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Rapid shear alignment of sub-10 nm cylinder-forming block copolymer films based on thermal expansion mismatch


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Abstract

Directed self-assembly of block copolymers (BCPs) provided by shear-stress can produce aligned sub-10 nm structures over large areas for applications in integrated circuits, next-generation data storage, and plasmonic structures. In this work, we present a fast, versatile BCP shear-alignment process based on coefficient of thermal expansion mismatch of the BCP film, a rigid top coat and a substrate. Monolayer and bilayer cylindrical microdomains of poly(styrene–b-dimethylsiloxane) aligned preferentially in-plane and orthogonal to naturally-forming or engineered cracks in the top coat film, allowing for orientation control over 1 cm² substrates. Annealing temperatures, up to 275 °C, provided low-defect alignment up to 2 mm away from cracks for rapid (<1 min) annealing times. Finite-element simulations of the stress as a function of annealing time, annealing temperature, and distance from cracks showed that shear stress during the cooling phase of the thermal annealing was critical for the observed microdomain alignment.

Directed self-assembly of block copolymer (BCP) microdomains in thin films has been used to enhance the correlation length of the periodic patterns for a wide variety of applications, including integrated electronics [1–3], data storage [4], photonic materials [5], and bio-functionalized surfaces [6]. The limited correlation length of BCP microdomain arrays has been overcome through engineering methods to produce both long-range order and local control over patterns. These alignment methods have been based on templates (chemoepitaxy or graphoepitaxy [7, 8]), on fields (magnetic or electric [9]) or zone/gradient annealing, such as scanned solvent annealing [10], and on shear alignment. Previous shear alignment approaches sought to investigate the rheology of BCP films, and found that the shearing of the polymer during annealing aligned the assembled microdomains [11–15]. More recent work has shown highly ordered, well-aligned line patterns over square-centimeter areas, as well as millimeter-area orientation control [16–20] and have used shear-aligned BCP patterns as templates for further directed self-assembly [21].

Different mechanical, light-based, and vapor-phase methods have been developed to shear the surface of a BCP thin film with a top coat. Many of the mechanical approaches produce shear by in-plane displacement of a weighted PDMS pad or rotation of silicone oil [11–13, 22–27]. Shear can also be produced by swelling a top PDMS pad with solvent vapor [19, 20, 28, 29] or by scanning a laser to locally heat substrates or PDMS top coats [18, 30]—in both cases, the expansion/contraction of the PDMS or substrate translates a shear stress to the adjacent BCP film. Other reports have observed shear-induced alignment during: viscous flow of BCP films [31, 32], specifically during nanoimprint lithography [33]; dewetting of a top coat poly(vinyl alcohol) pad [34, 35]; or scanned zone heating [16, 17, 36]. Chaikin et al have investigated shear alignment extensively via rheological measurements for both sphere and cylinder forming BCPs [11–13, 22, 24–27, 37, 38]. Yager et al have developed rapid alignment of cylinder domains with scanned-laser heating [17, 18, 30, 39].

Shear alignment has been effective for a variety of BCP chemistries, molecular weights, and numbers of microdomain layers within the film thickness. The variety of BCPs include different morphologies (body-centered...
cubic spheres, lamellae and hexagonally-packed cylinders) \[11, 13, 17, 22, 28, 33, 30, 34, 36\], and a wide variety of chemistries, including poly(styrene-b-dimethylsiloxane) (PS-b-PDMS) \[19, 28, 30, 34, 35\], poly(styrene-b-methyl methacrylate) (PS-b-PMMA) \[17, 19, 22, 30, 33, 36\], and poly(styrene-b-isoprene) (PS-b-PI) \[11, 30\]. The majority of the investigations have focused on thicker films consisting of many layers of microdomains, but shear alignment of monolayers of microdomains has also been shown \[17, 19, 20, 22–30, 35\].

The work noted above has progressed towards obtaining highly-ordered BCP line arrays via shear, though questions remain to be answered. The top-coat materials used in previous work were predominantly soft pads or oils \[11–13, 22–27\] with limited investigation of hard or inorganic materials. From a scientific perspective, the sheared assembly of BCPs near the order–disorder transition and under time-varying shear stress is not fully understood.

Here we present a shear alignment method based on the coefficient of thermal expansion mismatch (CTEM), which induces alignment of BCP nanopatterns via a thin rigid top coat. The shear was produced around cracks in the top coat, silica in our case, because the differing coefficient of thermal expansions of silica, silicon (the substrate) and BCP film. An example of the alignment is highlighted with the BCP cylinders in figure 1(a). We first present and discuss the experimental investigation of aligning BCP cylinders and then analyze a finite element model which elucidates the time- and temperature-dependent nature of the thermal annealing, including the importance of the BCP viscoelasticity. Finally, we present the hand-scribing of crack lines for controllable BCP domain orientation in multiple directions and over large-areas. By making use of an inorganic top coat, the mechanical stress can be higher than other soft top coats and processed at somewhat higher temperatures, possibly making the technique amenable to well-established industrial processes. Finally, we demonstrate the ability to achieve long range order using pre-engineered cracks in the top coat in a highly desirable short time of less than 1 min.

Methods

Step 1 in figure 1 illustrates spin coating of a thin film of PS-b-PDMS and electron-beam evaporation of a thin film of silica. Silicon wafers (3″ diameter, p-type, (100), from Silicon Valley Microelectronics, Inc.) were used as-is from the manufacturer, or coated with PDMS or PS brush \[53\]. A solution of poly(styrene-b-dimethylsiloxane) (PS-b-PDMS) (from Polymer Source, Inc., Montreal, Canada, 16 kg mol\(^{-1}\), fraction of PDMS = 31%, polydispersity index \(\sim 1.08\), natural period of \(\approx 18\) nm) (SD16) as 0.7 wt% in cyclohexane was used. The polymer was dissolved at room temperature in the solvent overnight via magnetic stirring. Thin films of SD16 were spin coated on the wafers to a thickness of 32–48 nm (resulting in 1 or 2 layers of cylinders), as measured by spectral reflectometry (Filmetrics, Inc., San Diego, CA, F20 Model). Silica of thickness 40, 70, 100 and 130 nm were thermally deposited by electron-beam evaporation on top of the SD16 layer.
Step 2 in figure 1 shows the thermal annealing of the BCP, during which the microdomains self-assembled and the top coat of silica cracked. The self-assembly formed in-plane cylindrical microdomains of PDMS in a matrix of PS. The annealing was completed either in an oven or on a hotplate in an ambient environment. Samples were annealed at 170 °C–250 °C (measured by infrared thermometer) for 1 min to 20 h and passively cooled in air after annealing. The top coat cracked during the heating, creating few-μm wide cracks (and thus free edges) in the silica and BCP films.

In Step 3 of figure 1, the top coat of silica was removed in order to expose the underlying BCP film. A Teflon beaker was filled with a 1% aqueous solution of HF acid (JT Baker, diluted from 48% solution). (Warning: HF is acutely hazardous and must be used with caution and training.) The samples were exposed to the room temperature solution for 5–10 min, enough time to completely etch away the silica. The PS block served as an etch stop, preserving the internal PDMS microdomain pattern. The samples were immediately put in a bath of deionized water, rinsed liberally with water, and blown dry with N2.

Step 4 in figure 1 shows RIE to remove a thin interface-wetting layer of PDMS and the PS block of the BCP nanopattern (Plasma-Therm, St. Petersburg, Florida, 790 Series). A two-step etch was used: CF4 plasma at 50 W and 15 mTorr for 3 s to remove the top wetting layer of PDMS directly under the silica, and O2 plasma at 90 W and 6 mTorr for 14 s to remove the PS block. The oxygen plasma partially oxidized the remaining PDMS lines on the surface, leaving the final nanopattern.

Inspection and metrology of samples were performed with optical microscopy, scanning electron microscopy (SEM), helium ion microscopy (HIM), profilometry, and scanning probe microscopy (SPM). Optical microscopy was used to inspect the cracking, undulations, and etching. SEM was performed on a Raith150 system (10 kV, 100–200 pA, ~6 mm working distance) or a Zeiss Sigma system (3 kV, ~240 pA, 4–6 mm working distance). HIM was performed on a Zeiss Orion system (35 kV, <1 pA, 6–8 mm working distance). Profilometry was performed on a Dektak 3. SPM was performed on a Digital Instruments AFM in tapping mode with a standard silicon tip.

Results and discussion

Alignment of BCP by cracks in the silica top coat

We first describe how naturally-forming cracks in the silica determined the shear stress in the PS-b-PDMS BCP film, and thus oriented the cylindrical microdomains as depicted in figure 1(a). Figure 1(b) shows a step-by-step overview of the experimental process. Briefly, silicon samples were spin-coated with a thin film of PS-b-PDMS (16 kg mol\(^{-1}\), fraction of PDMS = 31%) and then a thin film of silica was deposited. The samples were thermally annealed to promote PDMS-cylinder-phase separation in the BCP and thermal expansion and cracking of the layers. The alignment of the cylinders was determined by the nearest crack. After annealing, the silica top coat was etched away with a hydrofluoric acid (HF) solution and the PS majority block was removed with reactive-ion plasma etching (RIE) to leave aligned PDMS line patterns on the surface.

Figure 2 provides a multiscale perspective on the cracking and alignment of the cylinder arrays. An example of a cracked sample is shown in figure 2(a), with a micrograph of one of the crack intersections in figure 2(b). These cracks, which formed within the first 15 s of annealing, created disconnected regions (islands) of BCP/silica films. Figure 2(b) shows the intersection of three such islands. In figure 2(c), the aligned cylinders from the highlighted region in figure 2(b) were oriented parallel to the direction of shear stress induced by the nearest crack. This alignment was observed many hundreds of micrometers from the cracks. For regions proximal to an intersection of multiple cracks (see figure S1(a) in the supplementary data, available online at stacks.iop.org/NANOFE/1/035006/mmedia), the orientation of the BCP domains was towards the crack junction (figure S1(b)). This orientation was dependent on the distance to the nearest crack line (the alignment was more towards the junction for regions closer to crack junctions, as will be discussed with figure 6), the shape/size of the silica island, and the annealing parameters. The described alignment was observed for all experimental samples, making it evident that the cracks determined the BCP orientation.

The silica islands produced by cracking ranged in size from 1 mm\(^2\) to half the area of ~1 cm\(^2\) samples, and varied in shape and orientation. We experimentally varied the thickness of the top layer (40, 70 and 100 nm) and qualitatively found that thinner films resulted in larger islands (3–5 mm diameter) compared with thicker films (1–3 mm diameter), as has been shown for silica films on polymers under small strain [42]. Top-down and side-angle SEMs were used to characterize the crack geometry (see supplemental section S2 and figure S2). We found that the crack penetrated the BCP thin film as well as the silica top coat, implying strong adhesion between top coat and BCP. These separations served as free edges which defined the orientation of the shear stress during the remainder of the annealing.
Most samples also exhibited long-period undulations in film thickness which led to defects in the self-assembled cylinder arrays. The supplemental section S3 discusses the undulations and defects in more detail, including the spatial frequency, alignment of cylinders, and film thickness. This non-uniform topography arose from buckling of the silica top coat during annealing (figures S3 and S4). While such undulations in previous reports have contributed to directed alignment through topographical templating or film flow [30, 32, 33, 43–45], microdomain alignment in this report is determined to not be due to thickness undulations, as we observed cylinders aligned normal to the cracks for both samples with undulating and uniform film thickness. In this report, we were not able to fully eliminate the undulations, though suggest mitigation in future work with thicker and stiffer top coats.

**Finite element modeling**

Finite element analysis (FEA) was used to model the shear in the three layers arising from CTEM during the thermal annealing and the shear stress as a function of the distance from free edges (cracks) as is discussed in detail in supplemental section S4. The model consisted of a cross-section of the film stack similar to the schematic in figure 3(a), where \( L \) is half the width of a silica island (modeled as 7.5 μm), \( x/L = 0 \) represents the middle of the island and \( x/L = 1 \) represents the edge of the island at the crack. The model was thermally cycled from 20 °C to a maximum temperature of 175 °C at a constant heating time of 30 s, and then cooled at 4 °C s\(^{-1}\) to model passive cooling of a silicon sample in air. The soft polymer was described by the William–Landel–Ferry (WLF) theory, discussed in supplemental section S4. The implementation of WLF is supported by the experimental study in Rosati et al [46], suggesting that the viscoelastic behavior of the BCP is controlled by the PS block. The shift factor \( \phi \) was found to be weakly dependent on the morphology of the BCP, with better agreement to the WLF theory taking place at lower volume fraction of the cylinder-forming PDMS block [46].

The thermal cycling of the three-layer stack caused a sequence of deformations and stresses during the heating and the cooling. During heating, the combination of the CTEM of the silicon substrate (compared to the top silica coat) and its high elastic modulus allowed the silicon free edge to advance, dominating the system deformation. The creation of a displacement field within the system caused a buildup of internal stresses that were mostly accommodated by the soft BCP film. Figure 3(b) shows the magnitude of the shear stress at the BCP interface with the top coat for different points within a pre-cracked island. The magnitude of the shear stress increased gradually as the system expanded during the early stage of heating. The magnitude of stress is significantly reduced when the temperature crosses \( T_g \) due to polymer softening under the effect of WLF. A sharp rise in the stress level is observed due to the abrupt increase in CTE of the BCP film above \( T_g \). About 30 °C above \( T_g \) until \( T_{\text{max}} \) the continuous heating remarkably relaxed the system and brought the shear stress to a negligible level.

As shown in figure 3(b), the cooling, modeled as passive cooling into the ambient air as performed experimentally, played a key role in the stress evolution. The top coat and substrate contracted during cooling until \( \sim 30 \) °C above \( T_g \), at which point the shear stress began to increase. Similar to the heating cycle, a sudden drop in the stress is observed by reduction of the CTE, but this is quickly overcome by the steady increase in stress. With further cooling, the BCP returned to a glassy state and shear stress increased, which we assume led to

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**Figure 2.** Optical image of cracked sample and scanning helium-ion micrographs of BCP microdomains aligning parallel to the shear stress induced by cracks in the silica top coat. (a) Photograph of the sample, where the top coat of silica is cracked (highlighted by drawn-in white lines). (b) Scanning helium-ion micrograph in which the BCP thin film (darker regions) was separated by cracks (lighter lines) that formed in the silica and BCP during thermal annealing. The cracks provided a free edge so the shear stress in the BCP film was normal to the crack line. (c) Scanning helium-ion micrograph of aligned PDMS cylinders (the lighter lines are the cylinders, and the darker lines are the gaps between the cylinders) from the highlighted region in (b). The cylinder array aligned toward the nearest crack and parallel to the shear stress direction induced by the top coat of silica. These micrographs were taken after etching of the silica and BCP. The dotted lines are intended to be heuristic guiding lines. Inset is a zoomed in section of (c) and the scale bar represents 200 nm.
the alignment of the microdomains. The stress was 100 s of kPa, much greater than the previously reported stress required to induce alignment in various BCPs \cite{11, 12, 19, 22, 25}. Furthermore, a significant residual compressive stress remained in the BCP at room temperature, with an areal-average magnitude of \( \sim \) 80 kPa. In the deformed structure in figure S9, the final-state free surfaces of the BCP and the top coat are retracted beyond their starting position. There was no significant difference between the shear stress magnitude at either the silica or silicon interfaces with the BCP.

This modeling showed that the shearing, and thus aligning of the BCP, can be accounted for by the CTEM between the different layers and is consistent with the experimental observation of PDMS domains orienting normal to nearby cracks. Other reports have also shown the importance of rapid time scales \cite{30}, large shear stresses \cite{12}, latent alignment \cite{47} and the cooling phase of the anneal \cite{16, 48} in producing highly aligned...

**Figure 3** (a) Schematic of the simulated three-layer stack. The cracks in the top coat and BCP create an island of width 2L. \( x \) represents the distance from the middle of the island towards a crack. (b) Magnitude of the shear stress on the top surface of the BCP film as a function of temperature during the heating and cooling phase as modeled by FEA. The magnitude of the shear stress is calculated at different distances from the free edge, which is located at \( x = L \). During heating, the stress builds up until \( \sim 30 \) °C above \( T_g \), after which the system becomes effectively stress-free. This lack of stress continues during cooling close to \( T_g \) but residual stresses are present when the system has cooled back to room temperature. The inset shows the shear stress variation as a function of time. (c) Shear stress during the heating and cooling as function of different thicknesses of the silica top coat. Different colored lines are different thicknesses. All data are recorded at \( x/L = 0.9 \). Blue is 50 nm, black is 100 nm, and red is 150 nm.
microdomains. To further investigate the critical importance of the large shear stresses from the mismatch in coefficients of thermal expansion, we modeled the annealing with a top coat of silicon (the same material as the substrate), and found that during-cycling shear stresses were at least one order of magnitude less than with a top coat of silica and the residual stress was less than 10 kPa (figure S10). This reduced stress further points to the importance of a mismatch between the top coat and the substrate material and motivates future work in which these layers have larger CTE mismatch.

Lastly, we modeled thermal cycling with different thicknesses of silica and found that a thicker silica film (150 nm versus 50 nm) almost doubled the shear stress in the BCP film (see figure 3(c)). Experimentally, we observed alignment for silica top coats of both 50 and 130 nm, suggesting that the reduction in shear stress was not large enough to eliminate the CTEM shear alignment. Future work with thicker top-coat films could be beneficial for exerting larger shear stress, though an increased thicknesses must be balanced with the increased crack density of thicker top coats (as discussed above). We also believe that the shear stress observed in the cooling of the film is the critical component to the microdomain alignment knowing that the reaching the high temperature is expected to put the BCP film in the disordered state. Experimentally, the temperature ramp rate, from room temperature to maximum temperature, was varied from a few second, by placing samples directly on a hotplate, to ~1 h, for samples heated with an oven, and we observed similar microdomain alignment for both regimes; therefore heating process time seems less influential than the cooling process.

While the continuum-based analysis of FEA overlooks the details of microphase separation of BCP, the mechanics of the trilayer system still provides insights on the loading state of the system, showing that the BCP is microphase-separating under an increasing shear stress during cooling. The initial loading of the sample, during the heating phase, and the residual cooling, might provide a faster pathway to a better ordered structure with fewer defects as was proposed by Majewski and Yang [47]. The efficiency of creating long range order was attributed to the fact that the BCP does not need to traverse a successive series of energy barriers to annihilate defects, but rather undergoes a concerted self-assembly under the influence of the external mechanical load.

**Controlled orientation via hand-scribing of crack lines**

Instead of relying on the natural cracking of the top coat, we show it was possible to engineer the microdomain alignment by ‘hand-scribing’ cracks. In one example, parallel scribe lines were used to align cylinders over 1 cm² sample areas, and in another example, crossed scribe lines were used to align cylinders in two different directions on the same sample. Figure 4(a) is an example of a sample with two parallel scribe lines which resulted in an aligned BCP line array over the 1 cm × 1 cm area. The three SEM images provide examples of the substrate-wide alignment of the BCP domains normal to the scribe lines for the optimized annealing conditions. Grazing-incidence small-angle x-ray spectroscopy (GISAXS) was performed on a sample with six scribe lines. The scattering plot in figure 4(b) shows 4 truncated grating peaks, two symmetric peaks on each side, suggesting that the cylinder array was aligned over the whole probed area (also see figure S12).

To characterize the shear alignment that resulted from hand-scribing, we obtained SEM images at varying distances away from the scribe lines. Samples with two parallel scribe lines spaced evenly on the substrate were annealed at 200 °C–275 °C in an oven (no vacuum) for 1 and 10 min with a BCP thickness of 36.5 nm on bare Si. After processing, SEM micrographs were used to determine the alignment versus distance from the scribe line, as summarized in figure 5(a) and exemplified in figure 5(b). The micrographs were classified as ‘well aligned’ (>65% of the cylinders were aligned toward the crack within 5° of the normal, and there were fewer than ~100 counted defects per μm²), ‘poorly aligned’ (<65% aligned cylinders or >100 defects per μm²) and ‘unaligned’ (fingerprint pattern with no correlation to crack direction, as exemplified in the SEM of 200 °C for 1 min in figure 5(b)). (While further attempts were made to quantitatively characterize the degree of alignment, the micrographs did not provide more information than the presented semi-quantitative measurements.)

Annealing for 10 min as opposed to 1 min increased the distance over which the BCP was oriented towards the scribe line and the defects were reduced. At annealing temperatures of 250 °C and 275 °C, the BCP microdomains were aligned over the entire sample for 10 min of annealing. This time-dependent ordering was unexpected, as FEA suggested residual (post-annealing) stress was roughly independent of heating time (figure S11). We suggest that by heating the films for longer times, the microdomains had more time to take advantage of the previously-discussed latent alignment before the residual stress of the cooling process completed the alignment. We must note that the well aligned region was surprisingly smaller for 275 °C annealing, and future work will be required to fully elucidate the alignment trend at temperatures higher than 250 °C. As an extension of this handscribing technique, the orientation of the BCP domains could be controlled in different directions on a single substrate by placing scribe lines at an angle. Figures 6 and S13 illustrate this technique with perpendicular and oblique scribe lines, respectively.
These results illustrate templating of the alignment via hand-scribed lines which define cracks upon thermal cycling. However, natural cracking was not eliminated even with hand-scribing. Natural cracking may be mitigated by optimizing the internal strain and/or thickness of the deposited silica films as well as the scribe density and annealing process. Although not investigated in this report, the engineering of the crack pattern is not limited to hand scribing and could also be accomplished with other microfabrication methods such as photolithography. We expect that the crack width could be scaled down to 1 μm, significantly increasing the surface coverage of the BCP patterning.

The alignment of the BCP cylinders could be accomplished in less than 1 min. Figure S14 shows an example of aligned cylinders annealed for 1 min, compared to cylinders which were annealed for 10 min without a top coat.

**Figure 4.** Sketch and scanning electron micrographs of substrate-wide shear alignment of cylinders oriented orthogonal to two scribe lines and GISAXS showing large-area orientation. (a) The sketch depicts the square sample with two lines scribed to divide the sample into three equal areas. The three SEMs show the BCP line array, oriented parallel to the normal of the scribe lines in each of the three sections. The light lines are oxidized PDMS cylinders after RIE, and the dark lines are the gaps in between. Images are false-colored to demonstrate regions with alignment within 10° of normal to the scribe line (green) and >10° (red). The alignment cutoff of 10° was chosen arbitrarily as a guide for the reader. The scale bars represent 200 nm. (b) Glancing-incidence small-angle x-ray pattern of truncated grating peaks showing the oriented, periodic nature of the BCP cylinders over the illuminated area of the x-ray beam.
coat that showed no preferred orientation. Rapid alignment like this, in as low as 15 s in many cases, was observed for annealing temperatures from 225 °C to 240 °C and up to 200 μm away from scribe lines. This result indicates that the effectiveness of the shear alignment process is on par with other rapid annealing procedures \[13, 18, 19, 29, 30, 49–52\], despite the fact that the small relaxation time of PS-\(b\)-PDMS means that it is less susceptible to shear alignment as other polymers such as PS-\(b\)-PI and PS-\(b\)-P2VP \[30\]. Such rapid alignment may be critical for industrial fabrication of nanopatterns where high throughput is required at sizes unattainable with currently lithographic processes.

Figure 5. Graph and SEMs of ordered and defective alignment versus distance from the scribe lines. (a) Graph of the distances from hand scribed cracks (within 100 μm error) for which BCP domains exhibited alignment and low defects (solid region) or poorer alignment with more defects (hatched region) as a function of annealing temperature. The blue and gray regions denote 1 and 10 min of annealing, respectively. (b) Example SEMs showing morphology versus temperature. Images are false-colored to demonstrate regions with alignment within 5° of normal to the scribe line (green) and >5° (red). The alignment cutoff of 5° was chosen arbitrarily as a guide for the reader to contrast the alignment areal density in the well and poorly aligned regions. Scale bars all represent 100 nm.
Conclusions

A CTEM-based shear method is demonstrated for rapid and large-area alignment of a monolayer of cylindrical microdomains with sub-10 nm diameter. This method differs from previous shear alignment approaches by utilizing a rigid inorganic top coat. The mismatch in the coefficient of thermal expansion between the top coat, BCP layer and substrate, here silica and silicon, led to cracking in both the top coat and BCP film, and produced a directional shear stress in the sandwiched BCP film, resulting in well aligned cylinder domains. Free edges in the BCP and top coat film, from either natural or pre-engineered cracking, controlled the orientation of the shear stress and the resulting cylinders. Our FEA modeling showed that the final stress on the BCP film was >100 kPa, orders of magnitude larger than that required for the shear alignment of BCPs with other soft shear approaches, and this stress extended many 100 s of μm away from the free edges. As a result, aligned line arrays occurred over ~1 cm² samples with 1–10 min of thermal annealing. We expect that further optimization and pairing with templated self assembly (chemo- or graphoepitaxy) may lead to reduced pattern defectivity and line roughness. We have laid the ground work for greater local control of the aligned nanopatterns by microfabrication of the top coat cracks, via mask deposition, nanoimprint lithography, optical lithography or laser micromachining, or with a combination of CTEM-shear and localized heating with laser or scanning probe systems. The demonstration of CTEM shear and the viscoelastic model developed to describe it will allow future exploration of other hard top coat materials, alternate methods for providing orientation, e.g. lithography, optimization of the annealing process, and shear assembly of a wide variety of polymers or macromolecules.

Figure 6. Sketch and scanning electron micrographs of shear alignment with orientation in multiple directions defined by crossed scribe lines. The sketch shows the square sample with the scribe lines intersecting at a right angle and the varying orientation of the BCP cylinders normal to the nearby scribe line or towards the nearby corner. The three SEMs show the BCP oriented normal to the scribe lines for the vertical and horizontal scribes; and oriented towards the corner for the scribe intersection. The light lines in the SEMs are oxidized PDMS cylinders after RIE, and the dark lines are the gaps in between. The scale bars represent 200 nm.
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