Diblock copolymers are two different types of polymer chains connected at one end with a covalent bond\(^1,2\). Most pairs of polymers are immiscible and blends of polymers tend to phase separate. In the case of diblock copolymers, however, the two polymers that constitute the material are unable to phase separate at macroscopic length scales and instead spontaneously form ordered structures at the molecular scale with domain dimensions of 5-50 nm. The size and shape of the domains in the bulk are dependent on the molecular weight and composition of the copolymer and typically assume morphologies of spheres, cylinders, and lamellae.

The obvious interest in using these materials for patterning is derived from the fact that they self-assemble to form dense arrays of nanostructures with dimensions and spacings that are difficult or impossible to create by other means or are prohibitively expensive to fabricate using conventional lithographic materials and processes. Block copolymer lithography refers to the use of these materials in the form of thin films in which the domain structure provides a template for additive or subtractive pattern transfer operations\(^3\).

Patterns of hexagonal arrays of spots, for example, can be fabricated using a single layer of spherical domains or a thin film of cylindrical domains with the domains oriented perpendicular to the substrate (Fig. 1). The latter morphology is advantageous in that high aspect ratio templates may be produced with vertical sidewalls and connectivity between the substrate and the free surface of the polymer film. Unfortunately, substrates are often preferentially wet by one of the blocks of the copolymer and the cylinders tend to orient parallel to the substrate. Strategies such as chemical modification\(^4-11\) and the application of external fields\(^12-17\) can be used to neutralize or overcome surface and interfacial forces that tend to drive the cylinders...
to form parallel to the plane of the film. Alternatively, nonequilibrium structures with the desired morphologies can be formed by solvent evaporation18-22 or spin casting23,24. Patterns of dense periodic arrays of spots fabricated with block copolymer templates have been demonstrated, and in some cases are being commercialized, for the fabrication of quantum dots3,25, magnetic storage media26,27, flash memory devices28, semiconductor capacitors29,30, nanowires13,31,32, photonic crystals33,34, and nanopores35-37. These applications capitalize on self-assembling block copolymer materials to pattern periodic, uniform-dimension features at the nanoscale at very little expense. The use of block copolymer films to pattern dense arrays of features is over a decade old and other reviews have covered this topic in detail38,39.

One strategy to integrate block copolymers with conventional lithography is known as graphoepitaxy and was first demonstrated for sphere-forming block copolymers by Segalman et al.40. In this technique, grooves with typically micron or submicron dimensions are patterned on the substrate by photolithography and etching, and the domain structure of block copolymer films deposited in the grooves nucleates on the walls of the topographic features and propagates inward so as to be well ordered across the width of the grooves and along their axes40-46. The primary purpose of graphoepitaxy is to enhance the resolution of the conventional lithographic process by subdividing the patterned features and to improve the perfection of ordering of the dense periodic arrays of nanostructures that are naturally formed by block copolymers.

Topographic features also allow some control over the placement (registration) of the patterns with respect to the underlying substrate44,46. If sufficient order can be achieved, addressable arrays for applications such as single-domain magnetic storage media could be fabricated. Graphoepitaxy has also been shown to be an effective strategy for ordering cylinder-forming block copolymers with the domains oriented either perpendicular47,48 (Fig. 2) or parallel49,50 to the substrate, and in geometries more complex than parallel grooves such as circles51 and bends49. Application of structures patterned from block copolymer templates assembled in this way include nanoparticle arrays for magnetic storage media27,47, nanowire field-effect transistors (FETs)52, and nanowires.

Recently, we reported the extension of graphoepitaxy to the ordering of lamellar-forming block copolymers such that the lamellae are oriented perpendicular to the substrate and aligned in arrays parallel to the axis of the grooves53. In contrast to sphere-forming40-46 and cylinder-forming47,49,50 systems, the grooved substrates must not only be topographically but also chemically patterned to achieve the desired configuration of microphase separated domains. The motivation for investigating graphoepitaxy in conjunction with lamella-forming polymers is to be able to pattern transfer by reactive ion etching (RIE) from the block copolymer template to the underlying substrate47,54.

In this review, we focus on a strategy to integrate block copolymers into the conventional lithographic process using lithographically defined chemically nanopatterned surfaces. In this technique, surface and interfacial forces between the substrate surface and the two blocks of the copolymer are carefully engineered to direct the assembly of nanostructures into thermodynamically stable device-oriented patterns. The rationale of this approach is not aimed at improved resolution (or sublithographic patterning) with respect to the exposure tool, but rather at enhancing process control as a first step and, ultimately, greatly enhancing information transfer from the exposure tool to the imaging material through the use of a self-assembling resist. Before expanding on these ideas, we first describe the lithographic process as currently practiced, including its essential attributes for manufacturing and its limitations.

**Conventional photolithography**

The conceptualization of the integrated circuit, the miniaturization of such devices to have sub-100 nm features, and the development of processes for fabricating components at these dimensions are some of the crowning achievements of engineering over the past half century.
Photolithography\textsuperscript{55}, the predominant technique used in the nanofabrication of complex devices, has advanced at a frenetic pace throughout this period. Hallmarks of the modern lithographic process used in the semiconductor industry include pattern perfection over macroscopic areas, dimensional control of features within exacting tolerances and margins, and registration and overlay (placement of features in each layer and with respect to overlying and underlying layers)\textsuperscript{55,56}.

A simplified overview of the lithographic process has four steps:

1. A substrate, typically Si or doped Si, is coated with a film of photosensitive polymer-based material known as a photoresist;
2. The photoresist is exposed to a pattern in the intensity of radiation by the exposure tool and is chemically modified from the photoresist in the unexposed regions. The current state-of-the-art uses 193 nm optical lithography to pattern 65 nm half-pitch structures with perfection over full 300 mm diameter Si substrates\textsuperscript{56};
3. A solvent-based development process selectively removes either the exposed or unexposed photoresist based upon differences in their chemistry and solubility rates;
4. The resulting topographic pattern in the photoresist is transferred to the substrate by selective etching or deposition processes.

These lithographic steps are iterated with the patterns and materials required to build up multiple layers in the integrated devices.

The semiconductor industry is continually striving toward the production of faster and smaller microprocessors and integrated circuits by shrinking the smallest or critical dimension (CD) of the fabricated devices. The International Technology Roadmap for the Semiconductor Industry (ITRS) provides detailed timelines and requirement lists for the development of new patterning techniques at future technology nodes (e.g. the 65 nm, 45 nm, 32 nm, 22 nm, and 16 nm nodes as defined by the half-pitch of dense features)\textsuperscript{56}.

Guidelines are provided about the projected lithographic techniques for each of the desired pattern dimensions, as well as the technological obstacles that remain to be overcome.

The current lithographic process, however, is limited by the available photoresist materials and cannot be scaled to the future technology nodes demanded by the semiconductor industry. Already significant roadblocks are being predicted and encountered in achieving some of the requirements set forth in the ITRS. Surprisingly, resolution is not the most pressing challenge. The most critical issues relate to dimension control and line edge roughness (LER) or, in other words, control in the processing of photoresists\textsuperscript{56-58}. A technology gap exists because significant resources have been allocated to the development of exposure tools in the past decade, particularly electron-beam and extreme ultraviolet sources, capable of resolving patterns with dimensions of 20 nm or less with the required registration and overlay capabilities, whereas relatively modest investments have been made in the development of imaging materials with the required properties at the 20 nm length scale\textsuperscript{57}. In addition to limitations with CD control and LER, standard photoresists are also encountering a problem known as pattern collapse, where dense arrays of patterned resist become deformed in response to capillary forces present during the development process\textsuperscript{59-61}.

Here we present recent advances in the incorporation of self-assembling materials, specifically block copolymers, into the conventional lithographic process for patterning at the 22 nm technology node and beyond. The directed assembly technique using chemical surface patterns to control and direct the ordering of block copolymer domains is introduced. A principal concept of this work is that the desired structures represent thermodynamic minima and, as such, facilitate process control in patterned nanoscale features within relevant tolerances and margins. The potential of self-assembling materials to reproduce the essential attributes of conventional photolithography, including pattern perfection, registration, nonregular device-oriented features, and sufficient process latitude, are discussed in detail. Block copolymers also provide the opportunity to overcome the CD control and LER barriers that are currently encountered with conventional photoresists. Our focus remains on the limits to which directed assembly and block copolymers can be pushed for advanced lithography and the emerging directions in this field.

**Perfection and registration**

The concept of using chemical surface patterns to control the long-range organization of phase-separating polymers was first considered by Boltau et al.\textsuperscript{62}. An octadecyl mercaptan self-assembled monolayer (SAM) was microcontact printed on a Au substrate to provide a surface patterned with regions of varying surface energy. A blend of polystyrene (PS) and polyvinylpyridine (PVP) homopolymers effectively replicated the SAM surface pattern when the period of the surface heterogeneity was commensurate with the coarsened, micron-scale domains of the phase-separated blend. Rockford et al.\textsuperscript{63} extended the use of patterned surfaces to nanoscale dimensions and to block copolymer materials that microphase, rather than macrophase, separate. Striped surfaces of alternating SiO\textsubscript{2} and Au with a period of 60 nm were generated by grazing angle evaporation on miscut Si wafers. Only when the period of the lamellar-forming block copolymer \(L_0\) matched the surface pattern period \(L_s\) were the domains oriented normal to and directed on the substrate surface. Numerous theoretical studies have predicted that dimensional commensurability is required for the guided assembly of block copolymers on chemical surface patterns\textsuperscript{64-70}. Experimentally, Yang et al.\textsuperscript{71} have demonstrated an alternative route for fabricating surface chemical patterns. SAMs of octadecyltrichlorosilane were deposited on Si substrates and chemically patterned by an interference lithography technique using X-ray light and low pressures of oxygen\textsuperscript{8,9}. These chemically striped surfaces were subsequently used to direct the assembly of poly(styrene-block-methyl methacrylate) (PS-\(b\)-PMMA) copolymers.
The aforementioned nanoscale techniques, while providing small areas of guided self-assembly riddled with defects, did not achieve the defect-free, registered ordering that is necessary for widespread lithographic application\textsuperscript{63,71,72}. Even the most basic requirements demanded by the ITRS were far from being satisfied. Only statistical measures such as a two-dimensional order parameter could be used to characterize the quality of the directed patterns that were achieved\textsuperscript{63}. The lack of defect-free ordering and registration most likely resulted from a high density of imperfections in the surface pattern being translated into the self-assembled morphologies.

Directed assembly of block copolymers using chemical surface patterns, however, has recently been improved to the point where it is now a promising approach for nanolithography\textsuperscript{11,73-76}. A functional directed-assembly process is outlined in Fig. 3 and begins with the deposition of an ultrathin imaging layer on a Si substrate. The imaging layer is chemically grafted to the native oxide of the substrate and can either be a hydroxy-terminated polymer brush\textsuperscript{73-76} or a self-assembled trichlorosilane monolayer\textsuperscript{11,77}. Alternative combinations of substrates and imaging layers should certainly be possible\textsuperscript{78-80}. Subsequently a lithographic exposure step is used to pattern the imaging layer with chemically distinct regions. This step is typically a two-fold process in which extreme ultraviolet interference lithography\textsuperscript{81,82} or electron-beam lithography\textsuperscript{55} is first used to pattern dense lines and spaces with a period \( L_s \) in a photoresist film that has been deposited on the imaging layer. Next the topographic pattern in the photoresist layer is transferred to a chemical pattern in the imaging layer by means of an oxygen plasma treatment step. The remaining photoresist material is then removed by solvent treatment to reveal the chemical surface pattern that has a period of \( L_s \). Regions of the imaging layer exposed to the oxygen plasma become chemically modified to contain oxygen-containing moieties and have a high surface energy\textsuperscript{83}. In comparison, the regions of the imaging layer covered by the photoresist are protected from the oxygen plasma and remain chemically unmodified with a lower surface energy.

A thin film (typically <100 nm) of block copolymer can be deposited on the patterned surface and thermally annealed such that microphase separation produces ordered block copolymer domains. The resultant block copolymer morphologies can be characterized in either a top-down or cross-sectional manner using scanning electron microscopy (SEM) or atomic force microscopy (AFM). Fig. 4 shows a top-down SEM image of PS-b-PMMA copolymer structures on both chemically patterned and unpatterned regions of the surface\textsuperscript{11}. The block copolymer on the left hand side of the image resides on a chemically homogeneous surface that induces the formation of

![Fig. 3 Generalized schematic of directed assembly using chemical surface patterns. A chemical surface pattern is first produced in an ultrathin imaging layer. The block copolymer film is then deposited by spin casting on the surface pattern and annealed to allow for the formation of the ordered microdomains.](image)

![Fig. 4 The transition in morphology of a lamellar-forming PS-b-PMMA copolymer at the edge of a chemically patterned substrate. On the left, the surface is chemically homogeneous and the lamellae form a fingerprint morphology that lacks long-range order. On the right, the surface is chemically striped with a periodicity \( L_s \) that matches the block copolymer periodicity \( L_0 \) and induces the lamellae to form perfectly ordered structures over arbitrarily large areas.](image)
perpendicular domains that lack any long-range order and instead form a 'fingerprint' morphology. On the right-hand side of the image, the block copolymer domains follow an underlying chemical surface pattern with \( L_s = 47.5 \) nm, which matches the natural lamellar period of the block copolymer, \( L_0 \). Block copolymer structures on patterned surfaces with \( L_s = L_0 \) can be ordered and directed with perfection over arbitrarily large areas. In our experience, as long as the underlying surface pattern is defect-free, which can readily be achieved using the aforementioned polymer brush imaging layers and patterning techniques, then the block copolymer structures are also self-assembled and directed with perfection\(^{11}\). Furthermore, cross-sectional SEM images indicate that the polymer domains are perfectly registered and positioned with respect to the underlying surface pattern\(^{11}\). In this case, the PMMA domains preferentially wet the chemically oxygenated regions of the surface pattern and the PS domains wet the unmodified regions of the surface pattern. The interfaces between domains are also observed to be perpendicular to the substrate.

**Dimensional and process latitude**

Directed assembly can, therefore, fulfill at least two of the essential attributes of photolithography: pattern perfection and registration. The block copolymer assembly demonstrated in Fig. 4 was performed on surface patterns with \( L_s = \) equal to the equilibrium block copolymer dimension \( L_0 \). But what happens when directed assembly is performed on surface patterns with \( L_s \) that deviates from \( L_0 \)? How does the choice of imaging layer and its chemistry influence the perfection of the assembly process? These questions speak directly to the process latitude of directed assembly and whether this patterning approach can accommodate the dimensional variability necessary for lithographic application.

The \( L_0 \) periodicity of lamellar block copolymers results from the thermodynamically controlled self-assembly process and minimization of the free energy in the system\(^1\).\(^2\). The simplest model for block copolymer assembly considers only the competing contributions of the elastic chain stretching energy and the repulsive interaction energy between the blocks. In directed assembly, however, the additional interfacial interactions imparted via the surface pattern can stabilize the block copolymer morphologies and induce the stretching or compression of the individual polymer chains\(^{73}\). Fig. 5a demonstrates that the final block copolymer structures are influenced by both \( L_s \) and the surface energy of the initial imaging layer. The chemically patterned PS brush imaging layer has alternating oxygenated and unmodified stripes that have high and low surface energies, respectively. The interfacial energy contrast between these two regions is large and strongly induces wetting by the appropriate blocks of the copolymer. Significant chain stretching and compression is also enabled by the stabilizing surface interactions. In Fig. 5a, perfect ordering on patterned PS brushes was achieved for \( 42.5 \) nm < \( L_s \) ± 25.5 nm or \( L_s = L_0 \pm 10\% \) \( L_0 \). In comparison, an imaging layer of poly(styrene-random-methyl methacrylate) (PS-r-PMMA) copolymer with 50 vol\% PS produces fairly low interfacial energy contrast between the chemically modified and unmodified stripes. The lower interfacial energy contrast allows for easier wetting by the appropriate blocks of the copolymer, leading to perfect ordering of the copolymer domains on patterned surfaces.

*Fig. 5 Directed assembly of lamellar PS-b-PMMA (\( L_0 = 48 \) nm) on surfaces chemically patterned with periodicities 42.5 nm < \( L_s \) < 52.5 nm. (a) The degree of interfacial energy contrast between the chemically modified and unmodified regions of the surface pattern and the corresponding block copolymer domains plays a significant role in directed self-assembly. The low contrast PS-r-PMMA 50:50 brush (top row) fails to provide perfect ordering for any \( L_s \), but the high contrast PS brush (bottom row) directs the assembly of well-ordered block copolymer domains for the entire range of \( L_s \). (Adapted and reprinted with permission from\(^{73}\). © 2004 Wiley-VCH.) (b) The block copolymer chains must compress and stretch for \( L_s < L_0 \) and \( L_s > L_0 \), respectively, to accommodate the periodicities imposed by the surface pattern.*
energy contrast provides less of a driving force for chain stretching or compression and, consequently, defect-free assembly can be achieved over a narrow range of \( L_S \) (only \( L_S = L_0 \)). The greatest process latitude for directed assembly can thus be achieved when using chemical surface patterns with the largest interfacial energy contrast.\(^7\)

Recently, Wilmes et al.\(^8\) have shown that arcs with radii of curvature as small as \( L_0/4 \) can be fabricated with perfection using pure block copolymers. The arc geometry is nearly identical to dense lines with an additional free energy penalty for bending the lamellar interfaces. For perfect directed assembly with \( L_S = L_0 \), this interfacial bending energy must therefore be balanced by the interfacial interactions between the surface pattern and the block copolymer domains.

Block copolymer blends may also be used to expand the range of dimensions accessible to directed assembly.\(^8\) The ability to control the self-assembled dimension is of significant importance in nanofabrication where multiple length scales are often required in close proximity. Fig. 6 details how block copolymer-block copolymer blends and block copolymer-homopolymer blends can precisely tune the natural lamellar periodicity of the blend system, \( L_B \). Binary blends of a low molecular weight (e.g. 51 kg mol\(^{-1}\)) and a high molecular weight (e.g. 104 kg mol\(^{-1}\)) symmetric PS-b-PMMA copolymer result in lamellar phases with periodicities intermediate to that of the pure copolymers.\(^8\) The 1:3 and 1:1 by volume blends in Fig. 6a have lamellar periodicities of \( L_B = 45 \) nm and 41 nm, respectively. These materials were also used for directed assembly on chemical surface patterns and were observed to behave identically to pure block copolymers.\(^8\) For example, defect-free assembly on a patterned PS brush was achieved when \( L_S = L_B \pm 10\% L_B \).

Ternary blends of a block copolymer and its corresponding homopolymers (e.g. PS-b-PMMA plus PS and PMMA homopolymers) can access an even wider range of self-assembled dimensions. Simply by tuning the composition of the blend, through parameters such as the volume fraction of the total homopolymer and the homopolymer molecular weight, it is possible to swell the blend domains to greater than twice the size of the pure block copolymer domains.\(^8\) Fig. 6b demonstrates how lamellar ternary blend dimensions scale with the total homopolymer volume fraction, \( \phi_H \). For example, a pure symmetric block copolymer (\( \phi_H = 0 \)) with \( L_0 = 48 \) nm can be adjusted by the addition of 40 vol.% total homopolymer (\( \phi_H = 0.4 \)) to create a lamellar phase with a periodicity of \( L_B = 70 \) nm. These lamellar-forming blend materials have also been used for directed assembly and have comparable process latitude to pure block copolymers and binary block copolymer blends.\(^8\)

Nonregular device-oriented structures
The directed assembly of block copolymers must demonstrate the ability to fabricate nonregular device-oriented structures prior to being
considered a viable nanofabrication and next-generation lithography technique. Integrated circuits and memory arrays contain elements that are more complex geometrically than the simple periodic arrays of lines or spots available from pure block copolymers. The gate layer of most integrated circuits, for example, requires the patterning of dense lines, bent lines with sharp corners, lines that end at specific positions, T-junctions, jogs, and arrays of spots. Recently, many of these geometries have been successfully patterned by the directed assembly of block copolymers (Fig. 7).

The periodic lines with corners geometry (Fig. 7a, top left) was considered both with experiments and molecular-level simulations. Experimentally 45°, 90°, and 135° bends with a surface periodicity of 65 nm < L < 80 nm were patterned. A block copolymer-homopolymer blend was found to assemble with perfection in both the linear and sharp corner sections, providing the first evidence that directed assembly could fabricate nonregular geometries. Single chain in mean field (SCMF) simulations performed on this system indicate that the bend corners have a higher homopolymer concentration, by 6-7 vol.%, than the linear sections of the lamellae. The localized redistribution of homopolymer in the film swelled the domains in the corners in order to accommodate the dimensional differences between the linear period and the corner-to-corner period in this geometry.

The remaining geometries in Fig. 7 were also fabricated with block copolymer blends and the success of the assembly process, particularly for the T-junction geometry, was undoubtedly enhanced by the redistribution of homopolymer in the thin films. It is expected that, while pure block copolymers may be suitable for many of the essential integrated circuit geometries, block copolymer blends will provide the necessary flexibility to achieve the entire spectrum of structures, dimensions, and feature densities.

**CD control and LER**

Self-assembling materials such as block copolymers are particularly attractive for nanolithography because they offer potential improvements in the CD control and LER of the fabricated structures. Conventional lithography with chemically amplified photoresists is a diffusion-limited process. Small deviations in the exposure dose or post-exposure bake temperature can lead to large variations in the final structure dimension. Thermodynamically controlled processes such as self-assembly, on the other hand, proceed until the resulting morphology achieves a minimized free energy at equilibrium. As discussed earlier, the thermodynamics of the block copolymer system determines the overall shape and size of the domains. The block copolymer assembly process is therefore able to correct or self-heal for irregularities, e.g. dimensional variations or defects, in the chemical surface pattern. The influence of the surface pattern duty cycle, defined as the ratio of the width of the chemically unmodified stripes to the overall periodicity, on directed assembly has been considered with both experiments and SCMF simulations. The symmetric block copolymer considered had a duty cycle of 0.5, while surface patterns...
with duty cycles ranging from 0.25 to 0.70 were fabricated. Perfect ordering of the block copolymer was achieved for pattern duty cycles between 0.35 and 0.65. For the largest duty cycles (Fig. 8c), the domain interfaces were tilted away from the substrate normal. However, molecular-level simulations indicate that the interface tilting is less than ~10° and less than what would be predicted on the basis of simple volumetric arguments (>20°). In addition, the widths of the lamellar domains at half the film thickness were exactly equal and corresponded to the block copolymer duty cycle of 0.5. The resulting polymer structures were self-corrected for the dimensional variation in the underlying surface pattern and are more suitable as templates for pattern transfer processes to the substrate. Furthermore, lateral roughness and gaps in the chemically modified regions of the surface pattern stripes can be overcome by the block copolymer such that defect-free structures are formed with long-range order.

The LER of the self-assembled structures is also a thermodynamic property of the system and is theoretically predicted to be sub-1 nm in dimension. The interfacial width or roughness between the block copolymer domains is in theory proportional to $\chi^{-0.5}$, where $\chi$ is the interaction parameter between the blocks of the copolymer. Simply by choosing polymer components that are more incompatible it may be possible to reduce the LER of the block copolymer structures further. At present it has not been demonstrated, however, that one can achieve the sub-2 nm LER requirement in the ITRS after removing one block or after pattern transfer operations.

Emerging directions and conclusions

The insertion of block copolymers into the conventional lithographic process has progressed appreciably over the past decade, from the first demonstrations of directed assembly on chemical surface patterns to the fabrication of complex device-oriented geometries. Directed assembly has been refined to the point where pattern transfer processes to the substrate. Furthermore, lateral roughness and gaps in the chemically modified regions of the surface pattern stripes can be overcome by the block copolymer such that defect-free structures are formed with long-range order.

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The challenges facing directed self-assembly for insertion in the ITRS were addressed at a recent workshop cosponsored by the Semiconductor Industry and National Nanotechnology Initiative. In addition to the materials issues addressed above, specific lithographic questions remain about the possibility of assembling full integrated circuit layouts using block copolymers. The feasibility of fabricating the essential and desired set of lithographic structures used in integrated circuit layouts will need to be explored, including periodic and isolated lines and contact openings. Once the individual lithographic elements have been demonstrated, it will be necessary to integrate these components into a complete circuit layout. The ability to fabricate features with multiple sizes and pitches in a single layer of the chip would also be desirable, but may be difficult to achieve because the structure dimensions are typically limited by the choice of self-assembling material (e.g. $L_0 = L_0 \pm 10\% L_0$). Multiple-layer devices have yet to be attempted by directed assembly and it will be necessary to demonstrate that this approach can satisfy the projected ITRS alignment and registration requirements. Achieving these goals for full integrated circuits by directed assembly may demand the redesign of the layouts to be more amenable for self-assembling materials. This concept of design for manufacturing should take advantage of the inherent periodicities, length scales, and geometries naturally formed by the block copolymers and is believed to be a viable option at future technology nodes. Furthermore, theoretical frameworks and molecular-level simulations will need to be developed for predicting whether the desired pattern geometries can be directed to assemble without defects. Alternatively, these computer tools could be used to determine the optimal block copolymer material for self-assembling a specific geometry or set of components.

Using block copolymers and self-assembling materials for the direct fabrication of complex three-dimensional structures in thin films promises to be an emerging area for directed assembly and nanolithography. In top-down lithography and all of the work described thus far, the structures formed are two-dimensional in nature. Control over the structure geometries, long-range ordering, and positioning has been achieved within the plane of the film. However, there has been no
variation in the structures in the direction normal to the substrate. It may be possible to encode additional information into the system through the choice of self-assembling material such that three-dimensional structures are formed in a single processing step. In the case of the semiconductor industry, the formation of three-dimensional structures can be conceptualized as a route for simultaneously patterning multiple layers in an integrated device, e.g. as a combined gate and contact feature. Already block copolymers on chemical surface patterns with mismatched geometries have been used to induce the formation of bicontinuous, network morphologies (Fig. 9)\textsuperscript{104,105}. These types of bicontinuous structures show more immediate potential as membranes, but through careful design of the chemical surface pattern it may be possible to fabricate structures relevant for integrated circuits. An alternative approach to three-dimensional structures could involve the directed assembly of a block copolymer using a chemically striped surface, followed by conversion of the structures to a more functional geometry\textsuperscript{106}. Fig. 10a demonstrates the directed assembly of a cylindrical poly(styrene-block-tert-butyl acrylate) (PS-b-PtBA) copolymer in a thin film. The aligned PtBA cylinder domains are subsequently converted through a thermochemical reaction at 160°C to a linear, hierarchical arrangement of spherical poly(acrylic anhydride) (PAA) nanodots in three dimensions (Fig. 10b)\textsuperscript{106}. These dot arrays, with row-to-row spacings controlled by the surface pattern dimension $L_s = 57.5$ nm and regular separations of $~49$ nm between nanodots within a row, could potentially be used in the fabrication of magnetic storage media.

In conclusion, the directed assembly of block copolymers on chemically heterogeneous surfaces is a promising route for patterning at the nanoscale. The directed assembly technique is able to replicate the perfection, registration, and geometries attained by photolithography, while achieving the advantageous atomic-level control inherent to self-assembling materials. Improvements to the materials and the assembly process will be critical in determining whether block copolymers or other smart materials are eventually considered the best option for fabrication at sub-22 nm length scales.

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