Multidirectional BCP Alignment by Thermal-Coefficient-of-Expansion Mismatch Shear

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Aligned arrays of nanopatterns are required for many applications such as integrated circuits, next-generation data storage, and plasmonic structures, though typical lithographic processes can be limited by high cost or high defectivity. Directed self-assembly of block copolymers (BCPs) provided by shear-stress can produce aligned sub-10-nm structures over large areas[1,2], though the speed, versatility, and process integration can be improved. In this work, we present BCP shear-alignment via a thermal-expansion-coefficient mismatch between the polymer, substrate and a top-coat of SiO_2. The key results of this approach include ordered alignment in different directions on a single substrate over long-ranges, short (1 minute) annealing times, thin layers of polymer, control over local changes in direction, and no need for a vacuum or chemical surface functionalization.

Here we show the experimental results of shear-aligned BCP domains induced by a SiO_2 top-coat. For the fabrication process: (1) a thin film of cylinder-forming BCP, poly(styrene-*b*-dimethylsiloxane) (PS-*b*-PDMS, 16 kg mol^{-1}, fraction PDMS 31%) was spin coated on Si samples, (2) ~100 nm of SiO_2 was deposited on top of the BCP, (3) thermal annealing for 1 and 10 minutes to assemble oriented in-plane cylinders of PDMS, and (4) removal of SiO_2 in 1% hydrofluoric acid and exposure of final line array by reactive-ion etch. During annealing, the SiO_2 (coefficient of thermal expansion CTE ~0.5 ppm/°C) expanded less than the silicon substrate (CTE ~2.6 ppm/°C). The resulting strain aligned the BCP cylinders perpendicular to cracks or scribes in the SiO_2 film. Naturally forming cracks formed below 225°C, though were greatly reduced with hotter annealing. Different BCP domain orientations were achieved on a single substrate by scribing in different directions, as exemplified in Figure 1a. Furthermore, rapid orientation was achieved with annealing as low as 1 minute (Figure 1b). As an experimental control, no alignment was observed without a top-coat, therefore without shear alignment, as shown in Figure 1c.

We also investigated the spatial variation in alignment as a function of experimental parameters. We found that the alignment near (within 2 mm) the scribe was more ordered and less defective than further away (greater than 2 mm), likely due to higher shear stress at the SiO_2 edge[3]. This was consistent with enhanced finite-element simulation of shear-stress at the BCP-SiO_2 and –Si interfaces (Figure 2). The measured distance away from the scribe of ordering and alignment is plotted (Figure 3) as a function of annealing time and temperature. An increase in time and temperature improved long-range directionality and reduced defects. Figure 4 shows examples of annealing at 250°C, in which order and alignment were observed up to 2 mm away from the scribe. Such results show promise for this method to provide improved local orientational control as well as long-range order over entire substrates.

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[1] D. Angelescu *et al.*, Adv. Mat. **16,** 19 (2004).
[2] Z. Qiang et al., Macromolecules **47,** 3 (2014).
[3] J. W. Eischen *et al.*, Trans. ASME **112**, 16 (1990).

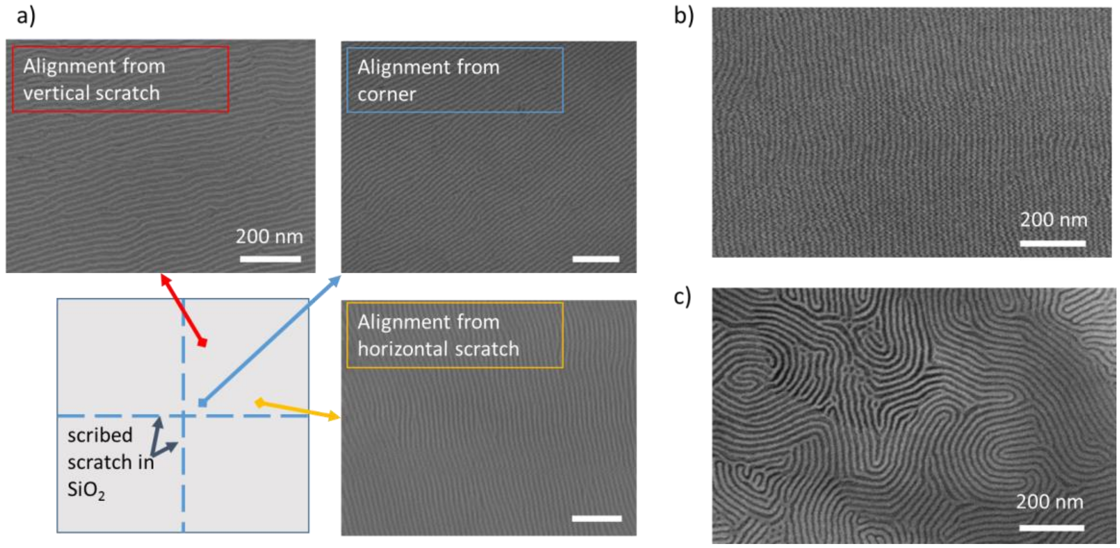

Figure 1: SEMs showing controlled shear-aligned BCP cylinders. a) Alignment orientation was controlled by scribes in the SiO_2 in different directions. b) Alignment induced for 1 minute of annealing at 250°C. c) No alignment was induced without shearing from a SiO_2 top-coat.

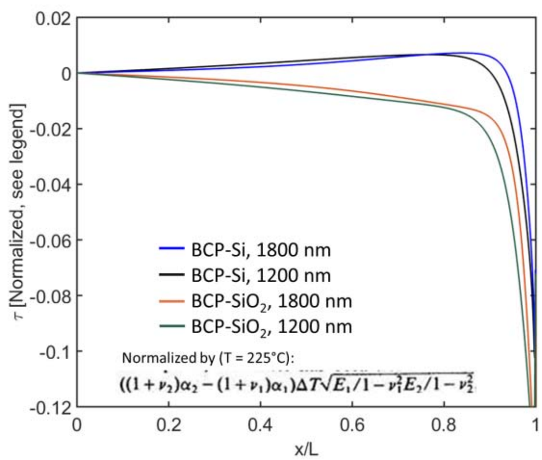

Figure 2: Plot of calculated normalized shear stress (τ) as a function of the distance (x) from the edge of a strip of SiO_2 (width = L) at 225°C. The stress is greatly enhanced near the edge, representing the experimental scribe marks.

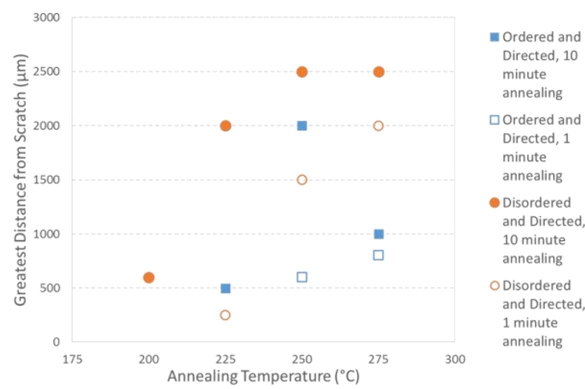

Figure 3: Maximum observed distance of ordering and direction vs. annealing temperature and time. Increases in temperature and time led to more order and shear-induced alignment of the BCP domains.

Figure 4: SEMs showing the order and alignment at distances of 300, 800, and 2000 µm from a scribe in the SiO_2 top-coat. The sample was annealed at 250°C for 10 minutes, and showed ordering up to 2 mm away from a scribe.