemplates in hybrid organic-inorganic devices. These systems self-assemble into microphase separated domains with a length scale tunable through the full range of the nanoscale; however, without further constraint, the domains have no preferred orientation and form a disordered fingerprint structure (Figure 1).

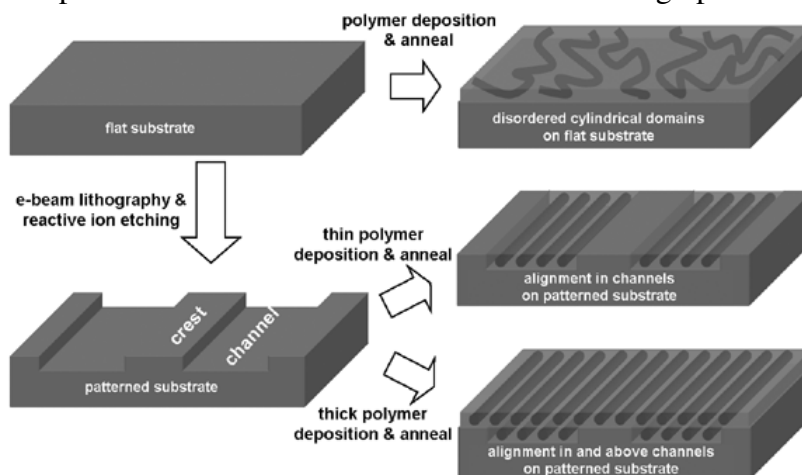


Figure 1. Schematic of alignment methodology

Localized alignment of cylindrical domains has been reported using a variety of techniques. These approaches, though, tend to produce either only short-range order or random domain orientation. In this work, we present a general method for defining an orientation and reducing defects via the introduction of geometric substrate anisotropy. Three novel results are presented:

(1) alignment of cylindrical polymer domains in confined volumes, (2) extension of this substrate-induced alignment above and beyond the confined volumes, and (3) virtually defect-free domains. Alignment is achieved using lithographically assisted self-assembly—a combined top-down/bottom-up methodology.

Asymmetric polystyrene-block-polyisoprene (PS-*b*-PI), obtained from Polymer Source, Inc. (Dorval Quebec, Canada), was 27 wt % PS with a molecular weight of 22,000 gm/mole and polydispersity of 1.08. Homogeneous Ni-Al catalyst was used to selectively hydrogenate the isoprene block to prepare polystyrene-block-poly(ethylene-alt-propylene) (PS-*b*-PEP). Polymer films were prepared by placing a drop size in the range 4-5 μl of 1.55% (w/w) PS-*b*-PEP/toluene solution on a grating and then spinning at selected speeds for 1 min. Subsequent thermal annealing of the samples was carried out at selected temperatures (388-408 K) under an argon atmosphere for periods ranging from 2-12 hrs.

RESULTS & DISCUSSION

In contrast to thin films on flat substrates, when a polymer film is prepared on a substrate patterned with grating lines, cylindrical domains exhibit remarkable behavior. The preferential interaction of PS with the trough sidewalls drives the alignment of cylindrical domains along the edges of the channels. Following sufficient annealing, the aligned domains ripen resulting in perfectly aligned cylindrical domains across the entire trough width (Figure 2).

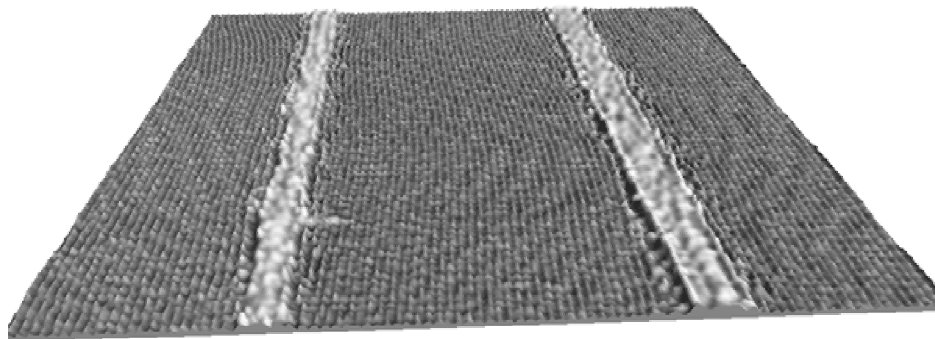


Figure 2. Macroscopic alignment of nanoscale polymer cylinders within 1 μm -wide channels prepared with e-beam lithography and reactive ion etching

In order to determine the mechanism of alignment, we have monitored the growth of cylinder alignment as a function of annealing time. At lower annealing times, at most two cylinders align along the channel edges and many defects are present in the center of the troughs. Subsequent annealing leads to improvement in alignment with larger aligned cylindrical domains, but there are still perpendicularly oriented defects present as a vestige of the original flow direction during annealing. Further annealing removes even these defects resulting in perfectly aligned cylindrical domains along the entire channel length. This perfection has been seen to extend the full 100 μm length of the lithographic channels, suggesting that this phenomenon is unbounded in length. Parallel flow along the channels cannot account for the observed alignment because there is no net flow along the length of the trough. The kinetics of this process varies with channel width, with wider troughs requiring more annealing. For templating applications, curved or angled geometries may also be useful. We have preliminary indications that the guided alignment presented here is not restricted to straight architectures.

This edge-ripening process is analogous to zone-refining. It is interesting to observe that cylinders closely follow the geometry of the trough edges. When there is a significant deviation in trough width along its length due to lithographic imperfections, defects are created. We have observed that the polymer accommodates structurally similar defects reproducibly. Elasticity of the confined polymer is demonstrated by the fact that there are regions where a given trough width can accommodate more than one number of polymer domains (Figure 3). The polymer avoids creation of high energy dislocation defects by expanding or contracting within the accessible range as necessary. At some point, this regulation becomes more costly than the energy required to create a dislocation and a single defect is formed.

Alignment has also been routinely observed, surprisingly, to extend beyond the confined volumes of the etched channels. We have observed that the alignment of cylindrical domains in underlying troughs induces alignment of cylinders both above the troughs and laterally onto the crests. This methodology can be utilized to align nanoscale polymer domains across an entire surface.

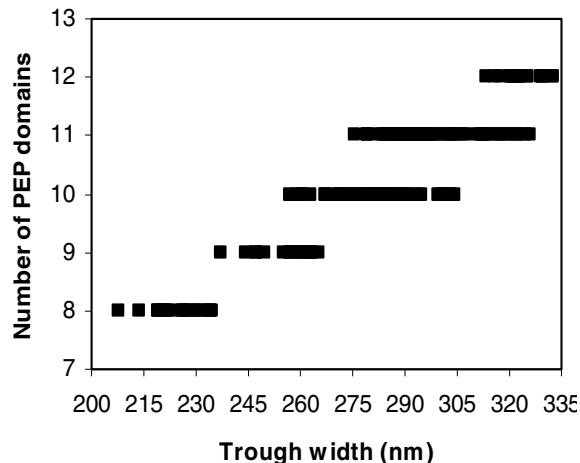


Figure 3. Elasticity of confined polymer domains

CONCLUSIONS

We report a new method for aligning nanoscale cylindrical diblock copolymer domains over large length scales. This approach merges top-down and bottom-up methods in order to achieve long-range order while maintaining the benefits of self-assembly. Alignment is initiated by a preferential wetting layer of PS on the sidewalls of the substrate channels and is extended throughout, and even beyond, the confined volume via defect annihilation. These domains display substantial compliance that enables them to accommodate lithographic imperfections without introducing structural defects. Ramifications of this work extend to applications in electronics, optics, and sensor technologies.

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REFERENCES

1. D. Sundrani, S.B. Darling, and S.J. Sibener, *Nano Letters* In Press.
2. D. Sundrani, S.B. Darling, and S.J. Sibener, Submitted to *Langmuir*.