BNL-104909-2014-CP

Block Copolymer Self Assembly for Design and Vapor Phase Synthesis of One-Dimensional Nanostructured Materials

A. Rahman and C.T. Black

Presented at the SPIE DSS 2014 Conference
Baltimore, MD
May 8-9, 2014

May 2014

Center for Functional Nanomaterials

Brookhaven National Laboratory

U.S. Department of Energy
Office of Science, Basic Energy Sciences

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

This preprint is intended for publication in a journal or proceedings. Since changes may be made before publication, it may not be cited or reproduced without the author's permission.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Block Copolymer Self Assembly for Design and Vapor Phase Synthesis of One-Dimensional Nanostructured Materials

A. Rahman and C. T. Black*
Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY, USA 11973

ABSTRACT

Block copolymer thin films provide a robust method for generating regular, uniform patterns with sub-100 nanometer length scales over arbitrarily large areas. A significant advantage of such block copolymer-based patterning is its ease of integration with all other aspects of traditional thin-film processing, including plasma-based etching and metallization. Such process compatibility ensures a host of application opportunities in designing material properties through control of their nanostructure. Here, we describe our use of block copolymer self assembly for design and vapor phase synthesis of quasi one-dimensional nanostructured materials made of metals, semiconductors, and insulators. The precise control of surface texture afforded by block copolymer-based patterning can influence macroscopic materials properties such as optical reflectance and hydrophobicity.

Keywords: block copolymer, self assembly, oblique angle deposition, reflectance, hydrophobicity, nanowire, vapor phase synthesis

1. INTRODUCTION

Block copolymer thin films provide a non-lithographic means of defining features on sub-100 nanometer length scales with a high degree of uniformity in feature size and density, and some degree of local order.[1, 2] Pattern formation in these materials occurs by self assembly, facilitated by phase separation of dissimilar polymer blocks into regular microdomains whose size, shape, and density depend on the total copolymer molecular weight and weight ratio of the constituent polymer blocks.[3]

Patterning applications of these materials include either combining with techniques of thin film fabrication, in which case the copolymer assumes a templating role otherwise played by a photoresist or electron-beam resist. Methods of pattern transfer include wet etching,[4-6] dry etching,[7, 8] or metallization[9, 10] – all of which have been used to good effect in

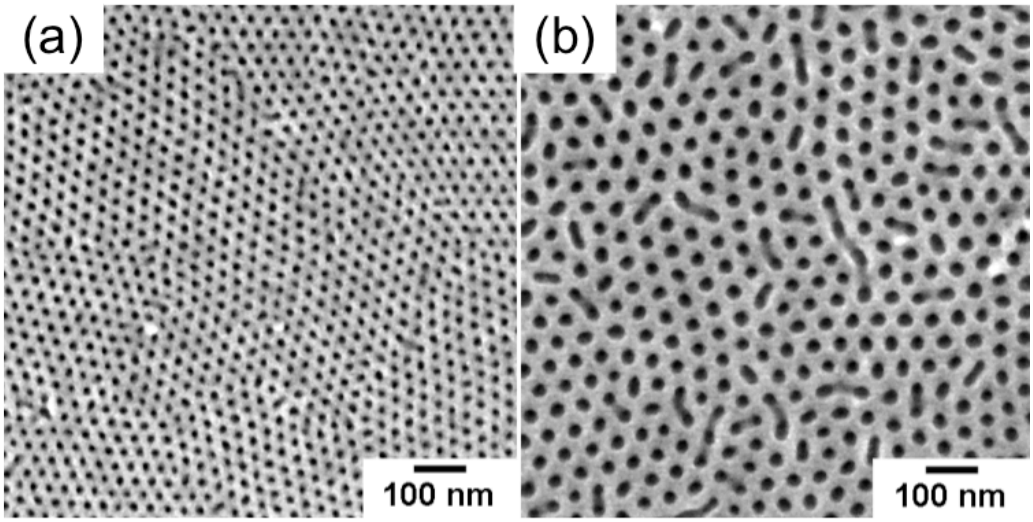

Figure 1. Topdown scanning electron microscope images of patterns formed by cylindrical phase PS-*b*-PMMA block copolymers with (a) 48 kg/mol molecular weight with 14 nm average diameter and 30 nm average separation, and (b) 99 kg/mol molecular weight with 25 nm average diameter and 50 nm average separation.

*ctblack@bnl.gov

applications such as electronics,[1] magnetic recording,[11] and optics.[12-15]

Alternatively, chemical differences between block copolymer microdomains can be used to carry out localized reactions in order to generate nanostructures in select pattern areas. Previous examples of this type of chemical synthesis route to nanostructure formation include loading block copolymer micelles[16] and phase separated microdomains from solution (e.g., [17-22]), as well as selective infiltration from the vapor phase.[23-25] Similar strategies have been useful in loading select block copolymer domains with nanoparticles through appropriate ligand chemistry.[26-29]

Here, we describe our efforts at synthesis of one-dimensional forms of materials by combining these two approaches for design of material properties. We present a versatile approach suitable for vapor phase synthesis of metals, semiconductors, and insulators over macroscopic areas. We combine infiltration of select block copolymer thin film domains from the vapor phase to create seeds for synthesis of 1D nanostructures via physical vapor deposition.

2. METHODOLOGY

In our experiments we leverage the chemical properties of polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) block copolymers for both their pattern forming abilities and also to perform chemical synthesis within select pattern areas. Asymmetric, cylindrical PS-*b*-PMMA block copolymers with total molecular weight greater than 40 kg/mol (and PS:PMMA weight ratio of ~70:30) self assemble into locally ordered hexagonal arrays of PMMA cylinders within a matrix of PS. The orientation of this pattern relative to the surface is controlled by the surface energy – appropriate neutralization prior to thin film formation results in perpendicular domain orientation[30]. We cast block copolymer thin films from toluene (1% wt) by spin coating, and facilitate self assembly by thermal annealing at ~200 °C for > 1 hour. Films made from copolymers with total molecular weight of 48 kg/mol form patterns with d = 14 nm average cylinder diameter and ℓ ~30 nm nearest neighbor separation, with cylinder density of $\rho \sim \left(2/\sqrt{3}\right) \cdot (1/\ell)^2 \sim 10^{11}/\mathrm{cm}^2$ (Figure

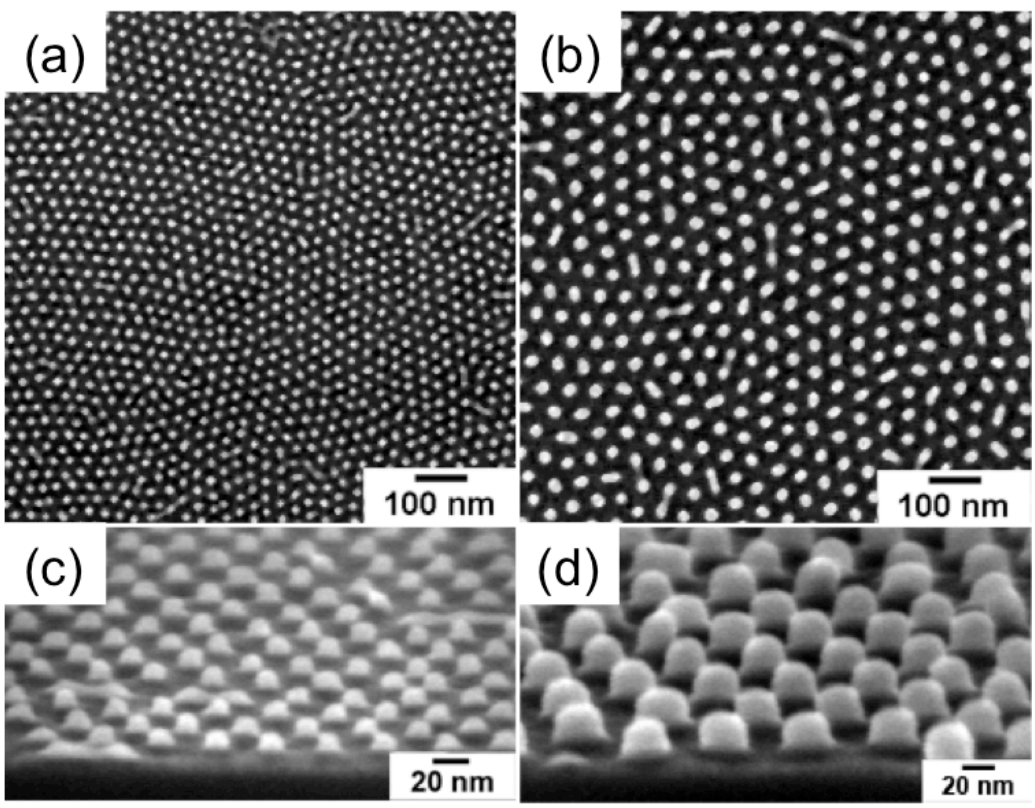

Figure 2. Topdown and 70 degree cross-sectional scanning electron microscope images of nanostructured alumina patterns formed by infiltration of cylindrical phase PS-*b*-PMMA block copolymers with (a, c) 48 kg/mol molecular weight and (b, d) 99 kg/mol molecular weight.

1a), while films cast from higher molecular weight materials (e.g., 99 kg/mol) form patterns with d = 25 nm, ℓ ~ 50 nm, and $\rho \sim 5 \cdot 10^{10}/\text{cm}^2$ (Figure 1b). PS-*b*-PMMA pattern feature sizes scale with molecular weight roughly according to $\ell \sim (M_w^{0.6})$[31, 32] with degraded pattern uniformity at higher molecular weights due to the slower self assembly kinetics. In this work we utilize the chemical functionality of the PMMA domain for nanostructure synthesis. In such a hexagonally arranged pattern, the PMMA domains occupy an areal fraction of:

$$f \equiv \frac{\pi}{2\sqrt{3}}\left(\frac{d}{\ell}\right)^2 \sim 0.9\left(\frac{d}{\ell}\right)^2, \tag{1}$$

which is approximately ~23% in every cylindrical phase block copolymer material, where $d \approx \ell/2$.

We convert these self-assembled polymer patterns into templates suitable for seeded growth of 1D materials using block selective synthesis of metal oxides within the PMMA microdomains.[23, 25] Sequentially exposing the copolymer films to an organometallic precursor and water vapor results in growth of metal oxide only within the PMMA domains. After removing the remaining PMMA and PS polymer by oxygen plasma (20 W rf, 100 mT O_2, 120 s), the resulting nanostructured metal oxide largely reflects the dimensions of the initial self-assembled PMMA microdomains.[33] For these studies, we have used 3 sequential exposures of tri(methyl aluminum) (TMA) and water to produce nanostructured alumina, with feature heights of ~10-12 nm for the case of a 48 kg/mol copolymer template (Figures 2a, c) and > 20 nm for 99 kg/mol templates (Figures 2b, d).

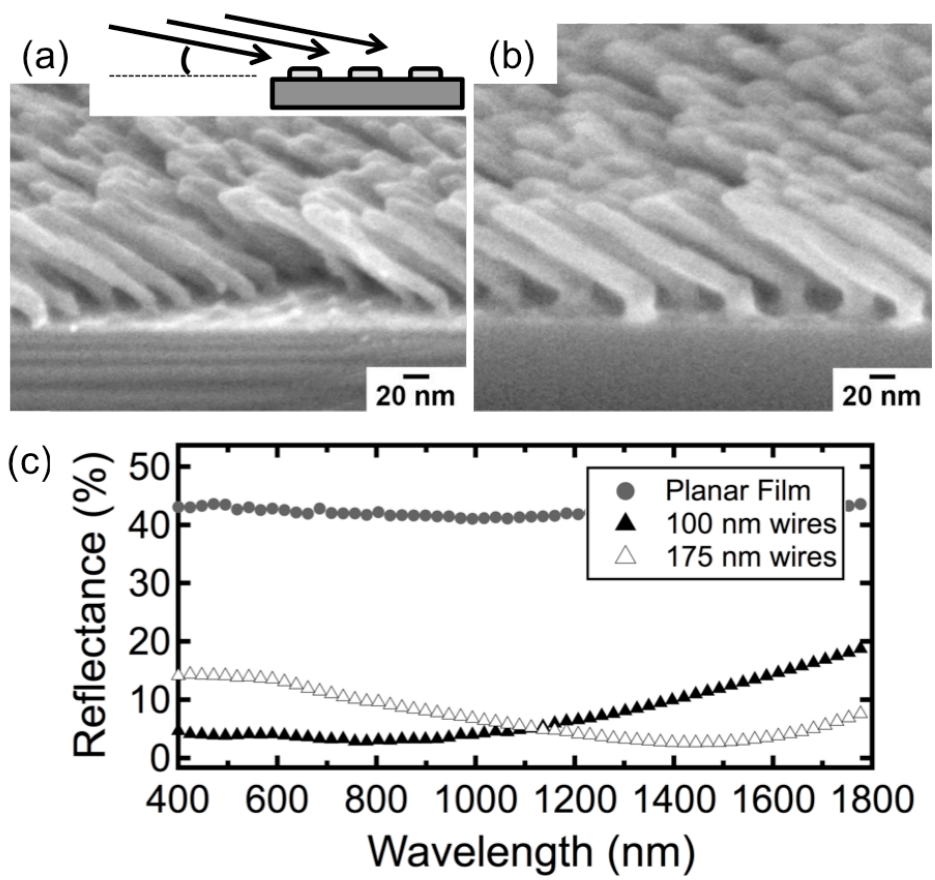

Figure 3. (inset) Schematic oblique angle deposition. (a, b) 70 degree cross-sectional scanning electron microscope images of germanium nanowires with (a) 14 nm average diameter and (b) 25 nm average diameter grown by oblique angle deposition onto alumina seed layers template by block copolymer thin films. (c) Reflectance versus wavelength of (grey circles) 100 nm thick Ge film on silicon, and 25 nm diameter germanium wires with length (black triangles) 100 nm and (red triangles) length 175 nm.

3. RESULTS AND DISCUSSION

We use the regular surface topography provided by these nanotextures for vapor phase synthesis of quasi-1D nanostructures using physical vapor deposition. This concept, first implemented in the 1990s and highly developed by groups around the world (e.g., [34, 35]) relies on surface shadowing when vapor flux is brought to the substrate surface at a near-parallel incident angle. Many previous studies have shown that atomic asperities can provide seeds for nanostructured film growth. Here, we use the block copolymer-defined seeds to provide a high degree of control over the nanostructure diameter. We are not the first group to employ this approach. For example, excellent prior work has been reported by the groups of Buriak and Brett at the University of Alberta, who have used glancing angle deposition onto block copolymer seed layers[36] for growth of organic semiconductors for solar applications.[37, 38]

3.1 Thin Film Reflectance

We synthesize close packed arrays of oriented germanium (Ge) nanowires by bringing the flux of Ge vapor to the sample at an angle of 5 degrees from sample parallel. Depositing the metal at a rate of ~0.1 nm/s results in growth of ~100 nm long wires inclined at an angle of ~30° from the plane of the substrate (Figures 3a, b). The average wire diameters reflect those of the initial alumina seed layer. Growing wires from 14 nm diameter alumina seeds, patterned from a 48 kg/mol block copolymer template (Figure 3a) are qualitatively thinner than those grown from initial 25 nm diameter seeds (patterned using a 99 kg/mol block copolymer) (Figure 3b).

Such thin films of densely packed, oriented nanowires can behave as effective optical media, because the lateral dimensions are deeply subwavelength.[39, 40] In this case, the oriented germanium wires form an effective medium with optical index given by:

$$n_{eff} = f \cdot n_{Ge} + (1 - f) \cdot n_{air} \tag{2}$$

where f is the germanium film volume fraction ~ 23% for our films, which yields $n_{eff} = 0.23 \cdot (4.5) + 0.77 \cdot (1) \approx 1.8$ for the porous material. A medium with intermediate optical index serves to improve the optical coupling at an interface between two different materials, such as in this example between air (n = 1) and silicon (n ~ 4). The effect of better optical coupling is reduced reflectance -- Ge thin films composed of wires grown on a silicon substrate reduce the reflectance across all incident wavelengths, from the ~40% of a polished silicon (not shown) to less than 20% (Figure 3c, black and white triangles). In contrast, a solid Ge film of similar thickness leaves the reflectance unchanged, because n_{Ge} is similar to n_{Si} ~ 4. The nanowire thin films minimize the optical reflectance at a wavelength given by:

$$\lambda_{min} = 4 \cdot n_{eff} \cdot t \tag{3}$$

where t is the film thickness. In this case, Eq. 3 predicts a 100 nm thick film of Ge wires will minimize reflectance at ~720 nm, while a 175 nm thick film has a minimum at 1260 nm. These value are similar, though smaller than those measured in our films (Figure 2c), where we find λ_{min} ~ 800 nm and 1450 nm, respectively. We understand the larger discrepancy between the predicted reflectance minimum and the measured value for the film of 175 nm long nanowires as being caused by wire diameters being broadened at their tip, relative to the base. The wider wires increase the Ge film volume fraction above that given by the estimate of Eq. (1), increasing n_{eff} and shifting λ_{min} to longer wavelengths.

3.2 Hydrophobicity

Nanostructures are known to strongly influence the nature of liquid interactions with surfaces, and in particular have been shown to induce increased hydrophobicity by providing textures that trap air between the solid-water interface. This effect is often described by the Cassie-Baxter model, in which the trapped air bubbles reduce the amount of solid-water contact and thereby increase the hydrophobicity.[41] This scenario represents only a metastable state, however, because finite pressures applied to the liquid drop will eventually cause infiltration of the surface texture. Importantly, the surface's ability to withstand finite pressures increases with decreasing space between textures.[42]

We have synthesized silicon surface nanotextures by oblique angle deposition of silicon by electron beam evaporation at an angle of 5 degrees from substrate parallel, onto a layer of alumina seeds templated by a 99 kg/mol molecular weight block copolymer film. The alumina seeds have dimensions of 25 nm average diameter, 50 nm separation, and 25 nm height (Figure 2b, d). In this case, substrate heating to ~70 °C during vapor phase synthesis changes the angle of nanowire growth relative to the substrate, resulting in more perpendicularly oriented wires with an angle of >65° relative to substrate parallel (Figure 4a). We rendered the silicon surface nanotextures hydrophobic by passivating with a 2.5 nm

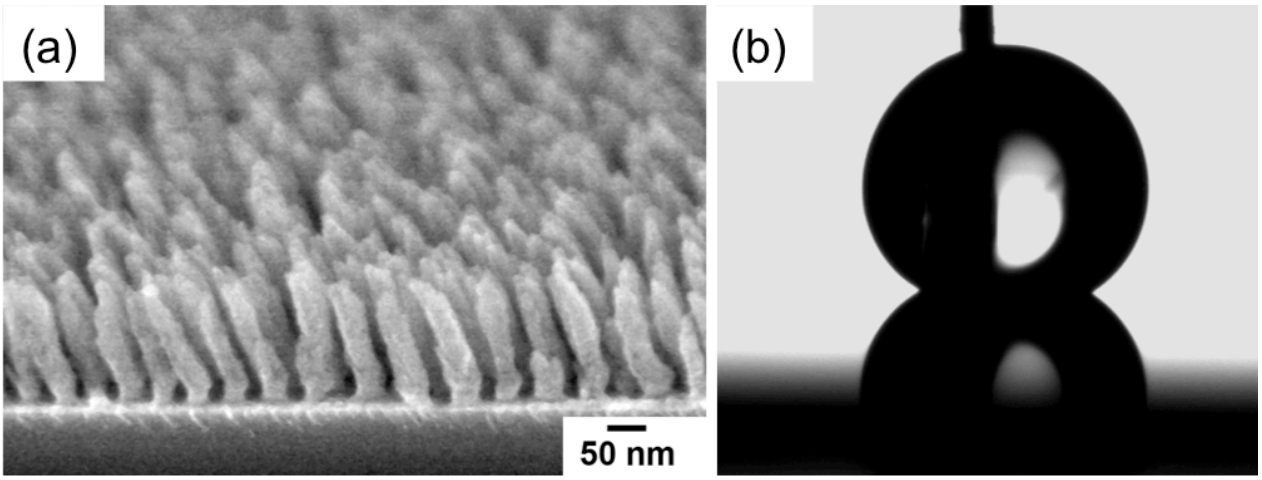

Figure 4. (a) Silicon nanowires with 25 nm average diameter and length ~100 nm grown by oblique angle deposition. (b) Optical microscope image of a water drop in contact with the silanized nanostructured silicon surface.

thick octadecyltrichlorosilane (OTS) monolayer (immersion in 5 mM solution of OTS molecules in bicyclohexyl for 10 h).

We measure a water contact angle for the silanized silicon nanotextures of θ_{CB} = 145 degrees (Figure 4b), a significant increase from the 110 degrees measured for a similarly silanized flat silicon surface. This value is similar to that predicted by the Cassie-Baxter model, in which:

$$\cos(\theta_{CB}) = f \cdot (\cos(\theta_F) + 1) - 1 \tag{4}$$

where θ_F is the contact angle on a flat surface and f is the area fraction of the surface nanotexture in contact with the liquid. For hexagonally arranged cylindrical pillars, $f \sim 0.9(d/\ell)^2 \sim 0.23$ (Eq. 1), so that $\theta_{CB} \sim$ 148 degrees. In this case, the silicon nanotextures display a significant amount of contact angle hysteresis ($\theta_R \sim$ 105 degrees) such that the structure does not display superhydrophobicity. These values are similar to other structures made previously using a block

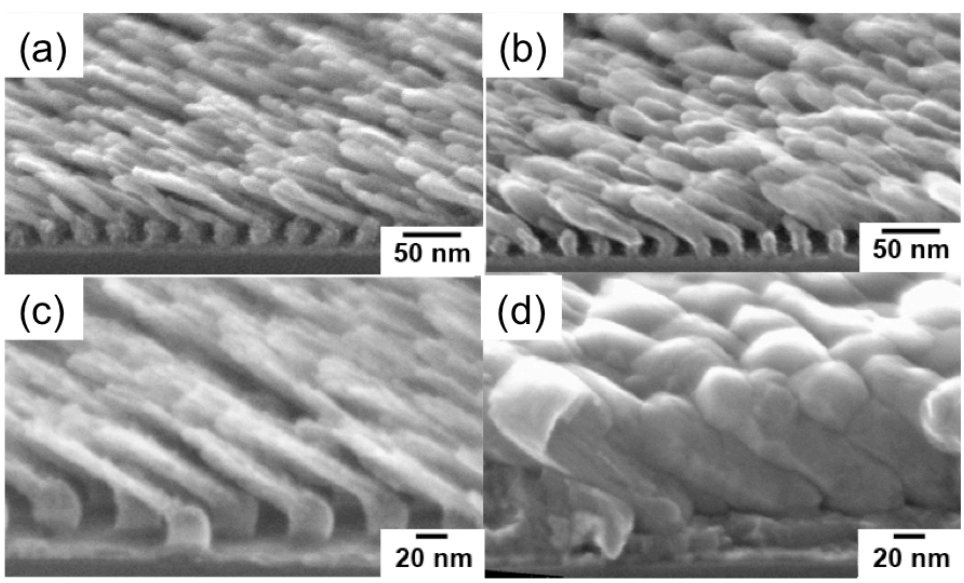

Figure 5. (a) Iron nanowires with 14 nm average diameter and length ~80 nm grown by oblique angle deposition. (b) Nanostructured Fe_2O_3 thin film synthesized by oxidation of sample (a). (c) Germanium nanowires length ~90 nm. (d) Composite germanium/titana core/shell structure grown by atomic layer deposition of TiO_2 onto sample (c).

copolymer based approach,[43] but are not as high quality as those obtained previously in our laboratory using a plasma-based etch approach to nanotexture formation,[7] rather than vapor-phase synthesis.

3.3 Complex Materials and Heterostructures

We may combine synthesis of oriented quasi-1D nanostructures by oblique physical vapor deposition onto block copolymer patterned seed layers with further material processing in order to create more complex materials. For example, we first synthesize iron nanowires by electron beam evaporation (~0.1 nm/s) at an angle of 5 degrees from substrate parallel onto a layer of 14 nm diameter alumina seeds (Figure 5a). Subsequent thermal oxidation of this structure by rapid thermal processing at 550 °C for 5 m in oxygen coverts the iron nanostructures into Fe_2O_3. The 1.5× volume expansion due to the density difference of 7.87 g/cm^3 (Fe) and 5.24 g/cm^3 (Fe_2O_3) results in a wire diameter increase of ~22%, which narrows the space between wires and completely swells it shut in some locations (Figure 5b).

Alternatively, we can use conformal deposition approaches to create core-shell heterostructure materials from aligned nanowires. We uniformly fill the spaces between ~20 nm diameter germanium wire arrays, inclined 30 degrees from the substrate surface (Figure 5c) by atomic layer deposition of 20 nm of titania. Because the germanium wires were grown from a 99 kg/mol block copolymer template pattern, the initial space between wires is of order ~25 nm. In this case, the entire wire interstitial region is filled with titania (Figure 5d), leaving a solid film with germanium wires embedded.

4. CONCLUSIONS

The self-assembled patterns formed by block copolymer thin films provide both physical and chemical templates for structuring materials on the nanometer length scale over macroscopic areas. We have utilized such patterns for nucleating growth of one-dimensional nanomaterials of metals, semiconductors, and insulators from the vapor phase by oblique angle deposition. We have presented results demonstrating the utility of this approach for design of porous materials for antireflective coatings as well as increasing the surface hydrophobicity.

5. ACKNOWLEDGEMENTS

The authors thank A. Checco for assistance with water contact angle measurements. Research carried out at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

REFERENCES

[1] Black, C. T., Ruiz, R., Breyta, G., Cheng, J. Y., Colburn, M., Guarini, K. W., Kim, H.-C., Zhang, Y., "Polymer self assembly in semiconductor microelectronics," IBM Journal of Research and Development 51, 605, (2007).

[2] Hawker, C. J., Russell, T. P., "Block copolymer lithography: Merging "bottom-up" with "top-down" processes," MRS Bulletin 30, 952, (2005).

[3] Bates, F., Fredrickson, G., "Block copolymers - Designer soft materials," Physics Today 52, 32, (1999).

[4] Guarini, K., Black, C., Zhang, Y., Kim, H., Sikorski, E., Babich, I., "Process integration of self-assembled polymer templates into silicon nanofabrication," Journal of Vacuum Science & Technology B 20, 2788, (2002).

[5] Li, R., Dapkus, P., Thompson, M. E., Jeong, W., Harrison, C., Chaikin, P., Register, R., Adamson, D., "Dense arrays of ordered GaAs nanostructures by selective area growth on substrates patterned by block copolymer lithography," Applied Physics Letters 76, 1689, (2000).

[6] Watanabe, R., Kamata, K., Iyoda, T., "Smart block copolymer masks with molecule-transport channels for total wet nanopatterning," Journal of Materials Chemistry 18, 5482, (2008).

[7] Checco, A., Rahman, A., Black, C. T., "Robust Superhydrophobicity in Large-Area Nanostructured Surfaces Defined by Block-Copolymer Self Assembly," Advanced Materials 26, 886, (2014).

[8] Johnston, D. E., Lu, M., Black, C. T., "Plasma etch transfer of self-assembled polymer patterns," Journal of Micro/Nanolithography, MEMS, and MOEMS 11, 031306, (2012).

[9] Hong, A. J., Liu, C.-C., Wang, Y., Kim, J., Xiu, F., Ji, S., Zou, J., Nealey, P. F., Wang, K. L., "Metal nanodot memory by self-assembled block copolymer lift-off," Nano Letters 10, 224, (2009).

[10] Xiao, S., Yang, X., Edwards, E. W., La, Y.-H., Nealey, P. F., "Graphoepitaxy of cylinder-forming block copolymers for use as templates to pattern magnetic metal dot arrays," Nanotechnology 16, S324, (2005).
[11] Hellwig, O., Bosworth, J., Dobisz, E., Kercher, D., Hauet, T., Zeltzer, G., Risner-Jamtgaard, J., Yaney, D., Ruiz, R., "Bit patterned media based on block copolymer directed assembly with narrow magnetic switching field distribution," Applied Physics Letters 96, 052511, (2010).
[12] Lohmuàller, T., Helgert, M., Sundermann, M., Brunner, R., Spatz, J. P., "Biomimetic interfaces for high-performance optics in the deep-UV light range," Nano Letters 8, 1429, (2008).
[13] Morhard, C., Pacholski, C., Lehr, D., Brunner, R., Helgert, M., Sundermann, M., Spatz, J. P., "Tailored antireflective biomimetic nanostructures for UV applications," Nanotechnology 21, 425301, (2010).
[14] Pàivanranta, B., Sahoo, P. K., Tocce, E., Auzelyte, V., Ekinci, Y., Solak, H. H., Liu, C.-C., Stuen, K. O., Nealey, P. F., David, C., "Nanofabrication of broad-band antireflective surfaces using self-assembly of block copolymers," ACS Nano 5, 1860, (2011).
[15] Hsueh, H.-Y., Chen, H.-Y., She, M.-S., Chen, C.-K., Ho, R.-M., Gwo, S., Hasegawa, H., Thomas, E. L., "Inorganic Gyroid with Exceptionally Low Refractive Index from Block Copolymer Templating," Nano Letters 10, 4994, (2010).
[16] Glass, R., Moller, M., Spatz, J. P., "Block copolymer micelle nanolithography," Nanotechnology 14, 1153, (2003).
[17] Aizawa, M., Buriak, J. M., "Block copolymer templated chemistry for the formation of metallic nanoparticle arrays on semiconductor surfaces," Chemistry of Materials 19, 5090, (2007).
[18] Chai, J., Wang, D., Fan, X., Buriak, J. M., "Assembly of aligned linear metallic patterns on silicon," Nature Nanotechnology 2, 500, (2007).
[19] Kim, D., Jia, X., Lin, Z., Guarini, K. W., Russell, T. P., "Growth of silicon oxide in thin film block copolymer scaffolds," Advanced Materials 16, 702, (2004).
[20] Chen, A., Komura, M., Kamata, K., Iyoda, T., "Highly ordered arrays of mesoporous silica nanorods with tunable aspect ratios from block copolymer thin films," Advanced Materials 20, 763, (2008).
[21] Harrison, C., Park, M., Chaikin, P. M., Register, R. A., Adamson, D. H., "Lithography with a mask of block copolymer microstructures," Journal of Vacuum Science & Technology B 16, 544, (1998).
[22] Li, J., Kamata, K., Watanabe, S., Iyoda, T., "Template and Vacuum Ultraviolet-Assisted Fabrication of a Ag-Nanoparticle Array on Flexible and Rigid Substrates," Advanced Materials 19, 1267, (2007).
[23] Peng, Q., Tseng, Y.-C., Darling, S. B., Elam, J. W., "Nanoscopic Patterned Materials with Tunable Dimensions via Atomic Layer Deposition on Block Copolymers," Advanced Materials 22, 5129, (2010).
[24] Ramanathan, M., Tseng, Y.-C., Ariga, K., Darling, S. B., "Emerging trends in metal-containing block copolymers: synthesis, self-assembly, and nanomanufacturing applications," Journal of Materials Chemistry C 1, 2080, (2013).
[25] Tseng, Y.-C., Peng, Q., Ocola, L. E., Elam, J. W., Darling, S. B., "Enhanced Block Copolymer Lithography Using Sequential Infiltration Synthesis," The Journal of Physical Chemistry C 115, 17725, (2011).
[26] Chiu, J. J., Kim, B. J., Kramer, E. J., Pine, D. J., "Control of nanoparticle location in block copolymers," Journal of the American Chemical Society 127, 5036, (2005).
[27] Lin, Y., Boker, A., He, J., Sill, K., Xiang, H., Abetz, C., Li, X., Wang, J., Emrick, T., Long, S., "Self-directed self-assembly of nanoparticle/copolymer mixtures," Nature 434, 55, (2005).
[28] Sohn, B.-H., Choi, J.-M., Yoo, S. I., Yun, S.-H., Zin, W.-C., Jung, J. C., Kanehara, M., Hirata, T., Teranishi, T., "Directed Self-Assembly of Two Kinds of Nanoparticles Utilizing Monolayer Films of Diblock Copolymer Micelles," Journal of the American Chemical Society 125, 6368, (2003).
[29] Son, J. G., Bae, W. K., Kang, H., Nealey, P. F., Char, K., "Placement control of nanomaterial arrays on the surface-reconstructed block copolymer thin films," ACS Nano 3, 3927, (2009).
[30] Mansky, P., Liu, Y., Huang, E., Russell, T., Hawker, C., "Controlling Polymer-Surface Interactions with Random Copolymer Brushes," Science 275, 1458, (1997).
[31] Xu, T., Kim, H.-C., DeRouchey, J., Seney, C., Levesque, C., Martin, P., Stafford, C., Russell, T., "The influence of molecular weight on nanoporous polymer films," Polymer 42, 9091, (2001).
[32] Guarini, K., Black, C., Yeuing, S., "Optimization of diblock copolymer thin film self assembly," Advanced Materials 14, 1290, (2002).
[33] Ruiz, R., Wan, L., Lille, J., Patel, K. C., Dobisz, E., Johnston, D. E., Kisslinger, K., Black, C. T., "Image quality and pattern transfer in directed self assembly with block-selective atomic layer deposition," Journal of Vacuum Science & Technology B 30, 06F202, (2012).

[34] Robbie, K., Brett, M., "Sculptured thin films and glancing angle deposition: Growth mechanics and applications," Journal of Vacuum Science & Technology A 15, 1460, (1997).
[35] van Kranenburg, H., Lodder, C., "Tailoring growth and local composition by oblique-incidence deposition: a review and new experimental data," Materials Science and Engineering: R: Reports 11, 295, (1994).
[36] Chai, J., Taschuk, M. T., Brett, M. J., Buriak, J. M., in NanoScience+ Engineering. (International Society for Optics and Photonics, 2008), pp. 704111-704111-10.
[37] Taschuk, M., Chai, J., Buriak, J., Brett, M., "Optical characterization of pseudo-ordered nanostructured thin films," Physica Status Solidi (C) 6, S127, (2009).
[38] Van Dijken, J., Fleischauer, M., Brett, M., "Controlled nanostructuring of CuPc thin films via glancing angle deposition for idealized organic photovoltaic architectures," Journal of Materials Chemistry 21, 1013, (2011).
[39] Xi, J.-Q., Schubert, M. F., Kim, J. K., Schubert, E. F., Chen, M., Lin, S.-Y., Liu, W., Smart, J. A., "Optical thin-film materials with low refractive index for broadband elimination of Fresnel reflection," Nature Photonics 1, 176, (2007).
[40] Chattopadhyay, S., Huang, Y., Jen, Y.-J., Ganguly, A., Chen, K., Chen, L., "Anti-reflecting and photonic nanostructures," Materials Science and Engineering: R: Reports 69, 1, (2010).
[41] Cassie, A., Baxter, S., "Wettability of porous surfaces," Transactions of the Faraday Society 40, 546, (1944).
[42] Reyssat, M., Pepin, A., Marty, F., Chen, Y., Quere, D., "Bouncing transitions on microtextured materials," EPL (Europhysics Letters) 74, 306, (2006).
[43] Krishnamoorthy, S., Gerbig, Y., Hibert, C., Pugin, R., Hinderling, C., Brugger, J., Heinzelmann, H., "Tunable, high aspect ratio pillars on diverse substrates using copolymer micelle lithography: an interesting platform for applications," Nanotechnology 19, 285301, (2008).