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Formation of sub-7 nm feature size PS-*b*-P4VP Block Copolymer Structures by Solvent vapour process

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ABSTRACT

The nanometer range structure produced by thin films of diblock copolymers makes them a great of interest as templates for the microelectronics industry. We investigated the effect of annealing solvents and/or mixture of the solvents in case of symmetric Poly (styrene-*block*-4vinylpyridine) (PS-*b*-P4VP) diblock copolymer to get the desired line patterns. In this paper, we used different molecular weights PS-*b*-P4VP to demonstrate the scalability of such high χ BCP system which requires precise fine-tuning of interfacial energies achieved by surface treatment and that improves the wetting property, ordering, and minimizes defect densities. Bare Silicon Substrates were also modified with polystyrene brush and ethylene glycol self-assembled monolayer in a simple quick reproducible way. Also, a novel and simple in situ hard mask technique was used to generate sub-7nm Iron oxide nanowires with a high aspect ratio on Silicon substrate, which can be used to develop silicon nanowires post pattern transfer.

Keywords: Block copolymers, solvent annealing, high χ polymers, polymer brushes, metal oxide inclusion

1. INTRODUCTION

1.1 Block copolymers in nanoscience and nanotechnology

Block copolymers are of technological importance for various reasons, as they are “combinations” of two types of polymers connected covalently. They can have properties of both polymers. In recent years, the importance of self-assembly of block copolymer in lithographic technique has attracted numerous research groups and industries. Block copolymers occupy a huge area of research because they offer a wide range of possibilities for architecture, size, and chemical composition. In bulk, due to thermodynamically incompatible and chemically immiscible blocks balance the entropic and enthalpic driven phase separation and the chemical bond constraints between the blocks driven the formation of ordered domains on nanometer features [1-7]. Nanoscale features with high precision and their rising demand for nanoscale fabrication methods, combined with the inherent feature-size limitations of optical lithography and the low throughput of electron-beam lithography, have motivated a search for cost-effective nanoscale fabrication technologies, including nanoimprint lithography [8], dippen nanolithography [9], and self-assembled block copolymer lithography [10-14]. For such nanostructured materials to be useful in thin-film applications, it should produce periodic arrays over a large area with

uniform thickness and well-ordered BCP microdomains. Accordingly, different approaches for controlling the orientation of microphase-separation have been developed such as solvent annealing [15-19]. Libera and co-workers [20] were the first to demonstrate the effect of solvent evaporation on the orientation of cylindrical microdomains normal to the film surface in a range of different BCP thin films. PS-*b*-PMMA is the system which has been extensively studied as it forms well-ordered and aligned line patterns by thermal annealing. However, it requires brush layer on top of the silicon substrate to form the well aligned structure which is time consuming method [21]. Etching of PS-PMMA suffers from rounding of the pattern, which can cause problems for device fabrication [22]. Another high chi system, PS-PDMS showed promising patterns but it also required the brush layer as well as poor pattern transferability [23, 24].

1.2 Lamellar PS-*b*-P4VP Block copolymer

In this paper, we have discussed the effect of solvents during solvent annealing of Polystyrene-*block*-Poly 4-vinyl pyridine (PS-*b*-P4VP). Solvent annealing is different from thermal annealing, where the solvent molecule is the extra component to be introduced in the films and that can lead to change in the morphology by the interaction of solvents and polymers which cannot be achieved through thermal annealing [25]. This orientation was found to be independent of the nature of substrate, but depends on the solvent used for annealing. It is well known that PS-*b*-P4VP belongs to non-ionic amphiphilic systems. Due to chemical incompatibility of both the blocks they dissolved in different solvents. Thus, the rich micellation behavior of the PS-*b*-P4VP system has been extensively investigated [26-29]. The high degree of dipolar polarization of the P4VP block leads to a strong repulsive interaction between the polystyrene and the P4VP blocks [30]. Flory-Huggins parameter, χ , of PS-*b*-P4VP exceeds the value of any other non-ionic system by at least one order of magnitude [31], which is supported by order-disorder transition temperatures well beyond 300°C. Therefore, the PS-*b*-P4VP diblock copolymers are strongly segregated and their bulk morphology is controlled by the block ratio. The supramolecular assemblies of PS-*b*-P4VP has been extensively studied, in which at least one of the blocks of the block copolymer should contain suitable functionality which can interact with the low-molecular weight additive through non-covalent interactions (in this case intermolecular H-bonding). The low-molecular weight additives which have been extensively used are 3-pentadecylphenol (PDP), dodecylbenzene sulfonic acid (DBSA), and 2'-(4'-hydroxybenzeneazo) benzoic acid (HABA). Herein we have studied, the self-assembly of lamellar PS-P4VP without using any additives. In this paper, we have also demonstrated a method to generate a patterned Iron oxide structure by using a simple inclusion technique.

2. EXPERIMENTAL SECTION

A series of Polystyrene-*block*-Poly-4-vinylpyridine (PS-*b*-P4VP) diblock copolymers with different molecular weights ($M_n = 20-17 \text{ kg mol}^{-1}$, $M_w/M_n = 1.08$; $M_n = 9.8-10 \text{ kg mol}^{-1}$, $M_w/M_n = 1.06$; $M_n = 7.4-7.7 \text{ kg mol}^{-1}$, $M_w/M_n = 1.08$; $M_n = 5-5 \text{ kg mol}^{-1}$; $M_w/M_n = 1.1$ and $M_n = 3.3-3.1 \text{ kg mol}^{-1}$; $M_w/M_n = 1.2$) were used without further purification. Reagent grade Toluene, Tetrahydrofuran (THF) and acetone were purchased from Sigma-Aldrich. Concentrated sulphuric acid and hydrogen peroxide were purchased from Sigma-Aldrich for piranha solution. All the chemicals were used as received without any further purification. Polymer brushes were prepared by simple method. Hydroxyl terminated polystyrene with molecular weight 4 kg mol^{-1} was dissolved in toluene to get 1 wt % solution. Silicon substrates were cleaned by piranha

treatment at 90°C for 1h and washed thoroughly with distilled water. Polystyrene solution were spin coated on piranha cleaned silicon substrate which further baked at 180°C for 12h and then rinsed with toluene to remove the unreacted polystyrene. Hydroxyl terminated PS brush chemically reacted to the oxide layer of silicon surfaces. All PS-*b*-P4VP polymers mentioned above were dissolved in Toluene, THF and Toluene/THF (80/20) to get 0.5 weight % solutions. The PS-*b*-P4VP solutions were kept for overnight stirring at room temperature to ensure complete solubility of the polymer. The silicon (100) wafers with an interfacial oxide of 2 nm were cleaned by sonicating for 15 min in Toluene and followed by 10 min in acetone and dried under stream of nitrogen prior to use. Thin films of desired thickness were prepared by spin-coating the polymer solutions on silicon wafers at 3000 rpm for 30 sec using a Specialty Coating Systems G3P-8 spin-coater. As the film is shrunk upon deposition, it may be again swollen in certain solvent for ordering or re-orientation purposes. So called solvent annealing is driven by the rate of solvent saturation and the time period in the swollen state. Here, the obtained films were kept in glass vial in 100 ml bottle containing 20 ml of solvents and were annealed at 50°C and in mixture of Toluene-THF for 30 min to 9 hours. Annealed samples were immediately removed from the vials and kept at room temperature for few minutes to allow the evaporation of the solvent is completed with to reduce the swelling of the films occurred due to different evaporation rate. All the annealed samples were sent for analysis.

Different concentrations (0.4-0.5 wt %) of iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) solutions were prepared in Ethanol and successively spin-coated onto the thin film. Spin coated thin film was send for UV/ozone treatment to oxidize the precursor and to remove the polymer.

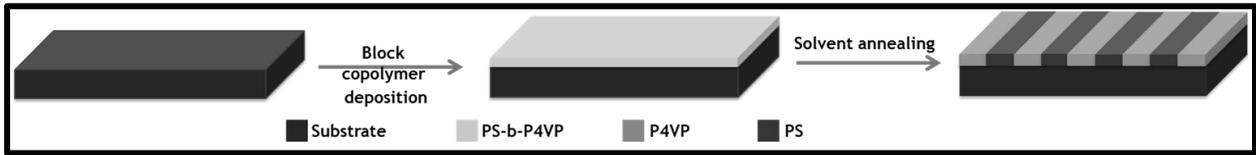
Characterization: An atomic force microscope (DME 2452 DualScope Scanner DS AFM) (SPM, Park Systems, XE-100) was used for studying the surface structure of the samples. AFM provides images of structural details without any chemical treatment (etching or staining) of the specimens. The film thicknesses were measured by optical ellipsometer (Woolam M2000). Surface morphologies of Iron oxide nanowires were imaged by scanning electron microscopy (SEM, FEI Company, FEG Quanta 6700 and Zeiss Ultra Plus).

3. RESULTS AND DISCUSSION

3.1 Self-assembly by solvent annealing

The thin film morphologies of BCP are profoundly influenced by various parameters, such as the block ratio, the strength of the interactions at the substrate interface, and surface fields of variable strength at a free surface. Microphase separation of PS-*b*-P4VP which contains approximately symmetric blocks phase-separates into lamellar structures and when spun-cast into thin films on silicon substrate, the surface morphology were characterized by the interaction between P4VP blocks and substrate and the lower surface tension of PS blocks that reduces the surface free energy at film-air interfaces. Here, we have demonstrated the phase separation in lamellar PS-*b*-P4VP block copolymer without using any organic moiety. Use of organic moiety, such as, PDP, HABA or other hydrogen bonding compounds increase the molecular weight of the system. We have obtained the phase separation with very simple technique. The use of organic solvent for solvent

annealing is well known. By using the series of solvents we have demonstrate the effect of solvents on the phase separation on bare silicon substrates.



Scheme 1: Schematic diagram describing the experimental procedure of self-assembly of PS-*b*-P4VP diblock copolymer

PS-*b*-P4VP with approximately symmetric blocks phase- separate into lamellar structures, when spin cast on silicon substrates were sent for solvent annealing in sealed glass bottle. The phase separation process is illustrated in scheme 1. The cleaned Silicon substrate was used to spin coat the block copolymer solution of 0.5 wt. % concentration dissolved in mixture of toluene and THF. The spin-coated BCP solution was sent for solvent annealing under solvent vapors of Toluene and THF atmosphere at 50°C for 3h.

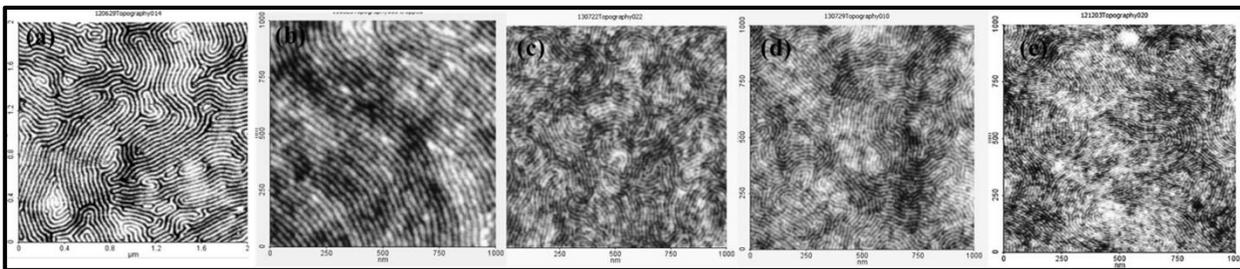


Figure 1. AFM images of solvent annealed microphase separated line patterns of different molecular weight PS-*b*-P4VP system (a)20k-17k, (b) 9.8k-10k, (c)7.4k-7.7k, (d)5k-5k and (e)3.3k-3.1k respectively.

Figure 1 shows atomic force microscopic (AFM) images of solvent-annealed PS-*b*-P4VP films on a silicon substrate with a native oxide layer. Solvent annealing method employed to achieve line structures, which could interpreted as perpendicularly oriented lamellae. The fingerprint-like pattern is consistent with a lamellar sample aligned perpendicular to the substrate. It is apparently that the annealing solvents can impart the mobility to the thin films so it can reorganize into more ordered structures after annealing, though the mobility of each component may be in different level. Center to center distance of microphase separated nanostructures of the polymer matrix with a period of 35nm, 22nm, 19nm, 15nm and 10.3nm for 20k-17k, 9.8k-10k, 7.4k-7.7k, 5k-5k and 3.3k-3.1k respectively was observed after annealed in solvent environment for 3h at 50°C from vapors of mixture of toluene and THF. The scalability of sub-12nm lamella forming PS-*b*-P4VP makes it one of the most potential candidates for nanofabrication industry.

3.2 Effect of film thickness within a same film

For lithographic applications, monolayer patterns are used as templates. Therefore, the orientation of block copolymer morphologies plays important role as it can change the pattern geometry. A mixed morphology was observed (Fig. 2) in PS-*b*-P4VP (20k-17k) after 1h of annealing from Toluene/THF mixture at 50°C, that transitioned into hexagonally packed dot structures, which could be interpreted as vertically oriented cylinders and small line formation. The thickness difference

between both the morphologies is of 3-4 nm. That shows importance of uniform and smooth film to get desired structure. The self-assembly of block copolymers is fundamentally influenced by the boundary conditions including film thickness.

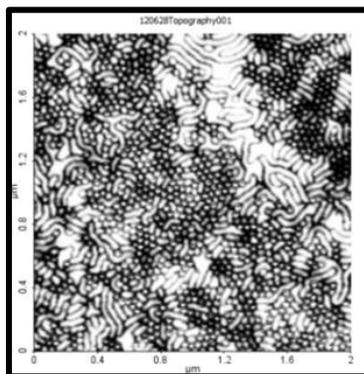


Figure 2. Topographic AFM image to demonstrate the effect of film thickness within a same film of PS-*b*-P4VP (20k-17k) after annealing for 1h at 50°C in Toluene/THF mixture.

3.3 Effect of annealing solvent(s) on the morphology of block copolymers

Morphological structures obtained were compared after annealing of PS-*b*-P4VP in different compositions of toluene and THF. Figure 3 shows the morphology obtained from pure toluene, THF and their different volume compositions. It should be noted that when spin coated thin film obtained from toluene/THF (80/20) was exposed to toluene, the hexagonally packed arrays of P4VP microdomains oriented normal to the surface in a PS matrix were formed as shown in Figure 3-a. Increasing the THF content in the annealing solvent mixture as shown in Figure 3b-c, orientation of the microdomains to the mixed lamellar forming structures was observed. It is due to the solvent evaporation and ability to dissolve one of the blocks. As toluene is more selective solvent for PS and THF is more selective solvent for P4VP, increasing the THF content in the mixture will flip the nanostructures to form the lamellar structure as shown in Figure 3d-g. Upon increasing addition of THF as annealing solvent with toluene as minor component, dewetting of the thin films was observed after annealed for longer time as shown in Figure 3-h. In presence of pure THF, lamellar structure was observed after 3h of annealing at 50°C (Figure 3-i).

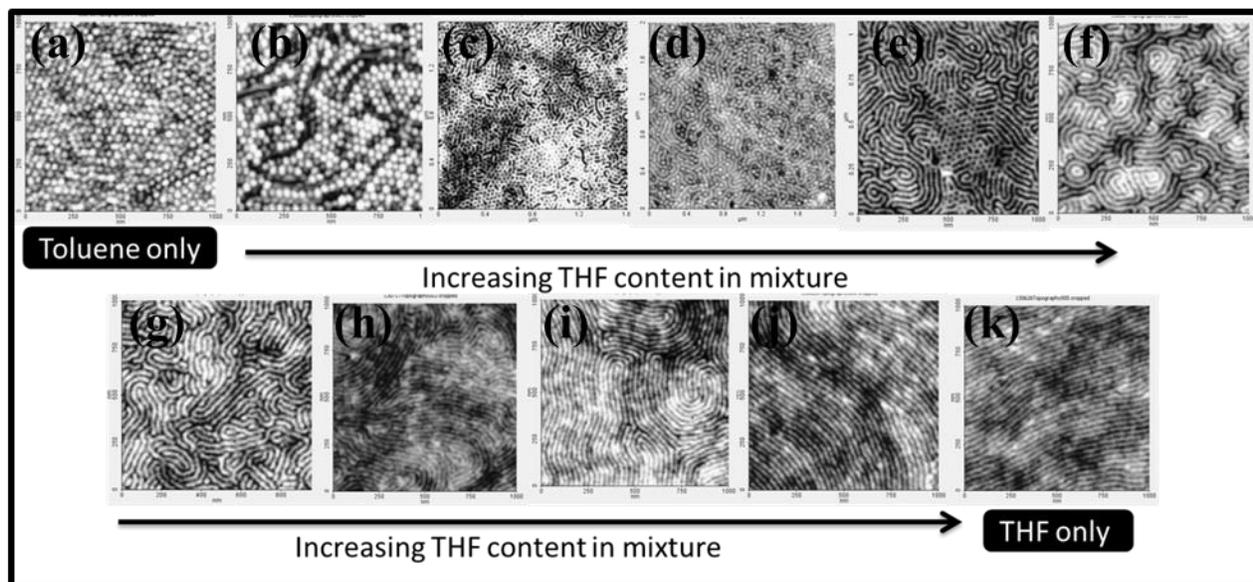


Figure 3: Topographic AFM images of phase separated PS-b-P4VP (9.8k-10k) thin films prepared from 0.5 wt% solutions in toluene/THF (80/20) followed by solvent annealing at 50°C for 3h from Toluene, THF and their various volume compositions. (a) pure toluene, (b) toluene/THF (90/10), (c) toluene/THF (80/20), (d) toluene/THF (60/40), (e) toluene/THF (50/50), (f) toluene/THF (40/60), (g) toluene/THF (20/80), (h) toluene/THF (90/10) and (i) pure THF.

Microphase separation was also achieved on different hard mask substrates. As explained in experimental section, BCP thin films of 28nm thickness were prepared by dissolving 9.8k-10k system in toluene/THF mixture on Alumina, silicon nitride (SiN) and carbon hard mask (CHM) substrates. The thin films obtained were solvent annealed at 50°C from mixture of vapors of toluene and THF to achieve microphase separation of pitch size of 23nm as showed in figure 4 a-c.

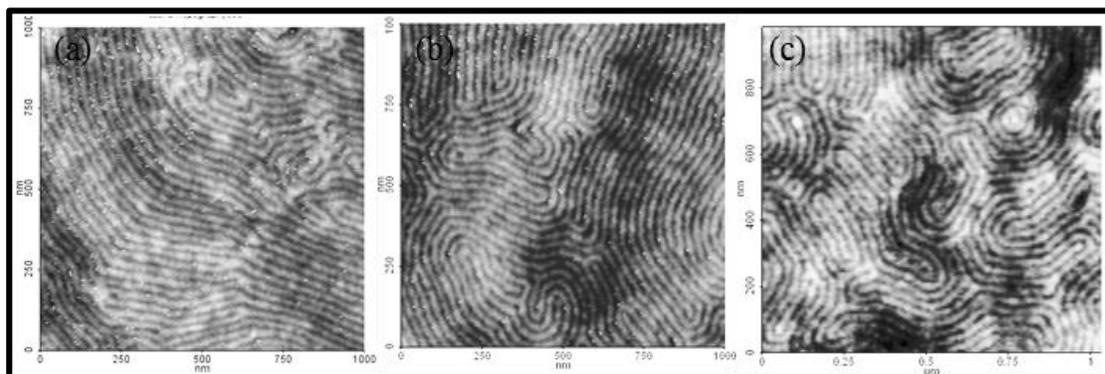


Figure 4: Topographic AFM images of phase separated PS-b-P4VP (9.8k-10k) thin films prepared on (a) Al₂O₃, (b) SiN and (c) CHM substrate.

3.4 Effect of polymer brushes on the morphology of block copolymers

Microphase separation of PS-*b*-P4VP (9.8k-10k) was also achieved on the polymer brushes deposited on silicon wafers. Polymer brushes were deposited by easy but time consuming method. Hydroxyl group of polystyrene chemically react with the native oxide layer on silicon wafer. The PS-*b*-P4VP on bare Silicon substrate shows a disordered structure with rough film which is because of strong interaction between the P4VP block and the hydroxyl-terminated polar native oxide surface. Similarly, ethylene glycol (EG) self-assembled monolayer (SAM) was prepared on silicon surface. While on both PS-brush and EG-brush coated substrates gives uniform film with good ordering. Thickness of both PS-brush and EG-brush were measured by using optical ellipsometry with thickness of 5nm and 1.7nm respectively. The center to center distance between two adjacent lines was measured to be 23nm.

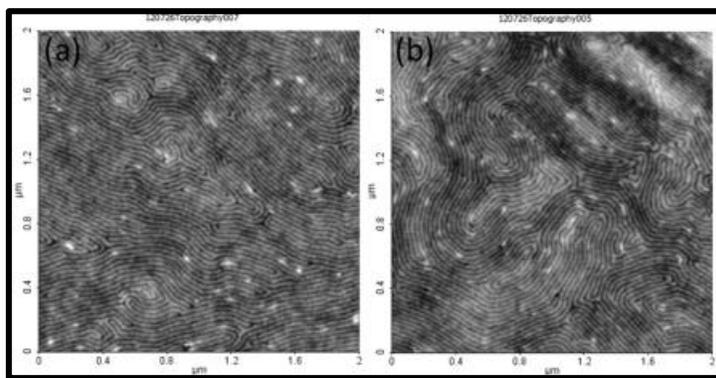


Figure 5: Topographic AFM images of phase separated PS-*b*-P4VP (9.8k-10k) by using PS brush (a) and ethylene glycol brush (b)

3.5 In-situ Iron oxide hard mask inclusion technique

Fabrication of Iron oxide nanowires were carried out by dissolving, Iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in ethanol to get 0.5 wt% solution and then it was spin-coated onto the patterned thin film of block copolymer, as shown in scheme 2(a). UV/Ozone treatment was used to oxidize the precursor and remove polymer (Scheme 2(b)). These iron oxide nanowires arrays will be used as a hard mask for pattern transfer onto the substrate.



Scheme 2: Schematic diagram of the fabrication of Iron oxide nanowires: (a) spin-coating of 0.4 wt% of Iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in ethanol, (b) UV/Ozone treatment to generate iron oxide nanowires on Silicon substrate

Unlike, as mentioned in Ghoshal *et al.*^{32, 33}, surface reconstruction of the block copolymer film was not performed. Immersing the thin film in ethanol leads to form nanoporous film in hexagonal nanodot arrays³⁴. For lamellar structure, the reconstruction cause swelling of lamella and eventually may hamper the structure. Generally, the low concentration (<0.5

wt%) solution was used (in this case 0.4 wt%) to avoid the overloading of iron nitrate solution. Spin coating of 0.4wt% iron nitrate solution in ethanol was carried out to follow by UV/ozone treatment for three hours which led to form the iron oxide nanowire structures on silicon substrate and remove the polymer matrix. After UV/ozone treatment, sample was sent to calcination at 800°C for 1h to show the thermal stability. Iron oxide nanowires formed is shown in figure 6. It was also noticed that the pitch size of iron oxide nanowires remained unchanged as expected (10.3 nm) with critical dimension of 5 nm.

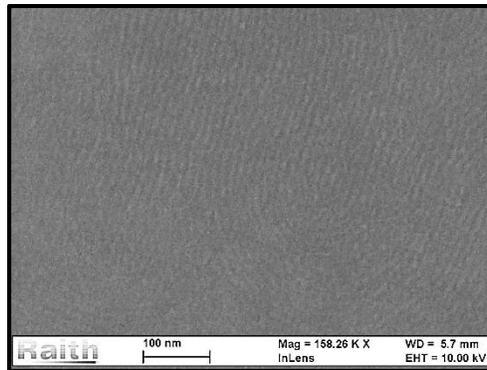


Figure 6. SEM image iron oxide nanowires formed by inclusion method on PS-*b*-P4VP (3.3k-3.1k).

4. CONCLUSION

Different molecular weights of symmetric and asymmetric PS-*b*-P4VP block copolymers for applications in self-assembled nanolithography were investigated. With high interaction parameter (χ) gives well-ordered structures. Extensive tunability of the self-assembly patterns were also demonstrated by controlling the annealing solvent parameters, their ratios and the vapor pressure. It leads to the different morphologies in a single polymer system. Fingerprint patterns of sub-12 nm were achieved on Si-OH as well as on different hard mask by using 3.3k-3.1k polymer system. We have achieved the minimum pitch size of 10.3nm (center to center distance of two adjacent lines). By lowering the molecular weight we have demonstrated the scalability of this polymer. The substrate-polymer interface requires careful control to orientate the BCP pattern (e.g. lamellae formed by self-assembly can be orientated parallel or vertical to the substrate). Successful interface control also ensures good surface wetting and hence coverage. Surface neutralization is achieved using PS-brush and EG-brush, which can be chemically attached to the substrate. The generated patterns were transferred to form the functional materials such as metal oxide nanostructures and can be used to pattern transfer to form silicon nanowires and can be used to make device elements.

REFERENCES

- [1] Leibler, L., "Theory of Microphase Separation in Block Copolymers," *Macromolecules* 13 (6), 1602–1617 (1980).
- [2] Bates, F. S. and Fredrickson, G. H., "Block copolymer thermodynamics: Theory and experiment," *Annu. Rev. Phys. Chem.* 41, 525-557 (1990).
- [3] Hamley, I. W., [The Physics of Block Copolymers], Oxford University Press: Oxford, (1998).
- [4] Hamley, I. W., [Developments in Block Copolymer Science and Technology], Wiley and Sons (2004).
- [5] Klok, H.-A., and Lecommandoux, S., "Supramolecular Materials via Block Copolymer Self-Assembly," *Advanced Materials* 13(16), 1217-1229 (2001).
- [6] Förster, S., and Plantenberg, T., "From Self-Organizing Polymers to Nanohybrid and Biomaterials," *Angewandte Chemie International Edition* 41(5), 688-714 (2002)
- [7] Ruzette, A.-V., and Leibler, L., "Block copolymers in tomorrow's plastics," *Nat. Mater* 4(1), 19-31 (2005)
- [8] Chou, S. Y., Krauss, P. R., Zhang, W., Guo, L., and Zhuang, L., "Sub-10 nm imprint lithography and applications," *J. Vac. Sci. Technol. B* 15(6), 2897–2904 (1997).
- [9] Piner, R. D.; Zhu, J.; Xu, F.; Hong, S.; Mirkin, C. A. "Dip-Pen Nanolithography," *Science* 283, 661-663 (1999).
- [10] Bates, F. S. and Fredrickson, G. H., "Block copolymer thermodynamics: Theory and experiment," *Annu. Rev. Phys. Chem.* 41, 525-557 (1990).
- [11] Cheng, J. Y., Ross, C. A., Chan, V.Z.H., Thomas, E. L., R.G.H. Lammertink, Vancso, G. J., "Formation of a Cobalt Magnetic Dot Array via Block Copolymer Lithography," *Adv. Mater.* 13(15), 1174-1178 (2001).
- [12] Cheng, J. Y., Ross, C.A., Smith, H. I., Thomas, E. L. "Templated Self-Assembly of Block Copolymers: Top-Down Helps Bottom-Up," *Adv. Mater.* 18(19), 2505-2521(2006).
- [13] Lee, K.B., Park, S.J., Mirkin, C.A., Smith, J.C., Mrksich, M., "Protein nanoarrays generated by dip-pen nanolithography," *Science* 295(5560), 1702-1705 (2002)
- [14] Vega, D. A., Harrison, C. K., Angelescu, D. E., Trawick, M., Huse, D. A., Chaikin, P. M., Register, R. A., "Ordering mechanisms in two-dimensional sphere-forming block copolymers," *Physical Review E* 71, 061803 (2005)
- [15] Kim, S. H., Misner, M. J., Xu, T., Kimura, M. S. H., Russell, T. P., "Highly Oriented and Ordered Arrays from Block Copolymers via Solvent Evaporation," *Adv. Mater.* 16(3), 226–231 (2004).
- [16] S. Park, J.-Y. Wang, B. Kim, W. Chen, T. P. Russell, "Solvent-induced Transition from Micelles in Solution to Cylindrical Microdomains in Diblock Copolymer Thin Films," *Macromolecules* 40(25), 9059-9063 (2007)
- [17] Park, S., Wang, J. Y., Kim, B., Xu, J., Russell, T. P., "A Simple Route to Highly Oriented and Ordered Nanoporous Block Copolymer Templates," *ACS Nano* 2(4), 766-772 (2008)
- [18] Park, S., Kim, B., Xu, J., Hofmann, T., Ocko, B. M., Russell, T.P., "Lateral Ordering of Cylindrical Microdomains Under Solvent Vapor," *Macromolecules* 42(4), 1278-1284 (2009)
- [19] Lee, D. H., Park, S., Gu, W. Y., Russell, T. P., "Highly Ordered Nanoporous Template from Triblock Copolymer," *ACS Nano* 5, 1207-1214, (2011).
- [20] Kim, G., Libera, M., "Morphological Development in Solvent-Cast Polystyrene–Polybutadiene–Polystyrene (SBS) Triblock Copolymer Thin Films," *Macromolecules* 31(8), 2569–2577 (1998).
- [21] Edwards, E. W., Stoykovich, M. P., Müller, M., Solak, H. H., de Pablo, J. J. and Nealey, P. F., "Mechanism and kinetics of ordering in diblock copolymer thin films on chemically nanopatterned substrates," *J. Polym. Sci. B Polym. Phys.* 43, 3444–3459 (2005)
- [22] Farrell, Richard A., Petkov Nikolay, Shaw Matthew T., Djara Vladimir, Holmes Justin D., Morris, Michael A. "Monitoring PMMA Elimination by Reactive Ion Etching from a Lamellar PS-b-PMMA Thin Film by ex Situ TEM Methods," *Macromolecules* 43 (20), 8651–8655 (2010)
- [23] Jung, Yeon Sik, Ross, C. A. "Orientation-Controlled Self-Assembled Nanolithography Using a Polystyrene–Polydimethylsiloxane Block Copolymer," *Nano Letters* 7(7), 2046-2050 (2007)
- [24] Jung, Y. S., Chang, J. B., Verploegen, E., Berggren, K. K., Ross, C. A., "A Path to Ultranarrow Patterns Using Self-Assembled Lithography," *Nano Letters* 10(3), 1000-1005 (2010)
- [25] Park, S., Kim, B., Xu, J., Hofmann, T., Ocko, B., and Russell, T.P., "Lateral ordering of cylindrical microdomains under solvent vapor," *Macromolecules* 42(4), 1278-1284 (2009)
- [26] Gohy J-F, "Block copolymer micelles," *Adv Polym Sci* 190, 65–136 (2005)
- [27] Antonietti, M., Heinz, S., Schmidt, M., Rosenauer, C., "Determination of the Micelle Architecture of Polystyrene/Poly (4-vinylpyridine) Block Copolymers in Dilute Solution," *Macromolecules* 27 (12), 3276–3281 (1994)
- [28] Forster, S., Zisenis, M., Wenz, E., Antonietti, M., "Micellization of strongly segregated block copolymers," *J. Chem. Phys.* 104 (24), 9956-9970 (1996)
- [29] Riess, G., "Micellization of Block Copolymers," *Prog. Polym. Sci.* 28, 1107-1170 (2003)

- [30] Zha, Weibin, Han, Chang D., Lee, Dong H., Han, Sung H., Kim, Jin K., Kang, Jin H., Park, Cheol, "Origin of the Difference in Order-Disorder Transition Temperature between Polystyrene-block-poly(2-vinylpyridine) and Polystyrene-block-poly(4-vinylpyridine) Copolymers," *Macromolecules* 40(6),2109-2119 (2007).
- [31] Clarke, C. J., Eisenberg, A., La Scala, J., Rafailovich, M. H., Sokolov, J., Li, Z., Qu, S., Nguyen, D., Schwarz, S. A., Strzhemechny, Y., "Measurements of the Flory-Huggins Interaction Parameter for Polystyrene-Poly(4-vinylpyridine) Blends," *Macromolecules* 30(14), 4184-4188 (1997).
- [32] Goshal, T.; Shaw, M. T.; Bolger, C. T.; Holmes, J. D.; Morris, M. A., "A general method for controlled nanopatterning of oxide dots: a microphase separated block copolymer platform," *Journal of Materials Chemistry* 22,12083-12089 (2012)
- [33] Ghoshal, T., Maity, T., Godsell, J. F., Roy, S., Morris, M.A., "Large scale monodisperse hexagonal arrays of superparamagnetic iron oxides nanodots: A facile block copolymer inclusion method," *Adv. Mater.* 24, 2390-2397 (2012)
- [34] C. Cummins, C., Borah, D., Rasappa, S., Chaudhari, A., Ghoshal, T., O'Driscoll, B. M. D., Carolan, P., Petkov, N., Holmes J. D., Morris, M. A., "Self-assembly of polystyrene-block-poly(4-vinylpyridine) block copolymer on molecularly functionalized silicon substrates: fabrication of inorganic nanostructured etchmask for lithographic use," *J. Mater. Chem.C* 1, 7941-7951 (2013)