

www.MaterialsViews.com

Nanometer Scale Alignment of Block-Copolymer Domains by Means of a Scanning Probe Tip

Jonathan R. Felts, M. Serdar Onses, John A. Rogers, and William P. King*

Block-copolymers (BCPs) comprise one set of materials useful for nanometer-scale lithography^[1] and nanomaterial patterning.^[2] Under certain conditions, a BCP thin-film can phaseseparate into discrete domains on a surface, with domain sizes much smaller and densities much higher than can be achieved using conventional lithography.^[3,4] The phase-separated films can then be used as an etch mask in a technique known as BCP lithography, where selectively etching one of the blocks in a spin-cast BCP thin film yields a polymer mask further used for liftoff or etching processes. BCP lithography has been used to construct functional nanostructured surfaces,^[5,6] thin film electronics,^[7] and organic electronic sensors.^[8] While BCPs provide great control over the size and periodicity of the nanoscale domains, the random domain orientation typically found in BCP thin films makes design of nanolithographic structures difficult.^[9] Incorporating BCP lithography into nanodevice fabrication requires the ability to both pattern BCP nanostructures and direct BCP domain self-assembly.

A variety of techniques exist to pattern and control domain alignment of BCPs, such as lithographically modifying the underlying substrate prior to adding the BCP film, applying an external field to the film, and patterning BCP nanostructures using imprint lithography and electrohydrodynamic-jetting.^[10,11] Modifying the chemistry or the geometry of the substrate changes the surface-polymer interaction such that one block prefers the modified areas of the substrate.^[12-14] While surface modification is effective at producing long range order in the BCP patterns, the modification itself requires an additional nanolithography technique with a resolution on the order of the BCP domain size. Long range BCP domain order can be achieved without the use of nanolithography techniques by applying an external electric field,^[15,16] temperature gradient,^[17] or shearing force^[18-20] to the BCP thin film. While applying external fields does not require high resolution lithographic techniques to align the BCP domains, the fields are applied to the entire thin film, with no translational or spatial control over domain self-assembly. Imprinting and jetting techniques can generate BCP nanostructures, but must often be combined with chemical or geometrical substrate modifications to direct

Dr. J. Felts, Prof. W. King Department of Mechanical Science and Engineering University of Illinois Urbana-Champaign 1206 W. Green St., Urbana, IL 61801, United States E-mail: wpk@illinois.edu Dr. M. Onses, Prof. J. Rogers Department of Materials Science and Engineering University of Illinois Urbana-Champaign 104 South Goodwin Ave., Urbana, IL 61801, United States

DOI: 10.1002/adma.201305481



BCP self-assembly. There is a need to arbitrarily control the patterning and alignment of BCP domains at the nanometer scale—and ultimately with single domain control—without the use of nanometer scale substrate modification or pre-fabricated lithographic masks. Atomic force microscope (AFM) tips provide a means for nanolithographic surface modification, and have been used previously to pattern a wide variety of organic materials, such as polymers,^[21–23] self-assembled monolayers,^[24,25] block-copolymers,^[26] and polymer-nanoparticle blends^[27] by controlling the tip speed, tip dwell time, and tip or surface temperature. The high level of control over shear force and mass flow rates at the tip makes AFM a useful tool for investigating nanometer scale patterning and alignment of BCP domains.

Here we demonstrate nanometer-scale control of BCP domain alignment and patterning using an AFM tip, achieving long range alignment of a lamellae-forming BCP with domains oriented perpendicular to the underlying substrate. The domains are aligned parallel to the tip travel with a spatial resolution of 200 nm (roughly 10 domains). The domains can undergo multiple realignment steps, providing a means for patterning micrometer sized regions of unique and different domain alignment. An AFM tip can also deposit BCP nanostructures onto a heated substrate, and we show that under certain conditions the BCP domains align themselves either parallel or perpendicular to the tip shear direction, a behavior not observed in studies of BCP at the macro scale.

Figure 1(a) shows the experimental setup. The BCP thin film sample was placed within the AFM in an inert nitrogen environment while a heater brought the sample to 220 °C, well above the glass transition temperature (see supporting information). Once the BCP film phase-separates, an AFM tip contacts the sample and scans in the direction of the desired BCP domain alignment. The block-copolymer in this experiment has a 37-37 K molecular weight and consists of poly(styreneblock-methyl methacrylate) (PS-b-PMMA). The silicon substrate is initially coated with a random copolymer mat which non-preferentially wets (i.e. neutral) both the PS and PMMA blocks, and the BCP is deposited onto the neutral surface using spin-casting with a thickness of ~35 nm. Figure 1(b) shows an AFM phase image of a patterned sample area. The left portion of the image shows the randomly oriented domains that resulted from the initial sample heating, and the right portion of the image shows a region of domains preferentially aligned in the direction of tip travel. The tip speed was 2 μ m/s with a scan line pitch of 100 nm, on the order of the 41 nm BCP domain periodicity. Figure 1(c) shows aligned BCP domains resulting from a single tip scan line, showing that the tip can align domains with a resolution of 200 nm, which for this BCP is roughly equivalent to 10 domains.

www.advmat.de

(a) Randomly AFM Aligned TIP Copolymer Domains Aligned Copolymer Domains Heater (b) Tip Travel Direction 400 **Randomly Aligned Aligned Domains** Domains (C) - 200 nm

Figure 1. (a) Schematic of the experimental setup. An AFM tip aligns block-copolymer domains along the direction of tip travel while a heater heats the surface to 220 °C. (b) An AFM phase image of a tip aligned region (right) next to a randomly aligned region (green overlay on left to aid the eye). (c) 200 nm wide aligned copolymer domains resulting from a single tip pass.

The BCP domain alignment direction can be controlled at the nanometer scale by changing the direction of tip travel, and subsequent tip scans are able to further change the alignment direction. **Figure 2**(a) shows an AFM phase image of the sample after multiple tip scans. The tip first scanned vertically over the entire area, followed by horizontal tip scanning in 1 μ m stripes. The results show that the initial vertical tip scans orient the random BCP domains along the tip travel direction,



and subsequent tip scans orthogonal to the original scan direction reoriented the previously aligned domains. A close-up view of the interface between the two orthogonally aligned regions shows that the transition between them occurs within 100 nm (5 domains), which is the distance between tip scan lines. Figure 2(b) shows an AFM phase image of domains aligned along a sinusoidal tip scan, after first aligning the domains vertically, further demonstrating that domain alignment follows the tip trajectory at the micrometer scale. In all cases, the smallest local alignment size achieved exceeded the nominal AFM tip radius of 10 nm, likely due to a combination of BCP domain size and the fluid shear dynamics within the film induced by the moving tip.

The measurements agree with previous studies of shearinduced alignment. Previous research studying macroscale shear alignment in perpendicular lamellar BCP domains showed that domains aligned parallel to the shear direction, with an orientational order parameter (a quantitative measure of the degree of long range alignment) of 0.8 for shear stresses between 10-40 kPa.^[28] In the current experiments, the local shear stress within the BCP thin film can be approximated by $\tau = \mu V/h$, where μ is the polymer viscosity, *V* is the tip velocity, and *h* is the distance over which the stress is applied. Assuming a typical viscosity value of 1000 Pa-s, a tip speed of 2 µm/s, and a characteristic shear length of 100 nm results in a shear stress of about 20 kPa, well above the threshold required to align the domains. The orientational order parameter was calculated to be 0.66 (see supplemental material), which could be improved in the future by using a smaller pitch between scan lines or undergoing multiple tip passes in each area. Increasing the speed of the tip did not noticeably enhance domain alignment, and tip speeds exceeding 5-10 µm/s (50 - 100 kPa) damaged the BCP film.

In addition to alignment of BCP domains, the tip can also deposit BCP nanostructures onto a neutral substrate. Figure 3(a) shows the experimental technique, where the tip - first coated with the BCP by dip-coating – scans along the heated substrate. The BCP melt flows from the tip to the substrate when the substrate is 220 °C. Figure 3(b) shows an AFM phase image of a BCP nanostructure written from a coated AFM tip with a width of 700 nm and a height of 100 nm, where the BCP domains are aligned in the direction of tip travel. Figure 3(c) shows a separate written nanostructure having a necked region in the center, resulting in 3 unique domain orientations. The structures on either side of the necked region are similar to the feature written in Figure 3(b) and have domains oriented perpendicular to the substrate and parallel to the tip travel direction. In contrast, the necked region shows domains oriented perpendicular to the substrate and transverse to the direction of tip travel, an orientation not previously seen in shear driven BCP domain alignment. The intermediate region between the perpendicular and transverse regions has a featureless area and visible transverse domains isolated at the edges of the nanostructure. We speculate that the intermediate region contains either BCP domains stacked parallel with respect to the surface, or a region of transverse domains covered by a single polymer overlayer, due to the presence of visible domains near the nanostructure edges.^[28] For tip speeds exceeding 10 µm/s, the tip deposited nanostructures with dimensions on the order of the domain size and smaller, as shown in Figure 3(d). The BCP nanoribbon

www.advmat.de



www.MaterialsViews.com



Figure 2. (a) An initial tip pass in the vertical direction aligns the copolymer domains vertically, and a subsequent horizontal tip pass aligns the domains horizontally (green overlay aids the eye in identifying vertical domains). (b) A sinusoidal tip scan trajectory shows that the domain orientation can be controlled on the micrometer scale.

has a width of 50 nm and a height of 0.8 nm, where the domains are again oriented perpendicular with respect to the substrate and transverse to the tip travel direction. Figure 3(e) shows a cross-section of the AFM tip phase in tapping mode, showing clearly the presence of distinct BCP domains, with a periodicity of 35 ± 7 nm.

The observed domain orientations and alignments are likely influenced by competition between interfacial surface energies, tip shear force, and geometrical constraints within the nanostructures. Film thickness and preferential polymer wetting of the silicon tip may influence the formation of featureless, parallel structures, as observed in Figure 3(c). This hypothesis is supported by the presence of perpendicular domains on the edges of the nanostructure, far the tip-feature contact and at smaller thickness. The orientation of domains perpendicular to the substrate is influenced by tip shear, confinement due to the nanostructure boundaries and the curvature of the nanostructure. For the structure in Figure 3(c), the domains labeled perpendicular are regions where tip shear and confinement act to orient the domains parallel to tip travel, while the parallel and transverse regions are likely dominated by the nanostructure curvature acting to orient the domains transverse to tip travel.^[29] In contrast, the dimensions of the nanoribbon in Figure 3(d) suggests that the domain structure is determined mainly by high tip shear, where the polymer chains are stretched flat along the direction of tip travel. Despite current uncertainties in the orientation mechanisms of tip-based BCP nanostructure deposition, nanometer sharp tips can pattern BCP structures with a wide range of feature sizes, geometries, and domain configurations not easily achieved using conventional BCP patterning methods.

In the future, tip-based nanolithography of BCPs can be further improved by optimizing the choice of BCP, tip, and substrate, and by improving the control of BCP nanostructure deposition. BCP compositions which form cylindrical domains have shown much better long range order when sheared.^[18] Coating the AFM tip with a neutral layer may reduce the presence of domains oriented parallel with respect to the surface. Improving the control of nanostructure deposition such that the size and geometry of the deposited structures can be routinely determined would provide additional understanding of the mechanisms involved in domain alignment, and ultimately the ability to design nanostructures with the desired alignment. Further, tip-based BCP patterning could be integrated with chemically and structurally heterogeneous surfaces as a way to control domain alignment within a single nanostructure or to discover and repair defects in structures aligned through other means.



www.MaterialsViews.com

the American Recovery and Reinvestment Act of 2009. The DOE SCGF program is administered by the Oak Ridge Institute for Science and Education for the DOE. ORISE is managed by Oak Ridge Associated Universities (ORAU) under DOE contract number DE-AC05–06OR23100.

Received: November 4, 2013 Revised: December 5, 2013 Published online: February 12, 2014

- R. Ruiz, H. M. Kang, F. A. Detcheverry, E. Dobisz, D. S. Kercher, T. R. Albrecht, J. J. de Pablo, P. F. Nealey, *Science* **2008**, *321*, 936.
- [2] R. B. Thompson, V. V. Ginzburg, M. W. Matsen, A. C. Balazs, Macromolecules 2002, 35, 1060.
- [3] F. S. Bates, G. H. Fredrickson, Ann. Rev. Phys. Chem. 1990, 41, 525.
- [4] D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548.
- [5] J. Y. Cheng, C. A. Ross, V. Z. H. Chan, E. L. Thomas, R. G. H. Lammertink, G. J. Vancso, Adv. Mater. 2001, 13, 1174.
- [6] R. R. Li, P. D. Dapkus, M. E. Thompson, W. G. Jeong, C. Harrison, P. M. Chaikin, R. A. Register, D. H. Adamson, *Appl. Phys. Lett.* 2000, 76, 1689.
- [7] J. W. Bai, X. Zhong, S. Jiang, Y. Huang, X. F. Duan, Nat. Nanotechnol. 2010, 5, 190.
- [8] Y. S. Jung, W. Jung, H. L. Tuller, C. A. Ross, Nano Lett. 2008, 8, 3776.
- [9] C. Harrison, D. H. Adamson, Z. Cheng, J. M. Sebastian, S. Sethuraman, D. A. Huse, R. A. Register, P. M. Chaikin, *Science* 2000, 290, 1558.
- [10] M. S. Onses, C. Song, L. Williamson, E. Sutanto, P. M. Ferreira, A. G. Alleyne, P. F. Nealey, H. Ahn, J. A. Rogers, *Nat. Nanotechnol.* 2013, *8*, 667.
- [11] J. Bang, U. Jeong, D. Y. Ryu, T. P. Russell, C. J. Hawker, Adv. Mater. 2009, 21, 4769.
- [12] M. P. Stoykovich, M. Müller, S. O. Kim, H. H. Solak, E. W. Edwards, J. J. de Pablo, P. F. Nealey, *Science* **2005**, *308*, 1442.
- [13] J. Y. Cheng, A. M. Mayes, C. A. Ross, Nat Mater 2004, 3, 823.
- [14] D. Sundrani, S. B. Darling, S. J. Sibener, Nano Lett. 2003, 4, 273.
- [15] P. Mansky, J. DeRouchey, T. P. Russell, J. Mays, M. Pitsikalis, T. Morkved, H. Jaeger, *Macromolecules* **1998**, *31*, 4399.
- [16] V. Olszowka, M. Hund, V. Kuntermann, S. Scherdel, L. Tsarkova, A. Böker, ACS Nano 2009, 3, 1091.
- [17] G. Singh, K. G. Yager, B. Berry, H. C. Kim, A. Karim, ACS Nano 2012, 6, 10335.
- [18] D. E. Angelescu, J. H. Waller, D. H. Adamson, P. Deshpande, S. Y. Chou, R. A. Register, P. M. Chaikin, *Adv. Mater.* 2004, *16*, 1736.
- [19] G. H. Fredrickson, J. Rheol. 1994, 38, 1045.
- [20] K. A. Koppi, M. Tirrell, F. S. Bates, K. Almdal, R. H. Colby, J. Phys. II 1992, 2, 1941.
- [21] J. R. Felts, S. Somnath, R. H. Ewoldt, W. P. King, Nanotech. 2012, 23, 215301.
- [22] P. E. Sheehan, L. J. Whitman, W. P. King, B. A. Nelson, Appl. Phys. Lett. 2004, 85, 1589.
- [23] M. Yang, P. E. Sheehan, W. P. King, L. J. Whitman, J. Am. Chem. Soc. 2006, 128, 6774.
- [24] S. Chung, J. R. Felts, D. Wang, W. P. King, J. J. De Yoreo, Appl. Phys. Lett. 2011, 99, 193101.
- [25] R. D. Piner, J. Zhu, F. Xu, S. H. Hong, C. A. Mirkin, Science 1999, 283, 661.
- [26] J. Chai, F. Huo, Z. Zheng, L. R. Giam, W. Shim, C. A. Mirkin, Proc. Natl. Acad. Sc. 2010, 107, 20202.
- [27] W. K. Lee, Z. T. Dai, W. P. King, P. E. Sheehan, Nano Lett. 2010, 10, 129.
- [28] S. Pujari, M. A. Keaton, P. M. Chaikin, R. A. Register, Soft Matt. 2012, 8, 5358.
- [29] B. H. Kim, H. M. Lee, J.-H. Lee, S.-W. Son, S.-J. Jeong, S. Lee, D. I. Lee, S. U. Kwak, H. Jeong, H. Shin, J.-B. Yoon, O. D. Lavrentovich, S. O. Kim, Adv. Funct. Mater. 2009, 19, 2584.



Figure 3. (a) Schematic depicting block-copolymer deposition from a tip onto a heated substrate. (b) AFM phase image of a deposited polymer structure showing copolymer domains aligned in the direction of tip travel. (c) An AFM phase image of a polymer line with a sub 200 nm domain where the domains order transverse to the direction of tip travel. (d) AFM phase image of a polymer nanoribbon 0.8 nm tall and 50 nm wide showing copolymer domain orientation transverse to trip travel direction. (e) Phase cross section of the copolymer nanoribbon showing a domain pitch of 35 \pm 7 nm.

In conclusion, we have demonstrated nanometer scale control over the alignment of domains within a BCP thin film and deposited BCP nanostructures using AFM tips. Scanning a tip over the BCP film aligns the domains parallel to the direction of tip travel with a spatial resolution of 200 nm. Further, subsequent alignment scans can alter the direction of already aligned domains, and adjacent sub-micron patterns with different domain alignment can be patterned with transitional boundaries on the order of 100 nm. AFM tips can also deposit BCP nanostructures onto a heated substrate, where the domains can be aligned parallel or transverse to tip travel, enabling the control of domain alignment within deposited BCP structures.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This research was supported in part by an award from the Department of Energy (DOE) Office of Science Graduate Fellowship Program (DOE SCGF). The DOE SCGF Program was made possible in part by