GRAPHOEPITAXIAL SELF-ASSEMBLY OF ARRAYS OF DOWNWARD FACING HALF-CYLINDERS

TECHNICAL FIELD

[0001] Embodiments of the invention relate to methods of fabricating thin films of self-assembling block copolymers, and devices resulting from those methods.

BACKGROUND OF THE INVENTION

[0002] As the development of nanoscale mechanical, electrical, chemical and biological devices and systems increases, new processes and materials are needed to fabricate nanoscale devices and components. Making electrical contacts to conductive lines has become a significant challenge as the dimensions of semiconductor features shrink to sizes that are not easily accessible by conventional lithography. Optical lithographic processing methods have difficulty fabricating structures and features at the sub-60 nanometer level. The use of self assembling diblock copolymers presents another route to patterning at nanoscale dimensions. Diblock copolymer films spontaneously assemble into periodic structures by microphase separation of the constituent polymer blocks after annealing, for example by thermal annealing above the glass transition temperature of the polymer or by solvent annealing, forming ordered domains at nanometer-scale dimensions.

[0003] The film morphology, including the size and shape of the microphase-separated domains, can be controlled by the molecular weight and volume fraction of the AB blocks of a diblock copolymer to produce lamellar, cylindrical, or spherical morphologies, among others. For example, for volume fractions at ratios greater than about 80:20 of the two blocks (AB) of a diblock polymer, a block copolymer film will microphase separate and self-assemble into a periodic spherical domains with spheres of polymer B surrounded by a matrix of polymer A. For ratios of the two blocks between about 60:40 and 80:20, the diblock copolymer assembles into a periodic hexagonal close-packed or honeycomb array of cylinders of polymer B within a matrix of polymer A. For ratios between about 50:50 and 60:40, lamellar domains or alternating stripes of the blocks are formed. Domain size typically ranges from 5-50 nm.

[0004] A lamellar-phase block copolymer material has been used for making line features on a substrate. However cylinders self-assemble more rapidly and corrects defects faster than lamellae. Researchers have reported producing lines of upward-facing, half-cylinders of a minority block of a block copolymer in a matrix of the majority block through self-assembly of a cylindrical-phase morphology block copolymer on a chemically neutral surface. After removal of the matrix material, the half-cylinders form a masking structure over the underlying substrate. However, subsequent etching tends to undercut and isotropically etch the matrix material that remains under the half-cylinder lines, which will negatively affect etch resolution of the substrate. Applications for forming structures in an underlying substrate for semiconductor systems require a complex layout of elements for forming contacts, conductive lines and/or other elements such as DRAM capacitors.

[0005] It would be useful to provide methods of fabricating films of line arrays of ordered nanostructures that overcome these problems.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] Embodiments of the invention are described below with reference to the following accompanying drawings, which are for illustrative purposes only. Throughout the following views, the reference numerals will be used in the drawings, and the same reference numerals will be used throughout the several views and in the description to indicate same or like parts.

[0007] **FIG. 1** illustrates a diagrammatic top plan view of a portion of a substrate at a preliminary processing stage according to an embodiment of the present disclosure, showing the substrate with a neutral wetting material thereon. **FIGS. 1A-1B** are elevational, cross-sectional views of the substrate depicted in FIG. 1 taken along lines 1A-1A and 1B-1B, respectively.

[0008] **FIG. 2** illustrates a diagrammatic top plan view of the substrate of FIG. 1 at a subsequent stage showing the formation of trenches in a material layer formed on the neutral wetting material. **FIGS. 2A-2B** illustrate elevational, cross-sectional views of a portion of the substrate depicted in FIG. 2 taken, respectively, along lines 2A-2A and 2B-2B.

[0009] **FIG. 3** illustrates a side elevational view of a portion of a substrate at a preliminary processing stage according to another embodiment of the disclosure, showing the substrate with trenches in a material layer formed on the substrate. **FIG. 4** illustrates a side elevational view of the substrate of FIG. 3 at a subsequent stage showing the formation of a neutral wetting material within the trenches.

[0010] **FIG. 5** is a diagrammatic top plan view of the substrate of FIG. 2 at a subsequent stage in the fabrication of a self-assembled, cylindrical phase, block copolymer film within the trenches according to an embodiment of the disclosure. **FIG. 5A-5B** illustrate elevational, cross-sectional views of a portion of the substrate depicted in FIG. 5 taken along lines 5A-5A and 5B-5B, respectively.

[0011] **FIG. 6** is a view of the substrate depicted in FIG. 5B at a subsequent stage showing positioning of a preferential wetting material over the block copolymer material within the trenches.

[0012] **FIG. 7** is a top plan view of the substrate shown in FIG. 6 at a subsequent stage, showing a cut-away of the preferential wetting material over the surface of the self-assembled block copolymer material within the trenches. **FIG. 7A-7B** illustrate cross-sectional views of the substrate depicted in FIG. 7, taken along lines 7A-7A and 7B-7B, respectively. **FIG. 7C** is a top plan view of a cross-section of the substrate shown in FIG. 7A taken along lines 7C-7C, showing the self-assembled half-cylinder lines within a polymer matrix within the trenches.

[0013] **FIG. 8** is a view of the substrate depicted in FIG. 7B at a subsequent stage showing removal of the preferential wetting material from the surface of the self-assembled block copolymer material according to an embodiment of the disclosure.

[0014] **FIG. 9** is a top plan view of the substrate shown in FIG. 7 at a subsequent stage, showing the removal of one of the polymer domain of the self-assembled block copolymer material within the trenches. **FIG. 9A-9B** illustrate cross-sectional views of the substrate depicted in FIG. 9, taken along lines 9A-9A and 9B-9B, respectively.

[0015] **FIGS. 10-11** are top plan views of the substrate of FIG. 9 at subsequent stages, illustrating an embodiment of the use of the self-assembled block copolymer film after removal of one of the polymer blocks, as a mask to etch the substrate and filling of the etched openings. **FIGS. 10A-11A** illustrate elevational, cross-sectional views of a portion of the substrate depicted in FIGS. 10-11 taken along lines 10A-10 and 11A-11A, respectively. **FIGS. 10B-11B** are cross-sectional views of the substrate depicted in FIGS. 10-11 taken along lines 10B-10B and 11B-11B, respectively.

[0016] **FIG. 12** is a view of the substrate depicted in FIG. 5A at a subsequent stage showing the application of a preferential wetting atmosphere over the block copolymer material within the trenches according to another embodiment of the invention.

[0017] **FIG. 13** is a top plan view of the substrate shown in FIG. 12 at a subsequent stage, showing the preferential wetting brush layer over the surface of the self-assembled block copolymer material within the trenches. **FIG. 13A-13B** illustrate cross-sectional views of the substrate depicted in FIG. 13, taken along lines 13A-13A and 13B-13B, respectively.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The following description with reference to the drawings provides illustrative examples of devices and methods according to embodiments of the invention. Such description is for illustrative purposes only and not for purposes of limiting the same.

[0019] In the context of the current application, the term "semiconductor substrate" or "semiconductive substrate" or "semiconductive wafer fragment" or "wafer fragment" or "wafer" will be understood to mean any construction comprising semiconductor material, including but not limited to bulk semiconductive materials such as a semiconductor wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term "substrate" refers to any supporting structure including, but not limited to, the semiconductive substrates, wafer fragments or wafers described above.

[0020] "L_o" as used herein is the inherent periodicity or pitch value (bulk period or repeat unit) of structures that self assemble upon annealing from a self-assembling (SA) block

copolymer. "L_B" as used herein is the periodicity or pitch value of a blend of a block copolymer with one or more of its constituent homopolymers. "L" is used herein to indicate the center-to-center cylinder pitch or spacing of cylinders of the block copolymer or blend, and is equivalent to "L_o" for a pure block copolymer and "L_B" for a copolymer blend.

[0021] In embodiments of the invention, a polymer material (e.g., film, layer) is prepared by guided self-assembly of block copolymers, with both polymer domains wetting the interface with the trench floor. Block copolymer materials spontaneously assemble into periodic structures by microphase separation of the constituent polymer blocks after annealing, forming ordered domains at nanometer-scale dimensions. In embodiments of the invention, one or more rows or lines of parallel-oriented half-cylinders are formed within a trench, with the face of the half-cylinder lines wetting a chemically neutral trench floor. Following self assembly, the parallel-oriented line(s) formed on the substrate can then be used, for example, as an etch mask for patterning nanometer-scale line openings into the underlying substrate through selective removal of one block of the self-assembled block copolymer. Since the domain sizes and periods (L) involved in this method are determined by the chain length of a block copolymer (MW), resolution can exceed other techniques such as conventional photolithography. Processing costs using the technique are significantly less than extreme ultraviolet (EUV) photolithography, which has comparable resolution.

[0022] A method for fabricating a self-assembled block copolymer material that defines an array of nanometer-scale, parallel-oriented, downward facing half-cylinder lines according to an embodiment of the invention is illustrated in **FIGS. 1-9**.

[0023] The described embodiment involves an anneal of a cylindrical-phase block copolymer in combination with a graphoepitaxy technique that utilizes a lithographically defined trench as a guide with a floor composed of a material that is neutral wetting to both polymer blocks and sidewalls and ends that are preferential wetting to one polymer block and function as constraints to induce self assembly of the block copolymer material. In some embodiments, an overlying material layer that is preferential wetting is placed over the block copolymer material in the trench. In other embodiments, the air interface can selectively wet the desired block. Upon annealing, the block copolymer material will self-assemble into one

or more rows or lines of half-cylinders in a polymer matrix and registered to the trench sidewalls, with the face of the half-cylinders oriented downward and wetting the trench floor. In some embodiments, an ordered array of two or more rows of half-cylinders can be formed in each trench.

[0024] As depicted in **FIGS. 1-1B**, a substrate **10** is provided, which can be silicon, silicon oxide, silicon nitride, silicon oxynitride, silicon oxycarbide, among other materials.

[0025] In the illustrated embodiment, a neutral wetting material **12** (e.g., random copolymer, blend of functionalized homopolymers, etc.) has been formed over the substrate **10**. A material layer **14** (or one or more material layers) can then be formed over the neutral wetting material and etched to form trenches **16**, **16a**, as shown in **FIGS. 2-2B**. Portions of the material layer **14** form a spacer **18** outside and between the trenches. The trenches **16**, **16a** are structured with opposing sidewalls **20**, opposing ends **22**, a floor **24**, a width (w_t, w_{t2}), a length (l_t) and a depth (D_t).

[0026] In another embodiment illustrated in **FIGS. 3-4**, the material layer **14'** can be formed on the substrate **10'**, etched to form the trenches **16'**, **16a'**, and a neutral wetting material **12'** can then be formed on the trench floors **24'**. For example, a random copolymer material can be deposited into the trenches and crosslinked or grafted to form a neutral wetting material layer. Material on surfaces outside the trenches such as on the spacers **18'** (e.g., non-crosslinked random copolymer) can be subsequently removed.

[0027] Single or multiple trenches **16**, **16a** (as shown) can be formed using a lithographic tool having an exposure system capable of patterning at the scale of L (10-100 nm). Such exposure systems include, for example, extreme ultraviolet (EUV) lithography, proximity X-rays and electron beam (e-beam) lithography, as known and used in the art. Conventional photolithography can attain (at smallest) about 58 nm features.

[0028] A method called "pitch doubling" or "pitch multiplication" can also be used for extending the capabilities of photolithographic techniques beyond their minimum pitch, as described, for example, in U.S. Pat. No. 5,328,810 (Lowrey et al.), U.S. Pat. No. 7,115,525 (Abatchev, et al.), US 2006/0281266 (Wells) and US 2007/0023805 (Wells). Briefly, a

pattern of lines is photolithographically formed in a photoresist material overlying a layer of an expendable material, which in turn overlies a substrate, the expendable material layer is etched to form placeholders or mandrels, the photoresist is stripped, spacers are formed on the sides of the mandrels, and the mandrels are then removed leaving behind the spacers as a mask for patterning the substrate. Thus, where the initial photolithography formed a pattern defining one feature and one space, the same width now defines two features and two spaces, with the spaces defined by the spacers. As a result, the smallest feature size possible with a photolithographic technique is effectively decreased down to about 30 nm or less.

[0029] Factors in forming a single line or multiple lines of parallel-oriented half-cylinders within the trenches include the width (w_t) of the trench, the formulation of the block copolymer or blend to achieve the desired pitch (L), and the thickness (t) of the block copolymer material.

[0030] There is a shift from two rows to one row of the half-cylinder lines as the width of the trench is decreased (e.g., from w_{t2} to w_t) and/or the periodicity (L value) of the block copolymer is increased, for example, by forming a ternary blend by the addition of both constituent homopolymers. The boundary conditions of the trench sidewalls **22** in both the x- and y-axis impose a structure wherein each trench contains "n" number of features (e.g., n lines of half-cylinders).

[0031] In the illustrated embodiment, trenches **16** are constructed with a width (w_t) of about 1.5-2*L (or 1.5-2 X the pitch value) of the block copolymer such that a cast block copolymer material (or blend) of about L will self assemble upon annealing into a single parallel-oriented, downward-facing half-cylinder line (line width at or about 0.5*L) that is aligned with the sidewalls down the center of each trench **16**. A relatively wider trench **16a** has been formed with a width (w_{t2}) of (n + 1)*L such that the block copolymer material (or blend) of about L will self assemble into n lines of downward-facing half-cylinders (line width $\simeq$ about 0.5*L) at a center-to-center pitch distance (p) of adjacent lines at or about the L value of the block copolymer material. For example, the width (w_{t2}) of a wider trench **16a** can be about 3-65*L to result in the formation of 2-64 rows, respectively, of the downward-facing half-cylinders.

[0032] For example, in using a cylindrical phase block copolymer with an about 50 nm pitch value or L, in trenches **16** with a width (w_t) of about 1.5-2*50 nm or about 75-100 nm, the block copolymer material will form a single downward-facing half-cylinder having a line width of about 25-nm. In trench **16a** with a width (w_{t2}), for example, of about 3*L or about 3*50 nm (or about 150 nm), the block copolymer material will form 2 rows of the half-cylinder structures (line width about 25-nm) at a center-to-center pitch distance (p) of adjacent half-cylinder lines of about the L value (about 50 nm).

[0033] In another example, with a cylindrical-phase block copolymer or blend having a pitch or L value of 35-nm, a single line of about 17.5 nm wide (about 0.5*L) of a downward facing half-cylinder will form in trench **16** having a width (w_t) of about 1.5-2*L or about 52.5-70 nm wide, and two parallel lines of half-cylinders (each about 17.5 nm wide) at a center-to-center pitch distance (p) of about 35 nm will form in trench **16a** having a width (w_{t2}) of about 3*L or about 3*35 nm (or about 105 nm).

[0034] The length (l_t) of the trenches **16, 16a** is according to the desired length of the half-cylinder line(s).

[0035] The depth (D_t) of the trenches is effective to direct lateral ordering of the block copolymer material during the anneal. In embodiments of the invention, the trench depth can be at or less than the final thickness (t_2) of the block copolymer material ($D_t \leq t_2$), which minimizes the formation of a meniscus and variability in the thickness of the block copolymer material across the trench width. In some embodiments, the trench depth is at about two-thirds to about three-fourths (⅔- ¾, or about 67%-75%) less than the final thickness (t_2) of the block copolymer material within the trench.

[0036] In some embodiments, the dimensions of the trenches **16, 16a** are a width of about 20-100 nm (trench **16**, w_t) and about 20-3200 nm (trench **16a**, w_{t2}), a length (l_t) of about 100-25,000 μm, and a depth (D_t) of about 10-100 nm.

[0037] As depicted in **FIGS. 5-5B**, a self-assembling, cylindrical-phase block copolymer material **26** having an inherent pitch at or about L_o (or a ternary blend of block copolymer and homopolymers blended to have a pitch at or about L_B) is deposited into the trenches **16**,

16a. A thin layer **26a** of the block copolymer material can be deposited onto the material layer **14** outside the trenches, e.g., on the spacers **18**.

[0038] The block copolymer or blend is constructed such that all of the polymer blocks will have equal preference for a neutral wetting material on the trench floor. In some embodiments of the invention, the block copolymer or blend is constructed such that the major domain can be selectively removed. In other embodiments, the minor domain polymer block can be selectively doped or structured to incorporate an inorganic component or species (e.g., a filler component) during annealing into microphase domains, which will remain on the substrate as an etch resistant material (e.g., mask) upon selective removal of the majority polymer domain or, in some embodiments, both the majority and minority polymer domains. Suitable inorganic precursors are thermally stable and do not volatilize at the anneal temperature.

[0039] Block copolymers that incorporate an inorganic species can be prepared by techniques known in the art, for example, by a direct synthesis technique, or by incorporating atoms of an inorganic species by complexation or coordination with a reactive group of one of the polymer blocks.

[0040] For example, as described in USP 6,565,763 (Asakawa et al.), the block copolymer can be blended with an inorganic heat resistant material or precursor thereof, which will segregate to one polymer phase, for example, a metal salt, a metal oxide gel, metal alkoxide polymers, metal oxide precursor, metal nitride precursor, and metal fine particles. Examples of the metal include silicon (Si), chromium (Cr), titanium (Ti), aluminum (Al), molybdenum (Mo), gold (Au), platinum (Pt), ruthenium (Ru), zirconium (Zr), tungsten (W), vanadium (V), lead (Pb), and zinc (Zn), among others.

[0041] Examples of metal alkoxides include alkoxysilanes such as tetramethoxysilane, tetraethoxysilane, tetraisopropoxysilane, tetraisopropoxyaluminum and tetraisopropoxytitanium, and alkylalkoxysilanes such as butyltriethoxysilane and propyltriethoxyaluminum. An example of the metal alkoxide polymer is polydiethoxysiloxane.

[0042] Examples of a metal oxide precursor or metal nitride precursor include polysilsesquioxane (e.g., polymethylsilsesquioxane, polymethylhydroxyl silsesquioxane, polyphenylsilsesquioxane, etc.), polyhedral oligomeric silsesquioxane (POSS), and polysilazane.

[0043] In some embodiments, a solution of a block copolymer can be combined with an additive such as an organic metal salt that has a high affinity to one of the polymer chains of the block copolymer and will segregate during an anneal to one of the polymer phases. For example, the block copolymer can be mixed with a metal salt combined with an organic compound. Examples of such organic metal salts include lithium 2,4-pentanedionate, lithium tetramethylpentanedionate, ruthenium 2,4-pentanedionate, magnesium 2,4-pentanedionate, magnesium hexafluoropentanedionate, magnesium trifuoropentanedionate, manganese (II) 2,4-pentanedionate, molybdenum (V) ethoxide, molybdenum (VI) oxide bis(2,4-pentanedionate), neodymium 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3.5-octanedionate, neodymium hexafluoropentanedionate, neodymium (III) 2,4-pentanedionate, nickel (II) 2,4-pentanedionate, niobium (V) n-butoxide, niobium (V) n-ethoxide, palladium hexafluoropentanedionate, palladium 2,4-pentanedionate, platinum hexafluoropentanedionate, platinum 2,4-pentanedionate, rhodium trifuoropentanedionate, ruthenium (III) 2,4-pentanedionate, tetrabutylammonium hexacholoroplatinate (IV), tetrabromoaurate (III) cetylpyridinium salt, among others.

[0044] As described in US 2007/0222995 and US 2007/0289943 (Lu; Agilent Technologies Inc.), atoms of an inorganic species such as a metal (e.g., iron, cobalt, molybdenum, etc.) can be incorporated into one block of a diblock copolymer by complexation of the atoms of the inorganic species with the pyridine units of poly(styrene)-b-poly(vinylpyridine) (PS-b-PVP), where the pyridine group forms a coordination bond with the inorganic species, e.g., iron (Fe), etc. or form as an acid-base conjugate. As an example of an acid-base conjugate, a solution of the PS-b-PVP block copolymer can be combined with dihydrogen hexachloroplatinate (H_2PtCl_6) wherein a single Pt atom can be complexed with each pyridine group (at maximum loading).

[0045] As also described in US 2007/0222995, block copolymers that incorporate an inorganic species can also be prepared by a direct synthesis technique. For example, a sequential living polymerization of a nonmetal-containing monomer (e.g., styrene monomer) followed by an inorganic species-containing monomer (e.g., ferrocenylethylmethylsilane monomer) can be used to synthesize an inorganic species-containing block copolymer (e.g., poly(styrene)-b-poly(ferrocenylmethylethylsilane) (PS-b-PFEMS).

[0046] Examples of diblock copolymers include, for example, poly(styrene)-b-poly(vinylpyridine) (PS-b-PVP), poly(styrene)-b-poly(methylmethacrylate) (PS-b-PMMA) or other PS-b-poly(acrylate) or PS-b-poly(methacrylate), poly(styrene)-b-poly(lactide) (PS-b-PLA), poly(styrene)-b-poly(tert-butyl acrylate) (PS-b-PtBA), and poly(styrene)-b-poly(ethylene-co-butylene (PS-b-(PS-co-PB)), and poly(styrene)-b-poly(ethylene oxide) (PS-b-PEO), polybutadiene-b- poly(vinylpyridine) (PB-b-PVP), poly(ethylene-alt-propylene)-b- poly(vinylpyridine) (PEP-b-PVP), among others, with PS-b-PVP diblock copolymers used in the illustrated embodiment. Other types of block copolymers (i.e., triblock or multiblock copolymers) can be used. Examples of triblock copolymers include ABC copolymers such as poly(styrene-b-methyl methacrylate-b-ethylene oxide) (PS-b-PMMA-b-PEO), and ABA copolymers such as PS-PMMA-PS, PMMA-PS-PMMA, and PS-b-PI-b-PS, among others.

[0047] Examples of diblock copolymers that incorporate an inorganic species include poly(styrene)-b-poly(dimethylsiloxane) (PS-b-PDMS), poly(isoprene)-b-poly(dimethylsiloxane) (PI-b-PDMS), PS-b-PFEMS, poly(isoprene)-b-poly(ferrocenylmethylethylsilane) (PI-b-PFEMS), poly(styrene)-b-poly(vinylmethylsiloxane) (PS-b-PVMS), poly(styrene)-b-poly(butadiene) (PS-b-PB) where the polybutadiene (PB) is stained by osmium tetroxide (OSO_4), and poly(styrene)-b-poly(vinylpyridine) (PS-b-PVP) where the pyridine group forms a coordination bond with an inorganic species, among others. After annealing and self assembly of the polymer blocks into the half-cylinders and matrix, an oxidation process (e.g., ultraviolet (UV)-ozonation or oxygen plasma etching) can be performed to remove the organic components of the block copolymer domains and convert the inorganic species to form a non-volatile inorganic oxide, which remains on the substrate and can be used as a

mask in a subsequent etch process. For example, the inorganic species of the PDMS and PFEM block copolymers are silicon and iron, which, upon oxidation, will form non-volatile oxides, e.g., silicon oxide (SiO_x) and iron oxide (Fe_xO_y).

[0048] The *L* value of the block copolymer can be modified, for example, by adjusting the molecular weight of the block copolymer. The block copolymer material can also be formulated as a binary or ternary blend comprising a block copolymer and one or more homopolymers (HPs) of the same type of polymers as the polymer blocks in the block copolymer, to produce a blend that will swell the size of the polymer domains and increase the *L* value. The concentration of homopolymers in a blend can range from 0 to about 60 wt-%. Generally, when added to a polymer material, both homopolymers are added to the blend in about the same ratio or amount. An example of a ternary diblock copolymer blend is a PS-b-PVP/PS/PVP blend, for example, 60 wt-% of 32.5 K/12 K PS-b-PVP, 20 wt-% of 10K PS, and 20 wt-% of 10K PVP. Another example of a ternary diblock copolymer blend is a PS-b-PMMA/PS/PMMA blend, for example, 60 wt-% of 46K/21K PS-b-PMMA, 20 wt-% of 20K polystyrene and 20 wt-% of 20K poly(methyl methacrylate). Yet another example is a blend of 60:20:20 (wt-%) of PS-b-PEO/PS/PEO, or a blend of about 85-90 wt-% PS-b-PEO and up to 10-15 wt-% PEO homopolymer.

[0049] The film morphology, including the domain sizes and periods (L_o) of the microphase-separated domains, can be controlled by chain length of a block copolymer (molecular weight, MW) and volume fraction of the AB blocks of a diblock copolymer to produce cylindrical morphologies (among others). For example, for volume fractions at ratios of the two blocks generally between about 60:40 and 80:20, the diblock copolymer will microphase separate and self-assemble into periodic half-cylindrical domains of polymer B within a matrix of polymer A. An example of a cylinder-forming PS-b-PVP copolymer material (L_o~35 nm) to form about 20 nm wide half-cylindrical PVP domains in a matrix of PS is composed of about 70 wt-% PS and 30 wt-% PVP with a total molecular weight (M_n) of 44.5 kg/mol.

[0050] Referring to **FIG. 5A**, the cylindrical-phase block copolymer material **26** can be cast or deposited into the trenches **16**, **16a** to an initial thickness (t_1) at or about the *L* value of

the block copolymer material (e.g., about ± 20% of L) such that the thickness (t_2) after annealing will be at or below the L value and the block copolymer material will self assemble to form a single layer of downwardly-facing half-cylinders registered parallel to the sidewalls **20** and extending the length (l_t) of each of the trenches (e.g., as in **FIGS. 7A-7B**). The thickness of the block copolymer material **26** can be measured, for example, by ellipsometry techniques.

[0051] The block copolymer material can be deposited by spin casting (spin-coating) from a dilute solution (e.g., about 0.25-2 wt% solution) of the copolymer in an organic solvent such as dichloroethane (CH_2Cl_2) or toluene, for example. Capillary forces pull excess block copolymer material **26** (e.g., greater than a monolayer) into the trenches **16, 16a**. As shown, a thin layer or film **26a** of the block copolymer material can be deposited onto the material layer **14** outside the trenches, e.g., on the spacers **18**. Upon annealing, the thin film **26a** will flow into the trenches leaving a structureless brush layer on the material layer **14** from a top-down perspective.

[0052] In the present embodiment, the trench floors **24** are structured to be neutral wetting (equal affinity for both blocks of the copolymer) to induce formation of half-cylinder polymer domains that are oriented facing downward on the trench floors, and the trench sidewalls **20** and ends **22** are structured to be preferential wetting by one block of the block copolymer to induce registration of the half-cylinders to the sidewalls **20** as the polymer blocks self-assemble. Entropic forces drive the wetting of a neutral wetting surface by both blocks, and enthalpic forces drive the wetting of a preferential-wetting surface by the preferred block (e.g., the minority block).

[0053] A chemically neutral wetting trench floor **24** allows both blocks of the copolymer material to wet the floor of the trench and provides for the formation of the half-cylinder line layout of the disclosure. The use of a neutral wetting trench floor in embodiments of the invention expands the number of block copolymer materials that can be utilized to produce self-assembled films having a series of parallel lines formed on a substrate surface that can be readily used as a mask for etching the underlying substrate to form a multiple line layout on a nanoscale level.

[0054] A neutral wetting material **12** can be provided, for example, by applying a neutral wetting polymer (e.g., a neutral wetting random copolymer) onto the substrate **10**, then forming an overlying material layer **14** and etching the trenches **16, 16a** to expose the underlying neutral wetting material, as illustrated in **FIGS. 2-2B**.

[0055] In another embodiment illustrated in **FIGS. 3-4**, a neutral wetting random copolymer material can be applied after forming the trenches **16', 16a'**, for example, as a blanket coat by casting or spin-coating into the trenches, as depicted in **FIG. 4**. The random copolymer material can then be thermally processed to flow the material into the bottom of the trenches by capillary action, which results in a layer (mat) **12'** composed of the crosslinked, neutral wetting random copolymer. In another embodiment, the random copolymer material within the trenches can be photo-exposed (e.g., through a mask or reticle) to crosslink the random copolymer within the trenches to form the neutral wetting material **12'**. Non-crosslinked random copolymer material outside the trenches (e.g., on the spacers **18'**) can be subsequently removed.

[0056] Neutral wetting surfaces can be specifically prepared by the application of random copolymers composed of monomers identical to those in the block copolymer and tailored such that the mole fraction of each monomer is appropriate to form a neutral wetting surface. For example, in the use of a PS-b-PVP block copolymer, a neutral wetting material **12** can be formed from a thin film of a photo-crosslinkable random PS-r-PVP copolymer that exhibits non-preferential or neutral wetting toward PS and PVP, which can be cast onto the substrate **10** (e.g., by spin coating). The random copolymer material can be fixed in place by chemical grafting (on an oxide substrate) or by thermally or photolytically crosslinking (any surface) to form a mat that is neutral wetting to PS and PVP and insoluble when the block copolymer material is cast onto it, due to the crosslinking.

[0057] In another embodiment, a blend of hydroxyl-terminated homopolymers and a corresponding low molecular weight block copolymer can be grafted (covalently bonded) to the substrate to form a neutral wetting interface layer (e.g., about 4-5 nm) for PS-b-PMMA and PS-b-P2VP, among other block copolymers. The block copolymer can function to emulsify the homopolymer blend before grafting. For example, an about 1 wt-% solution

(e.g., in toluene) of a blend of about 20-50 wt-% (or about 30-40 wt-%) OH-terminated homopolymers (e.g., M_n=6K) and about 80-50 wt-% (or about 70-60 wt-%) of a low molecular weight block copolymer (e.g., 5K-5K) can be spin coated onto a substrate **10** (e.g., SiO_2), heated (baked) (e.g., at 160°C), and non-grafted (unbonded) polymer material removed, for example by a solvent rinse (e.g., toluene). For example, the neutral wetting material can be prepared from a blend of about 30 wt-% PS-OH (M_n=6K) and PMMA-OH (M_n=6K) (weight ratio of 4:6) and about 70 wt-% PS-b-PMMA (5K-5K), or a ternary blend of PS-OH (6K), P2VP-OH (6K) and PS-b-2PVP (8K-8K), etc.

[0058] In embodiments in which the substrate **10** is silicon (with native oxide), a neutral wetting surface for PS-b-PMMA can be provided by hydrogen-terminated silicon. The floors **24** of the trenches **16**, **16a** can be etched, for example, with a hydrogen plasma, to remove the oxide material and form hydrogen-terminated silicon, which is neutral wetting with equal affinity for both blocks of a block copolymer material. H-terminated silicon can be prepared by a conventional process, for example, by a fluoride ion etch of a silicon substrate (with native oxide present, about 12-15 Å) by exposure to an aqueous solution of hydrogen fluoride (HF) and buffered HF or ammonium fluoride (NH_4F), by HF vapor treatment, or by a hydrogen plasma treatment (e.g., atomic hydrogen).

[0059] An H-terminated silicon substrate can be further processed by grafting a random copolymer such as PS-r-PVP, PS-r-PMMA, etc. selectively onto the substrate resulting in a neutral wetting surface for the corresponding block copolymer (e.g, PS-b-PVP, PS-b-PMMA, etc.). For example, a neutral wetting layer of a PS-*r*-PMMA random copolymer can be provided by an *in situ* free radical polymerization of styrene and methyl methacrylate using a di-olefinic linker such divinyl benzene which links the polymer to an H-terminated silicon surface to produce about a 10-15 nm thick film.

[0060] Referring again to **FIGS. 3-4**, in another embodiment, a neutral wetting random copolymer material **12'** can be applied after formation of the material layer **14'** and trenches **16'**, which reacts selectively with the trench floor **24'** (composed of the substrate **10'** material) and not the trench sidewalls **20'** or ends **22'** (composed of the material layer **14'**). For example, a random copolymer (or appropriate blend of homopolymers with block

copolymer surfactant) containing epoxide groups will react selectively to terminal amine functional groups (e.g. –NH- and -NH_2) on silicon nitride and silicon oxynitride surfaces relative to silicon oxide or silicon. In another example in which the trench floor **24'** is silicon or polysilicon and the sidewalls **20'** are a material such as an oxide (e.g., SiO_x), the floor can be treated to form H-terminated silicon and a random copolymer material **14'** (e.g., PS-r-PVP, PS-r-PMMA, etc.) can be formed by *in situ* polymerization only at the floor surface.

[0061] In yet another embodiment, a neutral wetting surface (e.g., for PS-b-PMMA and PS-b-PEO) can be provided by grafting a self-assembled monolayer (SAM) of a trichlorosilane-base SAM such as 3-(para-methoxyphenyl)propyltrichorosilane grafted to oxide (e.g., SiO_2) as described for example, by D.H. Park, *Nanotechnology* 18 (2007), p. 355304.

[0062] A surface that is neutral wetting to PS-b-PMMA can also be prepared by spin coating a blanket layer of a photo- or thermally cross-linkable random copolymer such as a benzocyclobutene- or azidomethylstyrene-functionalized random copolymer of styrene and methyl methacrylate (e.g., poly(styrene-r-benzocyclobutene-r- methyl methacrylate (PS-r-PMMA-r-BCB)). For example, such a random copolymer can comprise about 42 wt-% PMMA, about (58-x) wt-% PS and x wt-% (e.g., about 2-3 wt-%) of either polybenzocyclobutene or poly(para-azidomethylstyrene)). An azidomethylstyrene-functionalized random copolymer can be UV photo-crosslinked (e.g., 1-5 MW/cm^2 exposure for about 15 seconds to about 30 minutes) or thermally crosslinked (e.g., at about 170°C for about 4 hours) to form a crosslinked polymer mat as a neutral wetting layer. A benzocyclobutene-functionalized random copolymer can be thermally cross-linked (e.g., at about 200°C for about 4 hours or at about 250°C for about 10 minutes).

[0063] In another embodiment, a neutral wetting random copolymer of polystyrene (PS), polymethacrylate (PMMA) with hydroxyl group(s) (e.g., 2-hydroxyethyl methacrylate (P(S-r-MMA-r-HEMA)) (e.g., about 58 wt-% PS) can be can be selectively grafted to a substrate **10** (e.g., an oxide) as a neutral wetting layer about 5-10 nm thick by heating at about 160°C for about 48 hours. See, for example, In et al., *Langmuir*, 2006, 22, 7855-7860.

[0064] To provide preferential wetting trench sidewalls, for example, in the use of a PS-b-PVP block copolymer, the material layer **14** can be composed of silicon (with native oxide), oxide (e.g., silicon oxide, SiO_x), silicon nitride, silicon oxycarbide, indium tin oxide (ITO), silicon oxynitride, and resist materials such as methacrylate-based resists and polydimethyl glutarimide resists, among other materials, which exhibit preferential wetting toward the preferred block (e.g., the minority block) , which is the PVP block in the illustrated embodiment. Upon annealing and self assembly of the block copolymer material, the preferred block (e.g., the PVP block) will form a thin interface layer along the preferential wetting sidewalls **20** and ends **22** of the trenches.

[0065] In other embodiments utilizing PS-b-PMMA, a preferential wetting material such as a polymethylmethacrylate (PMMA) polymer modified with an –OH containing moiety (e.g., hydroxyethylmethacrylate) can be selectively applied onto the sidewalls of the trenches in embodiments where a neutral wetting material **12** is in place on the trench floor **24** (as in **FIGS. 2-2B, FIG. 4**). For example, a neutral wetting layer can be formed on the trench floor **24** (e.g., **FIG. 4** layer) by an *in* situ polymerization of a random copolymer on H-terminated silicon in the presence of SiO_x sidewalls, and OH-modified PMMA then grafted to the sidewalls. An OH-modified PMMA can be applied, for example, by spin coating and then heating (e.g., to about 170°C) to allow the terminal OH groups to selectively end-graft to the sidewalls **20** and ends **22** (e.g., of oxide) of the trenches. Non-grafted material can be removed by rinsing with an appropriate solvent (e.g., toluene). See, for example, Mansky et al., *Science*, 1997, 275, 1458-1460, and In et al., *Langmuir*, 2006, 22, 7855-7860.

[0066] Referring to **FIG. 6**, the surface **28** of the block copolymer material **26** in the trenches is then contacted by a material **30** that will preferentially wet one of the blocks of the copolymer material **26**, which is the minority block in the illustrated embodiment.

[0067] In an embodiment of the invention, the preferential wetting material **30** is composed of a solid material that is placed onto the surface of the block copolymer material **26**. For example, the preferential wetting material **30** can be composed of a soft, flexible or rubbery solid material such as a cross-linked, poly(dimethylsiloxane) (PDMS)

elastomer (e.g., Sylgard-184 by Dow-Corning) or other elastomeric polymer material (e.g., silicones, polyurethanes, etc.).

[0068] A cross-linked, solid PDMS material **30** provides an external surface that is hydrophobic, which can be altered, for example, by a plasma oxidation to add silanol (SiOH) groups to the surface to render the PDMS surface hydrophilic. For example, in using a PS-b-PVP (70:30) block copolymer, a PDMS material **30** having a hydrophobic surface placed into contact with the PS-b-PVP block copolymer material **26** will be preferentially wetted by the PS block, while a PDMS material **30** modified with a hydrophilic surface will be preferentially wetted by the PVP block. After annealing, a PDMS material **30** can be removed, for example, by lifting or peeling the material **30** from the surface **28** of the block copolymer material **26**, which can include applying a solvent such as water, alcohols, etc. (e.g., by soaking) to permeate and swell the PDMS material to enhance physical removal, and which is compatible with and does not dissolve the block copolymer. A dilute fluoride solution (e.g., NH_4F, HF, NaF, etc.) can also be applied to etch and dissolve away a PDMS material.

[0069] In another embodiment, the preferential wetting material **30** can be formed as an inorganic film on the surface **28** of the block copolymer material **26**. For example, a layer of a spin-on dielectric (SOD) material can be formed by applying, for example, a spin-on liquid silicon-containing polymer, removing the solvent (e.g., by heating), and then oxidizing the polymer layer (e.g., oxygen atmosphere, steam-oxidation process, wet chemical oxidation, etc.) to form a hard silicon dioxide (SiO_2) layer, a hydrophilic surface that will be preferentially wetted by the PVP (minority) block. In embodiments of the method, the oxidation can be conducted simultaneously with a thermal anneal of the BCP material. Examples of silicon-containing polymers include a silicates, siloxanes (e.g., hydrogen silsesquioxane (HSQ), hexamethyldisiloxane, octamethyltrisiloxane, etc.), silazanes (e.g., polysilazanes such as hexamethyldisilazane (HMDS), tetramethyldisilazane, octamethylcyclotetrasilazine, hexamethylcyclotrisilazine, diethylaminotrimethylsilane, dimethylaminotrimethylsilane, etc.) and silisesquioxanes (e.g., hydrogen silsesquioxane (HSQ). The spin-on polymer material can be applied, for example, by casting, spin applying, flow coating or a spray coating technique. The solvent of the spin-on polymer material is

compatible with and does not dissolve the block copolymer, for example, water or an alcohol. After annealing, the dielectric preferential wetting material layer **30** can be removed using a controlled etch back process, for example, by applying a fluoride-based etchant whereby the dielectric material is etched at a low etch rate (e.g., less than about 200 Å/minute).

[0070] With the preferential wetting material **30** in contact with the surface **28** of the block copolymer material **26**, an annealing process is conducted (arrows ↓, **FIG. 6**) to cause the polymer blocks to phase separate in response to the preferential and neutral wetting of the trench surfaces and the preferential wetting of the overlying material **30**, and form a self-assembled polymer material **32** as illustrated in **FIGS. 7-7C**.

[0071] Thermal annealing can be conducted at above the glass transition temperature of the component blocks of the copolymer material. For example, a PS-b-PVP copolymer material can be globally annealed at a temperature of about 150-275°C in a vacuum oven for about 1-24 hours to achieve the self-assembled morphology. The resulting morphology of the annealed copolymer material **32** (e.g., parallel orientation of the half-cylinder lines) can be examined, for example, using atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM).

[0072] The block copolymer material can be globally heated or, in other embodiments, a zone or localized thermal anneal can be applied to portions or sections of the block copolymer material **26**. For example, the substrate can be moved across a hot-to-cold temperature gradient **34** (**FIG. 6**) positioned above (as shown) or underneath the substrate (or the thermal source can be moved relative to the substrate, e.g., arrow →) such that the block copolymer material self-assembles upon cooling after passing through the heat source. Only those portions of the block copolymer material that are heated above the glass transition temperature of the component polymer blocks will self-assemble, and areas of the material that were not sufficiently heated remain disordered and unassembled. "Pulling" the heated zone across the substrate can result in faster processing and better ordered structures relative to a global thermal anneal.

[0073] Upon annealing, the cylindrical-phase block copolymer material **26** will self-assemble into a polymer material **32** (e.g. film), as depicted in **FIGS. 7-7C**. In response to the character of the cylinder-phase block copolymer composition (e.g., 70:30 PS-b-PVP having an inherent pitch at or about L) combined with the boundary conditions, including the constraints provided by the width (w_t) of the trenches **16** and the wetting properties of the trench surfaces (i.e., a trench floor **24** that exhibits neutral or non-preferential wetting toward both polymer blocks, e.g., a random graft copolymer, and trench sidewalls **20** and an overlying material **30** that are preferential wetting to the minority block), the minority (preferred) block (e.g., PVP) will self-assemble to form parallel-oriented, downward-facing, half-cylinder domain (line) **36** on the non-preferential (neutral) wetting material **12** on the trench floor, which is parallel to the trench floor **24** and registered to the sidewalls **20** for the length (l_t) of trenches **16**, **16a**. Within the trenches, a matrix **38** of the majority polymer block (e.g., PS) overlies and surrounds the half-cylinder(s) **36**. Generally, the half-cylinder lines **36** (both blocks considered) will have a width (w_c) at or about $0.5*L$.

[0074] In addition, the minority (preferred) block (e.g., PVP) will segregate to and wet the preferential wetting sidewalls **20** and ends **22** of the trenches **16**, **16a** to form a thin interface or wetting (brush) layer **36a**, and will segregate to and wet the overlying preferential wetting material layer **30** to form an overlying thin wetting layer **36a$_s$**. The thickness of the wetting layers **36a**, **36a$_s$** (both blocks considered) is generally about $0.5*L$, which includes $\leq 0.25*L$ of the minority block and about $0.25*L$ of the majority block. For example, a $\leq 0.25*L$ thick layer of the PVP block will wet oxide interfaces with attached PS domains (about $0.25*L$ thick) directed outward from the oxide material.

[0075] In embodiments of the invention, the self-assembled polymer material **32** has a post-anneal thickness (t_2) at or below the L value, or $t_2 = b + (0.5*L)$ (where b is the thickness of the overlying wetting layer **36a$_s$**, both blocks considered), or $t_2 = [(\leq 0.5*L) + (0.5*L)]$, or $t_2 \leq L$.

[0076] In embodiments in which the block copolymer material **26** includes an inorganic species such as a metal (e.g., Si, Fe, etc.), the inorganic species will segregate to one polymer phase upon annealing. For example, with a PS-b-PVP copolymer combined with an silicon-

and/or iron-containing additive where the pyridine group selectively solvates the Si and Fe species, during the anneal, the Si and Fe species will segregate to the PVP half-cylinders **36** (and wetting layers **36a**). Suitable inorganic precursors are thermally stable and will not volatilize at the anneal temperature.

[0077] In the illustrated embodiment, the width (w_t) of trenches **16** are about 1.5-2**L* (or 1.5-2 X the pitch value) of the block copolymer **26**, resulting in the formation of a single half-cylinder down the center of the trench **16** from a block copolymer having a pitch value of about *L*. As depicted in **FIGS. 7A** and **7C**, within a wider trench **16a** having a width (w_{t2}) of about (n +1)**L* (or (n +1) X the pitch value), the block copolymer material will self assemble to form multiple (n) lines of half-cylinders **36** (shown as two lines) with a center-to-center pitch distance (p) of adjacent lines at or about the pitch distance or *L* value of the block copolymer material. The number (n) of half-cylinder lines **36** within a trench can be varied, for example, according to the width of the trench and/or the pitch distance (p) or *L* value of the block copolymer material.

[0078] After the block copolymer material is annealed and ordered, the preferential wetting material **30** can be removed from contact with the assembled block copolymer material **32**, as shown in **FIG. 8**.

[0079] For example, in the use of a solid, elastomeric material **30** such as PDMS, the material can be lifted or peeled from the surface of the block copolymer material **32**. To facilitate removal, a solvent that is compatible with and does not dissolve or etch the assembled polymer domains such as water, alcohol, etc. can be applied (e.g., by spraying, soaking the material) to permeate and swell the material and enhance removal without altering or damaging the assembled polymer structure. A dilute fluoride solution (e.g., NH_4F, HF, NaF, etc.) can also be applied to mediate the removal and decomposition of a PDMS material.

[0080] In embodiments of the invention in which the preferential wetting material **30** is composed of an inorganic material such as a spin-on dielectric (SOD), the material **30** can be removed by a controlled etch back process, for example, by applying a fluoride-based etchant

whereby the dielectric material is etched at a low etch rate (e.g., less than about 200 Å/minute) without altering or damaging the assembled polymer structure.

[0081] In embodiments in which an elastomeric material **30** is used with a block copolymer material that includes an inorganic species (e.g., Si, Fe, etc.), a process that dissolves or etches the polymer components but not the inorganic species can be used to selectively remove the organic components of the block copolymer domains, leaving the inorganic species on the substrate to form a mask material. For example, an oxygen plasma etch will remove the carbonaceous major domains, leaving inorganic material (e.g., Si, Fe, etc.) as lines on the substrate surface.

[0082] Generally, a block copolymer thin film **26a** outside the trenches (e.g., on spacers **18**) will not be not thick enough to result in self-assembly. Optionally, the unstructured thin film **26a** can be removed, for example, by an etch technique or a planarization process to provide an about uniformly flat surface .

[0083] Optionally, the copolymer material can be treated to crosslink one of the polymer domains (e.g., the PVP half-cylinders) to fix and enhance the strength of the polymer blocks. For example, one of the polymer blocks can be structured to inherently crosslink (e.g., upon exposure to ultraviolet (UV) radiation, including deep ultraviolet (DUV) radiation), or the polymer block can be formulated to contain a crosslinking agent. For example, the trench regions can be selectively exposed through a reticle (not shown) to crosslink only the self-assembled polymer material **32** within the trenches **16**, **16a** and a wash can then be applied with an appropriate solvent (e.g., toluene) to remove the non-crosslinked portions of the block copolymer material **26a**, leaving the registered self-assembled polymer material **32** within the trench and exposing the surface of the material layer **14** above/outside the trenches. In another embodiment, the annealed polymer material **32** can be crosslinked globally, a photoresist material can be applied to pattern and expose the areas of the polymer material **26a** outside the trench regions, and the exposed portions of the polymer material **26a** can be removed, for example by an oxygen (O_2) plasma treatment.

[0084] An embodiment of the application of the self-assembled polymer material **30** is as an etch mask to form openings in the substrate **10**. After annealing and self assembly of the

polymer blocks into the half-cylinders **36** and matrix **38**, and removal of the preferential wetting material **30**, the assembled polymer material **32** can be processed to form a structure that can be used as an etch mask to form openings in the substrate **10**.

[0085] In some embodiments of the invention, the surface wetting layer **36a$_s$** (**FIGS. 7A, 7C**) composed of the minority block (e.g., PVP) can be selectively removed to expose the matrix **38** of the self-assembled polymer material **32**. For example, a surface wetting layer **36a$_s$** of PVP can be removed by an RIE process using an oxygen, fluorocarbon, or argon plasma, for example.

[0086] In embodiments of the invention in which one of the polymer domains includes an inorganic species (e.g., Si, Fe, etc.), an oxidation process such as a UV-ozonation or oxygen plasma etching, can be performed to remove the organic material (i.e., the polymer domains) and convert the inorganic species to a non-volatile inorganic oxide, e.g., silicon oxide (SiO_x), iron oxide (Fe_xO_y), etc., which remains on the substrate and can be used as a mask in a subsequent etch process.

[0087] For example, as depicted in **FIGS. 9-9B**, in the illustrated embodiment in which the block copolymer material (**26**) is composed of PS-b-PVP combined (e.g., doped) with an Si- and/or Fe-containing additive, and the Si and/or Fe species are segregated to the PVP half-cylinders **36** and wetting layers **36a**. An oxidation process (arrows ↓↓) can be performed to remove both the PS matrix **38** and PVP polymer component of the half-cylinders **36** (and neutral wetting layer **12**) and convert the Si and/or Fe species within the half-cylinders to inorganic oxide, e.g., SiO_x and/or Fe_xO_y, resulting in non-volatile, inorganic oxide lines **40** on the substrate **10**.

[0088] In other embodiments, the matrix domain **38** of the self-assembled polymer material **32** can be selectively removed relative to the half-cylinder lines **36**, which can be used as a mask to etch the exposed substrate **10** at the trench floor. For example, in using a PS-b-PMMA block copolymer, PMMA domains can be selectively removed by UV exposure/acetic acid development or by selective reactive ion etching (RIE), and the remaining PS domains can then be used as a mask to etch the substrate.

[0089] The oxide lines **40** can then be used as a mask to etch line openings **42** (e.g., trenches) in the substrate **10**, as depicted in **FIGS. 10-10B**, for example, using an anisotropic, selective reactive ion etch (RIE) process.

[0090] Further processing can then be performed as desired. For example, as depicted in **FIGS. 11-11B**, the residual oxide lines **40** can be removed, for example, using a fluoride-based etchant, and the substrate openings **42** can be filled with a material **44** such as a metal or metal alloy such as Cu, Al, W, Si, and Ti_3N_4, among others, to form arrays of conductive lines, or with an insulating material such as SiO_2, Al_2O_3, HfO_2, ZrO_2, $SrTiO_3$, and the like.

[0091] Referring now to **FIG. 12**, in another embodiment of the invention, an atmosphere **46'** can be applied to form an air interface at the surface **28'** of the block copolymer material **26'** in the trenches that is preferentially wetting to one of the blocks of the copolymer material **26'**.

[0092] In some embodiments, a preferentially wetting atmosphere can be composed of clean, dry air to preferentially wet the polymer block having the lower surface tension. For example, in the use of PS-b-PVP and PS-b-PEO, the PS block has a relatively lower surface tension and will preferentially wet a clean dry air atmosphere. In the use of PS-b-PDMS, the PDMS block has a lower surface tension and will preferentially wet a clean dry air atmosphere. In other embodiments, a humid atmosphere (air) can be applied to preferentially wet PEO over PS (e.g., using PS-b-PEO), or a near-saturated solvent atmosphere (e.g., ethanol, dimethylformamide (DMF), and the like) can be applied as a vapor phase to preferentially wet PVP over PS (e.g., using PS-b-PVP).

[0093] An anneal of the block copolymer material **26'** in the presence of the preferentially wetting atmosphere **46'** can then be conducted such that the polymer blocks phase separate in response to the preferential and neutral wetting of the trench surfaces and the preferential wetting of the overlying atmosphere **46'** at the air-interface to form a self-assembled polymer material **32'** as illustrated in **FIGS. 13-13B**. In response to the constraints provided by the width (w_t) of the trenches **16'**, **16a'**, a floor **24'** that is neutral wetting to both polymer blocks, and sidewalls **20'** and an air interface that are preferential wetting to the minority block, a

cylinder-phase block copolymer composition (e.g., 70:30 PS-b-PVP (inherent pitch $\simeq L$) will self-assemble such that the minority (preferred) block (e.g., PVP) will form parallel-oriented, downward-facing, half-cylinder domains **36'** on the neutral wetting material **12'** on the trench floors surrounded by an overlying matrix **38'** of the majority polymer block (e.g., PS). In addition, the minority (preferred) block (e.g., PVP) will segregate to and wet the sidewalls **20'** and ends **22'** of the trenches **16'**, **16a'** and the air interface (e.g., using a near-saturated solvent atmosphere), which are preferential wetting to the minority block, to form an thin interface or wetting layer **36a'** (on the sidewalls) and **36a$_s$'** (at the air interface) (e.g., at a thickness of about $0.25*L$). As another example, in the use of a cylindrical-phase PS-b-PDMS, PDMS half-cylinders **26'** would assemble on the neutral wetting material **12'** within an overlying PS matrix **38'**, and PDMS would form a brush layer **26a'** on the trench sidewalls **20'** and ends **22'** and a brush layer **26a$_s$'** at the interface with a clean, dry air atmosphere that would preferentially wet PDMS.

[0094] Following the anneal, the polymer material can be optionally crosslinked as previously described. In some embodiments, the surface wetting layer **36a'$_s$** at the air interface (e.g., the minority block, PVP) can be selectively removed to expose the underlying matrix **38'**, e.g., by an RIE process. The self-assembled polymer material can then be processed as desired, for example, to form a masking material to etch the underlying substrate **10'**.

[0095] Embodiments of the invention provide methods of forming structures of parallel lines that assemble via graphoepitaxy rapidly and defect-free over large areas in wide trenches. The structures formed from cylinder-forming block copolymers can be produced considerable faster than for lamellar-forming block copolymers, and have improved pattern transfer to an underlying substrate when used as an etch mask compared to arrays of minority block cylinders fully suspended in majority block matrix due to undercutting of the matrix underneath the cylinders during etching. The methods also provide ordered and registered elements on a nanometer scale that can be prepared more inexpensively than by electron beam lithography, EUV photolithography or conventional photolithography. The feature sizes produced and accessible by this invention cannot be easily prepared by conventional photolithography. The described methods and systems can be readily employed and

incorporated into existing semiconductor manufacturing process flows and provide a low cost, high-throughput technique for fabricating small structures.

[0096] Although specific embodiments have been illustrated and described herein, it will be appreciated by those of ordinary skill in the art that any arrangement which is calculated to achieve the same purpose may be substituted for the specific embodiments shown. This application is intended to cover any adaptations or variations that operate according to the principles of the invention as described. Therefore, it is intended that this invention be limited only by the claims and the equivalents thereof. The disclosures of patents, references and publications cited in the application are incorporated by reference herein.

WHAT IS CLAIMED IS:

1. A method of forming a nanostructured polymer material on a substrate, comprising:

forming a self-assembling block copolymer material within a trench in a material layer on the substrate, the trench having a length, a neutral wetting floor, and opposing sidewalls and ends that are preferentially wetting to a minority block of the block copolymer;

applying a material preferentially wetting to the minority block over and in contact with the block copolymer material within the trench; and

annealing the block copolymer material such that the block copolymer material self-assembles into half-cylindrical domains of the minority block of the block copolymer within a matrix of a majority block of the block copolymer, the half-cylindrical polymer domains oriented parallel to the trench floor and extending the length of the trench, the half-cylindrical domains having a face oriented toward and wetting the neutral wetting trench floor.

2. The method of Claim 1, wherein the minority block of the block copolymer comprises a metal.

3. The method of Claim 2, wherein the metal is selected from the group consisting of silicon, chromium, titanium, aluminum, molybdenum, gold , platinum, ruthenium, zirconium, tungsten, vanadium, lead, and zinc.

4. The method of Claim 2, wherein the minority block of the block copolymer is selected from the group consisting of poly(vinylpyridine), poly(methylmethacrylate), poly(lactide), poly(tert-butyl acrylate) poly(ethylene-co-butylene), poly(ethylene oxide), poly(butadiene), and polystyrene.

5. The method of Claim 2, wherein the minority block of the block copolymer is selected from the group consisting of polydimethylsiloxane, poly(vinylmethylsiloxane), and poly(ferrocenylmethylethylsilane).

6. The method of Claim 1, wherein the majority block of the block copolymer is selected from the group consisting of poly(styrene), poly(isoprene), poly(butadiene), and poly(ethylene-alt-propylene), and poly(methylmethacrylate).

7. The method of Claim 1, wherein applying the preferentially wetting material comprises contacting the block copolymer material within the trench with an elastomeric material.

8. The method of Claim 7, wherein the preferentially wetting material comprises poly(dimethylsiloxane) or poly(urethane).

9. The method of Claim 8, wherein the preferentially wetting material comprises poly(dimethylsiloxane) having a hydrophilic surface.

10. The method of Claim 9, wherein the preferentially wetting material comprises poly(dimethylsiloxane) comprising silanol groups on a surface.

11. The method of Claim 1, wherein applying the preferentially wetting material comprises depositing an inorganic material to form a layer over the block copolymer material within the trench.

12. The method of Claim 11, wherein the preferentially wetting material comprises a spin-on dielectric material.

13. The method of Claim 1, further comprising removing the preferentially wetting material to expose the annealed block copolymer material within the trench.

14. The method of Claim 13, wherein removing the preferentially wetting material comprises separating the preferentially wetting material from the annealed block copolymer material.

15. The method of Claim 14, further comprising, applying a solvent to the preferentially wetting material to enhance removal.

16. The method of Claim 13, wherein the preferentially wetting material comprises an oxide material and removing the preferential wetting material layer comprises applying a fluoride-based etchant.

17. The method of Claim 1, further comprising selectively removing the majority polymer block to expose the half-cylindrical domains and the substrate adjacent to said half-cylindrical domains.

18. The method of Claim 1, further comprising selectively removing polymeric material to expose the substrate and forming a metal component of the minority block into an inorganic metal material such that said inorganic metal material forms a line on the substrate.

19. A method of forming a nanostructured polymer material on a substrate, comprising:

forming a block copolymer material within a trench in a material layer overlying the substrate, the trench having a width, a length, a depth, a neutral wetting floor, and opposing sidewalls and ends that are preferentially wetting to a minority block of the block copolymer;

applying a material preferentially wetting to the minority block over and in contact with the block copolymer material within the trench; and

causing a microphase separation in the block copolymer material to form a half-cylinder domain comprising the minority block of the block copolymer in a matrix of a majority block of the block copolymer, the half-cylinder domain polymer domain oriented parallel to the trench floor and registered to the sidewalls in a line extending the length of the trench, the half-cylinder polymer domain having a face situated on the neutral wetting trench floor.

20. The method of Claim 19, wherein the trench has a width of about 1.5-2 times the L value of the block copolymer, and a single half-cylinder domain is formed within the trench having a width of about $0.5*L$.

21. The method of Claim 19, wherein the trench has a width greater than about 2 times the L value of the block copolymer, and two or more half-cylinder domains are formed within the trench at a center-to-center distance of about the L value of the block copolymer.

22. The method of Claim 21, wherein the trench has a width of about 3 or more times the L value of the block copolymer.

23. The method of Claim 19, wherein the neutral wetting floor comprises a blend of grafted homopolymers.

24. A method of forming a nanostructured polymer material on a substrate, comprising:

forming a self-assembling block copolymer material within a trench in a material layer on the substrate, the trench having a length, a neutral wetting floor, and opposing sidewalls and ends that are preferentially wetting to a minority block of the block copolymer;

applying an atmosphere preferentially wetting to the minority block over and in contact with the block copolymer material within the trench; and

annealing the block copolymer material such that the block copolymer material self-assembles into half-cylindrical domains of the minority block of the block copolymer within a matrix of a majority block of the block copolymer, the half-cylindrical polymer domains oriented parallel to the trench floor and extending the length of the trench, the half-cylindrical domains having a face oriented toward and wetting the neutral wetting trench floor, and the minority block forming a layer over the block copolymer material.

25. The method of Claim 24, wherein the preferentially wetting atmosphere is selected from the group consisting of clean dry air, humid air, and a near-saturated solvent atmosphere.

26. A method of etching a substrate, comprising:

forming a self-assembling block copolymer material within a trench in a material layer on the substrate, the trench having a length, a neutral wetting floor, and opposing sidewalls and ends that are preferentially wetting to a minority block of the block copolymer;

applying a material preferentially wetting to the minority block over and in contact with the block copolymer material within the trench;

annealing the block copolymer material such that the block copolymer material self-assembles into half-cylindrical domains of the minority block of the block copolymer within a matrix of a majority block of the block copolymer, the half-cylindrical polymer domains oriented parallel to the trench floor and extending the length of the trench, the half-cylindrical domains having a face oriented toward and wetting the neutral wetting trench floor;

further comprising removing the preferentially wetting material to expose the annealed block copolymer material within the trench;

selectively removing the majority polymer block to expose the substrate wherein at least at portion of the half-cylindrical domains remains as a continuous line on said substrate; and

etching exposed portions of the substrate to form a trench therein.

27. The method of Claim 26, wherein the minority block comprises a metal, and removing the majority block further comprises removing the minority polymer block and forming the metal into an inorganic metal material as a line on the substrate.

28. The method of Claim 26, further comprising filling the trench with a fill material.

29. The method of Claim 28, wherein the fill material comprises a metal or a metal alloy.

30. The method of Claim 28, wherein the fill material comprises an insulator material.

31. A method of etching a substrate, comprising:

forming a self-assembling block copolymer material within a trench in a material layer on the substrate, the trench having a length, a neutral wetting floor, and opposing sidewalls and ends that are preferentially wetting to a minority block of the block copolymer;

applying an atmosphere preferentially wetting to the minority block over and in contact with the block copolymer material within the trench; and

annealing the block copolymer material such that the block copolymer material self-assembles into half-cylindrical domains of the minority block of the block copolymer within a matrix of a majority block of the block copolymer, the half-cylindrical polymer domains oriented parallel to the trench floor and extending the length of the trench, the half-cylindrical domains having a face oriented toward and wetting the neutral wetting trench floor, and the minority block forming a layer overlying the block copolymer material.

comprising removing said overlying layer of the minority block to expose the annealed block copolymer material within the trench;

selectively removing the majority polymer block to expose the substrate wherein at least at portion of the half-cylindrical domains remains as a continuous line on said substrate; and

etching exposed portions of the substrate to form a trench therein.

32. A polymeric material situated within a trench in a material layer overlying a substrate, the trench having sidewalls, ends, a floor, a width and a length, the polymeric material comprising a self-assembled block copolymer material comprising half-cylinder polymer domains of a minority polymer block in a matrix of a majority polymer block, the half-cylinder polymer domains oriented parallel to the trench floor and extending the length of the trench, the half-cylindrical domains having a face situated on the trench floor.

33. The polymeric material of Claim 32, wherein the trench floor comprises a neutral wetting material, and the sidewalls and ends comprise a material preferentially wetting to the minority polymer block.

34. The polymer material of Claim 32, further comprising a material preferentially wetting to the minority block overlying the polymeric material.

35. The polymer material of Claim 32, wherein the minority block selectively comprises a metal.