TWO-DIMENSIONAL ARRAYS OF HOLES WITH SUB-LITHOGRAPHIC DIAMETERS FORMED BY BLOCK COPOLYMER SELF-ASSEMBLY

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

[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. Optical lithographic processing methods are not able to accommodate fabrication of structures and features at the nanometer level. The use of self assembling diblock copolymers presents another route to patterning at nanometer dimensions. Diblock copolymer films spontaneously assembly 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. Following self assembly, one block of the copolymer can be selectively removed and the remaining patterned film used as an etch mask for patterning nanosized features into the underlying substrate. Since the domain sizes and periods (L_o) involved in this method are determined by the chain length of a block copolymer (MW), resolution can exceed other techniques such as conventional photolithography, while the cost of the technique is far less than electron beam (E-beam) lithography or EUV photolithography, which have comparable resolution.

[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] Periodic cylindrical structures have been grown in parallel and perpendicular orientations to substrates. A primary requirement for producing perpendicular cylinders by thermal annealing is that the substrate floor must be neutral wetting to the blocks of the copolymer. Periodic hexagonal close-packed cylinders can be useful as etch masks to make structures in an underlying substrate for applications such as magnetic storage devices. However, that layout is not useful for making structures such as DRAM capacitors, which require a rectangular or square shaped array layout.

[0005] Graphoepitaxy techniques using substrate topography have been used in an attempt to influence the orientation, ordering and registration of the microphase-separated domains. Although one-dimensional arrays have been formed in trenches, no efforts have been made to address ordering of the domains over a large area, or to control the location and orientation of ordered domains in two dimensions.

[0006] Although there is a single report of forming ordered sphere-forming block copolymer films by Cheng et al. (*Nano Lett.*, 6 (9), 2099-2103 (2006)), these have been limited to one-dimensional ordered arrays with adjacent arrays not aligned, the cylinders being off-set along the y-axis in neighboring trenches.

[0007] It would be useful to provide methods of fabricating films of two-dimensional arrays of ordered nanostructures that overcome these problems.

[0008] 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.

[0009] **FIGS. 1A-4A** illustrate diagrammatic top plan views of a portion of a substrate during various stages of fabrication of a film composed of a two-dimensional rectangular array of perpendicular oriented cylinders in a polymer matrix according to an embodiment of the present disclosure. **FIGS. 1B/1C-4B/4C** are elevational, cross-sectional views of the

substrate fragment depicted in **FIGS. 1A-4A**, taken along lines **1B/1C-1B/1C** to lines **4B/4C-4B/4C**, respectively.

[0010] **FIGS. 5A-11C** illustrate various stages of the fabrication of a film composed of a two-dimensional square array of perpendicular oriented cylinders in a polymer matrix according to another embodiment of the present disclosure. **FIGS. 5A-5C** illustrate elevational, cross-sectional views of a portion of a substrate during stages of producing a material layer. **FIG. 6** is a cross-sectional view of the substrate depicted in **FIG. 5C** in a subsequent step with a self-assembling block copolymer material within trenches. **FIGS. 7A-11A** are diagrammatic top plan views of a portion of the substrate of **FIG. 6**, during subsequent stages of the fabrication of a film composed of a two-dimensional square array of cylinders in a polymer matrix. **FIGS. 7B-11B** are elevational, cross-sectional views of the substrate depicted in **FIGS. 7A-11A**, taken along lines **7B-7B** to lines **11B-11B**, respectively. **FIG. 11C** is a cross-sectional view of the substrate of **FIG. 10A** in a subsequent processing step showing selective removal of the matrix of the annealed film in another embodiment.

[0011] **FIGS. 12A-18A** illustrate diagrammatic top plan views of a portion of a substrate during various stages of fabrication of a film composed of a two-dimensional rectangular array of perpendicular oriented and parallel oriented cylinders in a polymer matrix according to another embodiment of the present disclosure. **FIGS. 12B, 13B and 15B-18B** are elevational, cross-sectional views taken along lines **B-B** of the substrate depicted in **FIGS. 12A, 13A and 15A-18A**, respectively. **FIG. 14** is an elevational, cross-sectional view of the substrate of **FIG. 13A** in a subsequent processing step.

[0012] 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.

[0013] 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.

[0014] "L_0" is the inherent pitch (bulk period or repeat unit) of structures that self assemble upon annealing from a self-assembling (SA) block copolymer or a blend of a block copolymer with one or more of its constituent homopolymers.

[0015] In embodiments of the invention, processing conditions are used that induce microphase separation of thin films of self assembling cylindrical-phase diblock copolymers to produce 2-D rectangular and square arrays of nanoscale cylinders by constraining one dimension by graphoepitaxy and the second dimension either by graphoepitaxy or by chemically differentiating the trench floor.

[0016] Steps in a method for fabricating two-dimensional (2-D) rectangular arrays of cylinders oriented perpendicular to a substrate from thin films of cylindrical phase self assembling (SA) block copolymers according to an embodiment of the invention are illustrated in **FIGS. 1A-4C**. The described embodiment is a graphoepitaxy-only technique, which utilizes topographical features, the sidewalls and ends of trenches, as constraints to induce orientation and registration of perpendicularly-oriented cylindrical copolymer domains in both one dimension (single row parallel to the trench sidewalls) and a second dimension (cylinders registered between adjacent trenches) to achieve 2-D rectangular arrays of nanoscale microstructures in the form of cylinders within a polymer matrix.

[0017] Referring to **FIGS. 1A-1B**, a substrate **10** with an overlying material layer **12** is provided, being a silicon layer **10** and a silicon oxide (SiO_x) layer **12** in the illustrated example.

[0018] To prepare a 2-D rectangular array of cylinders according to a first embodiment of a method of the invention, the material layer **12** is patterned to form an array of adjacently aligned trenches **$14a_{1-3}$**, **$14b_{1-3}$**, **$14c_{1-3}$**. Each trench is structured with sidewalls **16**, a floor or bottom surface **18**, a width (*w*), and a length (*l*). Substrate **10** is exposed as the floor **18** of the

trench, and portions of the material layer **12** form a spacer interval **12a** between the trenches. The width (*w*) of the trenches is equal to about the inherent pitch value (L_o) of the polymer, typically ranging from about 10-100 nm. The length (*l*) of the trenches is equal to about nL_o ("n*L_o"), typically ranging from about n*10-n*100 nm (with n being the number of features or structures (i.e., cylinders)). The first edges (ends or tips) **20a** and the second edges **20b** of each adjacent trench (e.g., trenches **14a**$_1$ – **14b**$_1$ – **14c**$_1$) are aligned, as shown in **FIG. 1A**. As such, each adjacent trench is substantially the same the length (*l*). In some embodiments, the trench dimension is about 55-80 nm wide (*w*) and 1600-2400 nm in length (*l*). The depth (*D*) of the trenches can range from about 50-500 nm. The spacing or pitch distance (p_l) between adjacent trenches can vary but is at least $2L_o$.

[0019] The trenches can be formed using a lithographic tool having an exposure system capable of patterning at the scale of L_o (10-100 nm). Such exposure systems include, for example, extreme ultraviolet (EUV) lithography, proximity X-rays, and electron beam lithography, as known and used in the art. Conventional photolithography can attain ~58 nm features.

[0020] The trench sidewalls **16** and edges **20a, 20b** influence the structuring of the array of cylinders within the trenches. The boundary conditions of the trench sidewalls **16** impose order in the x-direction (x-axis) and the ends **20** impose order in the y-direction (y-axis) to impose a structure wherein each trench contains n number of features (i.e., cylinders). Factors in forming a single 1-D array of cylinders aligned within the center and for the length of each trench include the width of the trench, the formulation of the block copolymer to achieve the desired pitch (L_o), and the thickness (*t*) of the copolymer film. To achieve a single array (row) of cylinders within each trench, the trench is constructed to have a width (*w*) of about the L_o value of the polymer and a length (*l*) of nL_o. The application and annealing of a block copolymer material having an inherent pitch value of L_o will result in a single array of "n" cylinders in the middle of a polymer matrix for the length (*l*) of the trench, with each cylinder being separated by a value of L_o.

[0021] For example, a block copolymer having a 35-nm pitch (L_o value) deposited into a 75-nm wide trench will, upon annealing, result in a zigzag pattern of 35-nm diameter

cylinders that are offset by a half distance for the length of the trench, rather than a single line of cylinders down the center of the trench. As the L_0 value of the copolymer is increased, for example, by forming a ternary blend by the addition of both constituent homopolymers, there is a shift from two rows to one row of cylinders within the center of the trench.

[0022] The lithographically-defined alignment of the trench edges **20a**, **20b** imposes a second dimension of ordering such that each one-dimensional (1-D) array of cylinders (i.e., in trench $\mathbf{14b_1}$) will line up with the adjacent 1-D arrays of cylinders (i.e., in trenches $\mathbf{14a_1}$ and $\mathbf{14c_1}$). Stresses due to trench length and/or width mismatch with the inherent pitch of the block copolymer can be relieved by elliptical variance from circularity in the x- or y-axis direction, as described, for example, by Cheng et al. (*Nano Lett.*, 6 (9), 2099-2103 (2006)).

[0023] As shown in **FIGS. 1A-1B**, an array or string of three adjacent trenches **14a-c** has been etched into material layer **12** (e.g., oxide). The trenches are structured such that the surfaces of the sidewalls **16** and edges **20a, 20b** are preferential wetting by the minority block of the copolymer and the trench floors **18** are neutral wetting (equal affinity for both blocks of the copolymer) to allow both blocks of the copolymer material to wet the floor of the trench. Entropic forces drive the wetting of a neutral-wetting surface by both blocks, resulting in a perpendicular orientation of the self-assembled morphology.

[0024] A neutral wetting surface can be provided, for example, by applying a neutral wetting polymer to form a neutral wetting film **22** on the surface of the substrate **10** forming the trench floors **18**, as illustrated in **FIGS. 1A-1B**. In the use of a SA diblock copolymer composed of PS-b-PMMA, a random PS:PMMA copolymer brush layer (P(S-r-MMA)), which exhibits non-preferential or neutral wetting toward PS and PMMA can be applied by spin-coating onto the trench floor **18** (i.e., the surface of substrate **10**). The brush can be affixed by grafting (on an oxide substrate) or by cross-linking (any surface) using UV radiation. In an embodiment shown in **FIG. 1C**, a random copolymer solution can be applied to substrate **10'** as a blanket film **22'** before deposition of the material layer **12'**. For example, a random copolymer solution composed of PS and PMMA (58% PS) can be applied to the surface of the substrate **10** as a layer about 5-10 nm thick and end-grafted by heating at about

160°C for about 48 hours. Etching through the material layer **12'** to form the trenches **14'** then exposes the underlying random copolymer film layer **22'** as the floor **18'** of the trench.

[0025] A surface that is neutral wetting to PS-b-PMMA can also be prepared by spin coating a photo- or thermally cross-linkable random copolymer such as benzocyclobutene- or azidomethylstyrene-functionalized random copolymers of styrene and methyl methacrylate (e.g., poly(styrene-r-benzocyclobutene-r-methyl methacrylate (P(S-r-PMMA-r-BCB)) onto the surface of the substrate **10** within the trenches and thermally crosslinking the polymer (e.g., 190°C, 4 hours) to form a cross-linked polymer mat. Capillary forces pull the random copolymer to the bottom of deep trenches. Non-crosslinked polymer material can be subsequently removed. In another embodiment, the cross-linkable polymer can be applied as a blanket film **22'** to the substrate **10'** before deposition of the material layer **12'**, and exposed upon etching of the trenches **14'**, as depicted in **FIG. 1C**. Another neutral wetting surface for PS-b-PMMA can be provided by hydrogen-terminated silicon, which can be prepared by a conventional process, for example, by a fluoride ion etch of silicon (with native oxide present, about 12-15 Å) (e.g., as substrate **10**), for example, by immersion in aqueous solutions of hydrogen fluoride (HF) and buffered HF or ammonium fluoride (NH_4F), HF vapor treatment, etc., by exposure to hot H_2 vapor or by a hydrogen plasma treatment (e.g., atomic hydrogen).

[0026] The surface of the sidewalls **16** and the edges **20a, 20b** of the trenches are preferential wetting by one of the components of the block copolymer to induce formation of the cylinders down the middle of each trench as the blocks self-assemble. For example, silicon oxide (SiO_x) exhibits preferential wetting toward the PMMA block to result in the assembly of a thin interface layer of PMMA on the trench sidewalls as well as PMMA cylinders in the center of a PS matrix within each trench. Other preferential wetting surfaces to PMMA can be provided, for example, by silicon nitride, silicon oxycarbide, and PMMA polymer grafted to a sidewall material such as silicon oxide, and resist materials such as such as methacrylate based resists. Upon annealing, the PMMA block of the PS-b-PMMA copolymer layer will segregate to the sidewalls and edges of the trench to form a wetting layer (**33** in **FIGS. 3A-3C**). The material layer **12** itself can be a preferential wetting material (e.g., SiO_x), although a layer of a preferential wetting material can be applied onto the surfaces of the trenches. For example, a polymethylmethacrylate (PMMA) that is modified with a moiety

containing one or more hydroxyl (-OH) groups (e.g., hydroxyethylmethacrylate) can be applied by spin coating and then heating (e.g., to about 170°C) to allow the terminal OH groups to end-graft to the oxide sidewalls **16** and edges **20a**, **20b** of the trenches. Non-grafted material can be removed from the neutral wetting layer **22** by rinsing with an appropriate solvent (e.g., toluene). See, for example, Mansky et al., *Science* 275: 1458-1460 (1997)).

[0027] Referring now to **FIGS. 2A-2B**, a cylindrical-phase SA block copolymer material **24** having an inherent pitch at or about L_0 (or a ternary blend of block copolymer and homopolymers blended to have a pitch at or about L_0) is then deposited, typically by spin casting (spin-coating), onto the floor **18** of the trenches. The block copolymer material can be deposited onto the patterned surface by spin casting 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.

[0028] The copolymer material layer **24** is deposited into the trenches to a thickness (t) of less than or about equal to the L_0 value of the copolymer material to up to about $3L_0$, such that the copolymer film layer will self assemble upon annealing to form a single row of perpendicular cylindrical domains having a diameter of about L_0 (e.g., 25-35 nm) in the middle of a polymer matrix within each trench. The film thickness can be measured, for example, by ellipsometry.

[0029] Depending on the depth (D) of the trenches, the cast block copolymer material **24** can fill the trenches as in **FIG. 2B** where the trench depth is about equal to L_0 ($D \sim L_0$), or form a thin film **24'** over the trench floor **18'** or optionally over the trench sidewalls **16'** and edges **20a', 20b'** as in **FIG. 2C** where the trench depth is greater than L_0 ($D > L_0$), e.g., a meniscus. The height (h) of the assembled cylinders (**FIGS. 3B-3C**) corresponds approximately to the thickness (t) of the deposited copolymer material **24, 24'** within the trench. Although not shown, a thin film of the copolymer material **24** can be deposited onto the surface of the oxide layer **12**; this material will not self-assemble, as it is not thick enough to form structures.

[0030] Although diblock copolymers are used in the illustrative embodiment, other types of block copolymers (i.e., triblock or triblock or multiblock copolymers) can be used. Examples of diblock copolymers include poly(styrene-block-methyl methacrylate) (PS-b-PMMA),

polyethyleneoxide-polyisoprene, polyethyleneoxide-polybutadiene, polyethyleleoxide-polystyrene, polyetheleneoxide-polymethylmethacrylate, polystyrene-polyvinylpyridine, polystyrene-polyisoprene (PS-b-PI), polystyrene-polybutadiene, polybutadiene-polyvinylpyridine, and polyisoprene-polymethylmethacrylate, among others. Examples of triblock copolymers include poly(styrene-block methyl methacrylate-block-ethylene oxide). An examples of a PS-b-PMMA copolymer material (L_o= 35 nm) is composed of about 70% PS and 30% PMMA with a total molecular weight (M_n) of 67 kg/mol, to form ~20 nm diameter cylindrical PMMA domains in a matrix of PS.

[0031] The block copolymer material can also be formulated as a binary or ternary blend comprising a SA block copolymer and one or more homopolymers of the same type of polymers as the polymer blocks in the block copolymer, to produce blends that swell the size of the polymer domains and increase the L_o value of the polymer. The volume fraction of the homopolymers can range from 0 to about 40%. An example of a ternary diblock copolymer blend is a PS-b-PMMA/PS/PMMA blend, for example, 46K/21K PS-b-PMMA containing 40% 20K polystyrene and 20K poly(methylmethacrylate). The L_o value of the polymer can also be modified by adjusting the molecular weight of the block copolymer.

[0032] Optionally, ellipticity ("bulging") can be induced in the structures by creating a slight mismatch between the trench and the spacer widths and the inherent pitch (L_o) of the block copolymer or ternary blend, as described, for example, by Cheng et al., "Self-assembled One-Dimensional Nanostructure Arrays,", *Nano Lett.*, 6 (9), 2099-2103 (2006), which then reduces the stresses that result from such mismatches.

[0033] Referring now to **FIGS. 3A-3B**, the block copolymer film **24** is then annealed as by thermal annealing above the glass transition temperature of the component blocks of the copolymer material to cause the polymer blocks to separate and self assemble according to the pattern of wettability on the underlying surfaces of the trenches to form the self-assembled block copolymer structure **28**. For example, a PS-b-PMMA copolymer film can be annealed at a temperature of about 180-195°C in a vacuum oven for about 1-24 hours to achieve the self-assembled morphology. The film can also be solvent annealed, for example, by slowly swelling both blocks of the film with a solvent, then slowly evaporating the solvent.

[0034] The annealed copolymer film comprises a rectangular array of perpendicularly oriented cylindrical domains **30** of a first block of the copolymer within a matrix **32** of a second block, the cylindrical domains in one dimension at a pitch distance of about L_o and aligned with cylindrical domains in a second dimension at a pitch distance of about $2*L_o$. The annealed copolymer film can be contained within adjacently spaced apart trenches with the ends (edges) **20a, 20b** of the trenches being aligned, and with the cylindrical domains within each trench in a single array and at a pitch distance of about L_o and aligned with the cylindrical domains in adjacent trenches at a pitch distance of about $2*L_o$.

[0035] The constraints provided by the width (w) of trenches and the character of the copolymer composition combined with a neutral wetting trench floor **18** and preferential wetting sidewalls **18** and edges **20a, 20b**, results, upon annealing, in a one-dimensional (1-D) array (single row) of perpendicularly-oriented, cylindrical domains **30** of PMMA within a matrix **32** of PS within each trench **14a-c**, with n structures according to the length of the trench, and a thin layer **33** of PMMA wetting the sidewalls **18**.

[0036] The additional feature of the alignment of the trench edges **20a, 20b** in combination with a pitch distance (p_t) of adjacent trenches substantially equal to $2L_o$, achieves two-dimensional (2-D) rectangular arrays **28a-28c** of cylindrical domains **30** in which the pattern period or pitch distance (p_c) of the cylinders **30** within a single trench (e.g., $\mathbf{14a_3}$) is substantially equal to L_o and the pitch distance (p_{c2}) between the cylinders **30** of adjacent trenches (e.g., $\mathbf{14a_3}$ and $\mathbf{14b_3}$) is substantially equal to $2*L_o$ ($2L_o$) as depicted in **FIG. 3A**.

[0037] The resulting morphologies of the block copolymer (i.e., perpendicular orientation of cylinders) can be examined, for example, using atomic force microscopy (AFM), transmission electron microscopy (TEM), and scanning electron microscopy (SEM).

[0038] After annealing and the copolymer material is ordered, one of the block components can be selectively removed from the film, leaving either the cylindrical domains **30** (**FIG. 4B**) or the matrix **32** (**FIG. 4C**) resulting in rectangular arrays **28a-28c** of openings or coverings (structures). After selective removal of one of the polymer domains, the resulting thin films can be used, for example, as a lithographic template or mask to pattern the underlying

substrate **10** in a semiconductor processing to define regular patterns in the nanometer size range (i.e., about 10-100 nm).

[0039] For example, referring to **FIGS. 4A-4B**, selective removal of the PMMA phase cylinders **30** will result in 2-D rectangular arrays of openings **34** within a thin film of polystyrene (PS) **32** within the trenches **14a-c** with the oxide layer **12a** remaining a spacer between each trench. Removal of the PMMA phase cylinders **30** can be performed, for example, by application of an oxygen (O_2) plasma, or by a chemical dissolution process such as acetic acid sonication by first irradiating the sample (ultraviolet (UV) radiation, 1 J/cm^2 254 nm light), then ultrasonicating the film in glacial acetic acid, ultrasonicating in deionized water, and rinsing the film in deionized water to remove the degraded PMMA.

[0040] In another embodiment illustrated in **FIG. 4C**, the selective removal of a PMMA phase matrix **32** will provide 2-D rectangular arrays of PS phase cylinders **30** and openings **34'**. Such an embodiment would require a majority PMMA block copolymer and sidewalls composed of a material that is selectively PMMA-wetting (e.g. oxide).

[0041] The resulting porous PS film can be used as an etch mask to pattern (arrows ↓↓) the underlying substrate **10**, for example, by a non-selective RIE etching process, to form a rectangular array of openings **35** in substrate **10** (shown in phantom in **FIGS. 4A-4B**) for the fabrication of devices such as capacitors. Further processing can then be performed as desired.

[0042] A method according to another embodiment of the invention utilizing a graphoepitaxy-only technique is illustrated with reference to **FIGS. 5A-11C**, for forming two-dimensional (2-D) square arrays of perpendicularly-oriented cylinders in a polymer matrix.

[0043] In an embodiment to form a 2-D square array, a construction as described with reference to **FIGS. 1A-1C** can be provided, which includes a substrate **10'** bearing a neutral wetting surface, for example, by application of a neutral wetting material layer **22"**, and an overlying material layer **12"** having trenches **$14a_{1-3}$"-$14c_{1-3}$"** formed therein to expose the neutral wetting material layer **22"** as the trench floors **18"**. In one embodiment, for example,

a neutral wetting material layer **22"** such as an end-grafted neutral wetting random (PS:PMMA) copolymer brush can be formed on the substrate **10"**, and then layer **12"** deposited, as described with reference to **FIG. 1C**. Neutral wetting trench floors **18"** can also be provided as H-terminated silicon, which can be prepared, for example, by a fluoride ion etch of a silicon substrate **10"** (with native oxide present, about 12-15 Å), for example, by immersion in aqueous solutions of hydrogen fluoride (HF) and buffered HF or ammonium fluoride (NH_4F), HF vapor treatment, etc., or by exposure to hot H_2 vapor or by a hydrogen plasma treatment (e.g., atomic hydrogen). As in **FIGS. 1A-1C**, each trench is separated by a spacer interval **12a"** of the material layer **12"** of a width (w_i) of about L_o.

[0044] In this embodiment, the sidewalls **16"** of the material layer **12"** are preferential wetting to the major block of the SA block copolymer, being PS in the illustrated example. Preferential wetting surfaces to PS can be provided, for example, by a metal such as gold or a PS-based photoresist containing a photoacid generator. For example, the material layer **12"** itself can be composed of metal (e.g., gold), or the sidewalls **16"** of the material layer **12"** can be coated with a thin film of metal, for example, by evaporation, sputtering, or a spin-on technique, with removal of the metal from the trench floors **18"** (e.g., by etching). For example, a metal (e.g., gold) layer of about 2-10 nm can be applied by thermal evaporation onto surfaces of the trenches formed within a material layer **12"** of oxide, which surface can be precoated with a seed layer (e.g., chromi um) as an adhesive interface.

[0045] In an embodiment with reference to **FIG. 5A**, a neutral wetting layer **22"** (e.g., a random copolymer, H-terminated silicon, etc.) is formed on the substrate **10"**. Then, as illustrated, a photoresist layer **36"** is applied onto the neutral wetting layer **22"**, baked, patterned and developed to form a series of grooves **37"**. For example, a random copolymer brush of PS (58% vol.) and PMMA can be grafted onto a silicon substrate to provide a neutral wetting layer **22"**, and a PMMA resist **36"** applied (e.g., by spin-coating), baked (about 130°C) to remove residual solvent, patterned (e.g., by electron beam lithography), and developed by immersing in solvent. As shown in **FIG. 5B**, a layer of metal can then be deposited to form the material layer **12"**. The remaining photoresist **36"** and overlying metal can then be removed. Such a liftoff process results in a structure as in **FIG. 5C** (and in top plan view in **FIG. 1A**). For example, a layer of chromium and of gold can be sequentially

deposited by evaporation, and the PMMA photoresist and overlying deposited metal removed to result in gold features with grooves between the features. As shown, a series of metal features (e.g., gold) form the material layer **12"** with sidewalls **16"** and spacer intervals **12a"** between adjacent trenches (e.g., between **$14a_3$"**, **$14b_3$"**, and **$14c_3$"**), and grooves or trenches **$14a_{1-3}$"-$14c_{1-3}$"** with the exposed neutral wetting layer **22"** as the trench floors **18"**. Upon annealing a block copolymer film (e.g., of PS-b-PMMA) within the trenches, the major block (e.g., PS) will wet the surface of the sidewalls of the trenches (as shown in **FIGS. 7A-7B**).

[0046] Referring now to **FIG. 6**, a cylindrical-phase SA block copolymer material **24"** (as described with reference to **FIGS. 2A-2B**) is then deposited into the trenches and annealed. The resulting self-assembled block copolymer structure **28"**, illustrated in **FIGS. 7A-7B**, is composed of 2-D rectangular arrays **28a"-28c"** of cylinders **30"** of the minor block (e.g., PMMA) within a matrix **32"** of the major block (e.g., PS), which also wets the sidewalls **16"** of the trenches.

[0047] Following the annealing and ordering of the copolymer material **24"**, the polymer film **28"** is crosslinked to fix and enhance the strength of the self-assembled polymer blocks. The polymers may be structured to inherently crosslink (e.g., upon UV exposure), or one or both of the polymer blocks of the copolymer material can be formulated to contain a crosslinking agent, which can be the same crosslinking agent if used in forming the neutral wetting film **22"** on the trench floors **18"** (as in the step of **FIGS. 1A-1C**).

[0048] Referring now to **FIGS. 8A-8B**, following the crosslinking of the film **28"**, the spacer interval **12a"** of the material layer **12"** (e.g., gold) situated between adjacent trenches (e.g., between **$14a_3$"**, **$14b_3$"**, and **$14c_3$"**) is then removed, for example, by a selective wet etch with aqua regia, to produce an intermediate structure with new trenches **$15a_{1-3}$"-$15b_{1-3}$"** of width (w_1) at or about L_0. As illustrated, the removal exposes the matrix **32** composed of the major block (e.g., PS) to form the sidewalls **40"** of the trenches **15"**, and exposes the neutral wetting layer **22"** as the trench floors **42"**.

[0049] In an embodiment in which the material layer **12"** is composed of a material such as silicon oxide (SiO_x), the spacer intervals **12a"** can be removed, for example by a fluoride ion wet etch. In an embodiment in which the material layer **12"** is composed of a negative resist

such as a methacrylate-based photoresist, the spacer intervals **12a"** between trenches **14a-c"** can be selectively developed and then removed by wet processing by applying an appropriate solvent to form new trenches **15a"-15b"**.

[0050] As shown, the spacer material **12a"** has been removed to define the trench ends or edges **38a"**, **38b"**, and to expose the matrix **32"** (e.g., of PS) of the first self-assembled block copolymer film **28"** to define the sidewalls **40"** of trenches **15a"-15b"**, which are preferential wetting. The removal of the spacer material **12a"** is conducted so as not to damage or disrupt the integrity of the first self-assembled block copolymer structure **28"**. A residual amount of the spacer material **12a"** (e.g. of gold) may remain (not shown) on the surface of the matrix **32"** (i.e., sidewalls **40"**). The trench edges **38a"**, **38b"** are aligned with the edges **20a"**, **20b"** of trenches **14a"-14c"**. As such, the length (*l*) of the trenches **14"**, **15"** is nL_o.

[0051] Next, as illustrated in **FIGS. 9A-9B**, a second SA block copolymer material is deposited (e.g., by spin casting) as a film **46"** into the newly formed trenches **$15a_{1\text{-}2}$"-$15b_{1\text{-}2}$"**. The second block copolymer material **46"** has a period of L_o and is neutral wetting to the trench floors **42"**, and the major block (e.g., PS) of the second copolymer material is preferential wetting to the sidewalls **40"** and trench edges **38"**, **38b"**. The second copolymer material **46"** can be the same or a different composition than the first copolymer material **24"**. The thickness (*t*) of the cast film **46"** is less than or about equal to the L_o value of the second block copolymer material.

[0052] The first self-assembled major block (matrix **32"**, optionally with a residual amount of spacer **12a"** (e.g., gold) thereon) which forms the sidewalls **40"** of trenches **15a"-15b"**, provides a template or boundary condition in the x-axis (↔) for the registration of the self-assembling second copolymer film **46"**. In addition, the edges **38a**, **38b** provide boundary conditions in the y-axis (↕). The trench floors **42"** are neutral wetting, and the matrix **32"** of the first assembled film is preferential wetting to the major block of the second copolymer, allowing graphoepitaxy and the formation of perpendicularly-oriented cylindrical domains within the trenches **15a"-15b"**. Optionally, ellipticity can be induced in the structures by creating a slight mismatch between the trench width and the inherent pitch (L_o) of the block copolymer or ternary blend, as previously described.

[0053] The second copolymer film **46"** is then annealed to form the self-assembled block copolymer structure **48"** depicted in **FIGS. 10A-10B**. The earlier performed cross-linking step contributes to the structural integrity of the first self-assembled film **28"** during the casting and annealing of the second block copolymer film. The annealed copolymer film comprises a square array of perpendicularly oriented cylindrical domains of a first block of the copolymer within a matrix of a second block, the cylindrical domains in one dimension in a single row at a pitch distance of about L_o and aligned with cylindrical domains in a second dimension at a pitch distance of about L_o.

[0054] Upon annealing, the second block copolymer film self-assembles into 1-D arrays of perpendicularly-oriented (PMMA) cylindrical domains **50"** (e.g., of PMMA) within a polymer matrix **52"** (e.g., of PS), which are registered to the sidewalls **40"** (matrix **32"**) of the trenches **15a$_{1-2}$"-15b$_{1-2}$"**, with the major polymer block (matrix **52"**, e.g., of PS) wetting the sidewalls **40"**. Each cylinder **50"** is spaced apart within each trench **15a"-15b"**) by a pitch distance (p_c") of L_o. The cylinders **50"** are also registered to and aligned with the cylinders **30"** within trenches **14a-c"**.

[0055] The alignment of the trench edges **38a"**, **38b"** with edges **20a"**, **20b"** of the first set of trenches **14a"-14c"** in combination with a trench width (w) and trench pitch (p_t) between adjacent trenches (e.g., **14a$_3$"**, **15a$_3$"**, **14b$_3$"**, etc.) of about L_o produces a self-assembled film **48"** containing two-dimensional (2-D) square arrays **48a"-48c"** of cylinders **30"**, **50"**, with each cylinder within an array being separated by a pitch distance (p_c) of L_o.

[0056] Referring now to **FIGS. 11A-11C**, selective removal of one of the polymer domains (i.e., matrix or cylinders) can then be performed to produce a template for use in patterning the substrate **10"**. For example, selective removal of the cylindrical domains **30"**, **50"** (e.g., of PMMA) will produce 2-D square arrays of openings **54"** contained within a polymer matrix **32"**, **52"** (e.g., of PS), as in **FIGS. 11A-11B**. Selective removal of the matrix phase **32"**, **52"** of the film will provide 2-D square arrays of cylinders **30"**, **50"** and openings **54"**, as shown in **FIG. 11C**. The resulting film can be then used in patterning (arrows ↓↓) substrate **10"** to form openings **35"** in substrate **10"** (shown in phantom). Processing can then be continued as desired.

[0057] Another method according to an embodiment of the invention, illustrated with reference to **FIGS. 12-18**, utilizes both graphoepitaxy (topographic features) and chemical pattern transfer techniques to form a film composed of 2-D rectangular arrays of parallel- and perpendicular-oriented cylinders in a polymer matrix. Graphoepitaxy is used to form arrays in one dimension, and a chemical pattern transfer technique is used to control formation of the arrays in a second dimension.

[0058] In the present embodiment, chemical pattern transfer is applied to differentiate and create patterns of wetting preferences in discrete areas on the floors of adjacently positioned trenches as a series of stripes oriented perpendicular to the trench sidewalls. The differing wetting patterns impose ordering on block copolymer films that are then cast on top of the substrate and annealed.

[0059] As shown in **FIGS. 12A-12B**, in a first step of preparing a patterned or chemically activated surface on the trench floor (**18'''**), a neutral wetting random copolymer brush **22'''** (e.g., a random PS-r-PMMA polymer) is coated onto a substrate **10'''**, which can be an inherently preferential wetting material such as silicon (with native oxide), oxide (e.g., silicon oxide, SiO_x), or inorganic film. The brush layer **22'''** is coated with a layer of photoresist **56'''**, which is patterned as shown, by optical lithography or other suitable method. The polymer brush layer **22'''** is then etched using the patterned resist layer **56'''** as a mask to expose the underlying preferential wetting substrate **10'''**, and the resist layer **56'''** is removed.

[0060] In another embodiment, layer **22'''** is composed of a photo-crosslinkable neutral wetting polymer as described, for example, in USP 6,890,703 and USP 6,992,115 (Hawker et al.), which can be photoexposed and selectively crosslinked in the desired regions **60'''** by exposure to light through a reticle. In another embodiment, selective crosslinking of the neutral wetting layer **22'''** in defined sections **60'''** can be performed with the use of a patterned photoresist mask. The non-crosslinked regions can then be removed by wet processing using an appropriate solvent.

[0061] The resulting structure, depicted in **FIGS. 13A-13B**, is patterned with discrete sections **58'''** of the exposed preferential wetting substrate **10'''** (e.g., silicon with native

oxide) adjacent to discrete sections **60'''** of the neutral wetting polymer layer **22'''**. In some embodiments, the floor pattern is a series of stripes, the neutral wetting stripes or sections **60'''** with a width (w_r) at or about nL_o and the preferential wetting stripes or sections **58'''** with a width at or about Lo. In another embodiment, each of the sections **58'''**, **60'''** has a width (w_r) at or about L_o.

[0062] A material layer **12'''** (e.g., of SiO_x) is then deposited over the substrate as illustrated in **FIG. 14**, and patterned with a series of trenches to expose the patterned substrate **10'''** as the floor of the trenches, as shown in **FIGS. 15A-15B**. In another embodiment, the material layer **12'''** can be deposited on the substrate **10'''**, the trenches etched into the material layer to expose the substrate, and the neutral polymer layer **22'''** deposited onto the floors of the trenches, masked and then etched to expose sections **58'''** of the substrate **10'''** within the trenches.

[0063] As illustrated in **FIG. 15A**, the structure has been patterned with three sets of adjacent trenches **$14a_{1\text{-}3}$'''-$14c_{1\text{-}3}$'''** of width (w) at or about L_o and a length (l) of about nL_o. The widths (w_s) of the spacer interval **12a'''** of the material layer **12'''** between adjacent trenches (e.g., between **$14a_3$'''**, **$14b_3$'''**, **$14c_3$'''**, etc.) is constant and at least L_o, being L_o in the present example. Thus, the pitch distance (p_t) of adjacent trenches is about $2*L_o$.

[0064] The trench sidewalls **16'''** and edges **20a'''**, **20b'''** (e.g., of SiO_x) are preferential wetting to one block (e.g., PMMA) of the copolymer. The trench floors **18'''** are defined by the alternating preferential wetting sections **58'''** (substrate **10'''**) and neutral wetting sections **60'''** (e.g., random copolymer brush **22'''**).

[0065] Referring now to **FIGS. 16A-16B**, with the trench floors chemically patterned, a block copolymer **24'''** with cylindrical morphology of pitch L_o or a ternary blend of a block copolymer and homopolymers formulated to have pitch L_o can then be cast into the trenches to a film thickness (t) of about L_o and annealed. As depicted in **FIGS. 17A-17B**, the block copolymer film will then self assemble in each trench into a 1-D array of a perpendicular-oriented cylindrical domain **62'''** (or a string of such perpendicular domains) extending the length (l_1) of each neutral wetting polymer section **60'''** situated between a

parallel-oriented cylindrical domain **64'''** (half-cylinder) (or string of such parallel domains) extending the length (l_2) of each preferential wetting section **58'''**.

[0066] The annealed copolymer film comprises a rectangular array of cylindrical domains of a first block of the copolymer within a matrix of a second block, the cylindrical domains in one dimension comprising a series of *n* perpendicular oriented cylinders **62'''** between two parallel-oriented cylinders **64'''** in a single row at a pitch distance of about L_o, with the cylindrical domains aligned with cylindrical domains in a second dimension at a pitch distance of about $2*L_o$. The annealed copolymer film can be contained within adjacently spaced apart trenches of length $m*(n+1)*L_o$ with the ends (edges) **20a'''**, **20b'''** of the trenches being aligned, and with the cylindrical domains within each trench in a single array and at a pitch distance of about L_o and aligned with the cylindrical domains in adjacent trenches at a pitch distance of about $2*L_o$, such that the single array within each trench comprises a perpendicular oriented cylinder **62'''** or *n* cylinders between two parallel-oriented cylinders **64'''**.

[0067] The edge **66'''** between the sections **58'''**, **60'''** provides a boundary condition for the sharp transition between parallel- and perpendicular-oriented cylinders and imposes order in one-dimension (1-D) within each trench. The resulting structure is an ordered 1-D array of alternating perpendicular- and parallel-oriented cylinders for the length (nL_o) of each trench. Alternatively, the structure is a repeating series of *n* perpendicular cylinders separated by a region of parallel cylinder morphology, e.g., the trench length is $m*(n+1)*L_o$, where *m* is the number of preferential-wetting chemically patterned stripes and *n* is the number of features or structures (e.g., where *m* and *n* are independently 1-50).

[0068] The inversion from perpendicular to parallel cylinders that occurs at the boundary edges **66'''** imposes a second dimensional constraint whereby the structures in adjacent trenches (rows) are also aligned in a second dimension. The resulting structure is a 2-D rectangular array of sublithographic cylindrical structures in alternating perpendicular and parallel orientations.

[0069] Referring now to **FIGS. 18A-18B**, selective removal of one of the polymer domains (i.e., matrix or cylinders) can then be performed to produce a template for use in patterning

the substrate **10'''**. For example, selective removal of the cylindrical domains **62'''**, **64'''** (e.g., of PMMA) will produce 2-D rectangular arrays of openings **68'''**, **70'''** contained within a polymer matrix **72'''** (e.g., of PS). The resulting film can be then used in patterning substrate **10'''**. The configuration of the openings will vary according to the orientation of the cylindrical domains within the trenches. Only openings **68'''** will extend to the trench floor **18'''**, thus the structure forms an etch mask which can selectively transfer the structural pattern of the perpendicular cylinders **62'''** to the underlying substrate (shown as phantom openings **74'''**).

[0070] Embodiments of the invention provide ordering of domains over a large area, and control the location and orientation of ordered cylindrical domains in two dimensions. Such features can be prepared more inexpensively than by electron beam lithography or EUV photolithography. The feature sizes produced and accessible by this invention cannot be prepared by conventional photolithography.

EXAMPLE I

[0071] Trenches 250 nm deep with widths ranging from 75nm to 600 nm having silicon oxide sidewalls and silicon oxycarbide floors were provided. On several of the wafers, oxide was deposited onto the sidewalls and the trench floors. Both types of trench floors were treated to be neutral wetting to PS and PMMA.

[0072] To get perpendicular cylinders, a random PS:PMMA copolymer solution (about 58% PS) containing a crosslinking agent was cast as a film of about 5-10 nm thick onto the features, and annealed at about 160°C for 4 hours. Capillary forces pulled the PS-r-PMMA to the trench floor prior to complete cross-linking, leaving oxide sidewalls that were preferential-wetting to PMMA. The resulting trench structure had sidewalls that were preferential wetting with the random copolymer layer as a mat on the bottom of the trenches, which provided a neutral wetting surface.

[0073] A 0.425% solution of cylinder-forming PS-b-PMMA in toluene was then cast onto the treated substrates so as to form a film about 30-40 nm thick. The PS-b-PMMA material (46K/21K PS:PMMA; 67K MW) was formulated to form PMMA-phase cylinders (diameter ~

20 nm) at repeat periods (pitch) of about 35 nm in the middle of a PS matrix. However, the arrays in adjoining trenches were not aligned.

[0074] In about 75 nm wide trenches, two rows of cylinders were formed that were slightly offset from each other, forming a "zigzag" structure in a regular registered pattern with each side being equidistant from the sidewall of the trench.

EXAMPLE 2

[0075] Ternary blends (10-40%) of homopolymers (20 K PS, 20 K PMMA) were prepared in 0.425% solutions of 46K/21K PS-b-PMMA in toluene. These solutions were cast onto the substrates described above at thicknesses of 30-40 nm. The addition of homopolymers swells the domain sizes of the two fractions, resulting in an increased inherent pitch value (L_o) of the polymer.

[0076] At 10-20% homopolymers, a two row zigzag pattern of cylinders was formed as seen by SEM. With 30% homopolymers content, the zigzag pattern began to break down and numerous errors and unusual morphologies were observed. When a ternary blend of 46/21 PS-b-PMMA block copolymer with 40% 20 PS and 20K PMMA homopolymers was cast and annealed onto the same substrate (i.e., 80 nm wide trenches, (P(S-r-BCB-r-MMA)) floor, oxide sidewalls), single rows of perpendicular cylinders with apparent diameter of about 35 nm formed in the 80 nm wide trenches. At 40% homopolymers, the mixture caused a pitch of about 50 nm, resulting in the formation of a one-dimensional (1-D) array (single row) of cylinders. This is an example of graphoepitaxy technique in which lithographically defined physical features are used to cause ordering of block copolymer films. The cylinder arrays in adjacent trenches were not aligned and were off-set along the y-axis.

[0077] The results show that the boundary condition of the preferential wetting sidewalls and neutral wetting floor within a trench of width equal to the inherent pitch value (L_o) of the self-assembling polymer film enforced the formation of a single row of cylinders. The results also demonstrate that, by increasing L_o so that it is a closer match to the sidewalls, there is a shift from a two row structure to a one row structure.

[0078] 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 for fabricating nanoscale microstructures, comprising:

forming a film comprising a self-assembling block copolymer within a plurality of trenches to a thickness of about L_o, each trench having a width of about L_o, a length of about nL_o, a pitch distance between adjacent trenches of at least about $2*L_o$, preferential wetting sidewalls and ends, and a neutral wetting floor, with ends of the trenches aligned; and

causing the copolymer film to form a single array of perpendicularly oriented cylindrical domains of a first polymer block of the block copolymer in a matrix of a second polymer block of the block copolymer within each trench, wherein the pitch distance between each cylindrical domain within a trench is about L_o, and the pitch distance between the cylindrical domains of adjacent trenches is about $2*L_o$.

2. The method of Claim 1, wherein the block copolymer comprises a blend of the block copolymer with a homopolymer of the first polymer block, the second polymer block, or both.

3. The method of Claim 1, wherein the block copolymer comprises polystyrene and polymethyl methacrylate.

4. The method of Claim 1, wherein the block copolymer comprises an about 60:40 to about 80:20 ratio of the first polymer block to the second polymer block.

5. The method of Claim 1, wherein the sidewalls and ends comprise an oxide.

6. The method of Claim 1, further comprising applying a neutral wetting material to the floors of the trenches.

7. The method of Claim 6, further comprising applying a preferential wetting material to the sidewalls and ends of the trenches.

8. The method of Claim 1, wherein the trench floor comprises a layer of a random copolymer.

9. The method of Claim 8, further comprising applying a layer of a neutral wetting random copolymer onto the trench floors.

10. The method of Claim 1, wherein the trench floor comprises hydrogen-terminated silicon.

11. The method of Claim 1, further comprising, after causing the copolymer film to form the single array of perpendicularly oriented cylindrical domains of the first polymer block, selectively removing the first polymer block to provide a rectangular array of cylindrical openings extending through the matrix of the second polymer block of the film.

12. The method of Claim 11, further comprising etching the substrate through the openings in the film.

13. The method of Claim 1, further comprising selectively removing the second polymer block to provide a rectangular array of cylinders masking portions of the substrate.

14. The method of Claim 13, further comprising etching unmasked portions of substrate.

15. A method for fabricating nanoscale microstructures, comprising:

forming a self-assembling block copolymer film comprising an about 60:40 to about 80:20 ratio of a first polymer block to a second polymer block within a plurality of trenches to a thickness of about L_o, each trench having a width of about L_o, a length of about nL_o, a pitch distance between adjacent trenches at least about $2*L_o$, preferential wetting sidewalls and ends, and a neutral wetting floor, with ends of the trenches aligned; and

annealing the block copolymer film to form a single array of perpendicularly oriented cylindrical domains of the second polymer block of the block copolymer in a matrix of the first polymer block of the block copolymer within each trench, wherein each trench contains a single row of *n* cylindrical domains at a pitch distance of about L_o and substantially parallel to

the sideswalls of the trench, with the cylindrical domains of adjacent trenches at a pitch distance of about $2*L_o$.

16. A method of forming nanoscale microstructures, comprising:

forming a self-assembling block copolymer film having a thickness of about L_o within a plurality of trenches within a material layer, wherein each trench has a width of at least about L_o, a length of about nL_o, a pitch distance between adjacent trenches of at least about $2*L_o$, preferential wetting sidewalls and ends, and a neutral wetting floor, with ends of the trenches aligned, the block copolymer comprising about 60:40 to about 80:20 ratio of a first polymer block to a second polymer block, and capable of microphase separating upon annealing into cylindrical domains within a matrix; and

causing a microphase separation in the block copolymer to produce a single array of perpendicularly-oriented cylindrical microstructures composed of the second polymer block in a matrix of the first polymer block within each trench, wherein the pitch distance between adjacent cylindrical microstructures within each trench is about L_o and the pitch distance between cylindrical microstructures of adjacent trenches is about $2*L_o$.

17. A method for fabricating nanoscale microstructures, comprising:

forming a neutral wetting material layer on a substrate;

forming a material layer on the neutral wetting material layer;

forming a plurality of trenches in the material layer, each trench having a width of about L_o, a length of about nL_o, a pitch distance between adjacent trenches of at least about $2*L_o$, preferential wetting sidewalls and ends, and a floor defined by the neutral wetting material layer, with ends of the trenches aligned;

forming a film comprising a self-assembling block copolymer within the trenches to a thickness of about L_o; and

causing the copolymer film to form a single array of perpendicularly oriented cylindrical domains of a first polymer block of the block copolymer in a matrix of a second polymer block of the block copolymer within each trench, wherein the pitch distance between each cylindrical domain within a trench is about L_o, and the pitch distance between the cylindrical domains of adjacent trenches is about $2*L_o$.

18. A method for fabricating nanoscale microstructures, comprising:

forming a first film comprising a self-assembling block copolymer within a first plurality of trenches within a material layer to a thickness of about L_o, each trench having a width of about L_o, a length of about nL_o, a pitch distance between adjacent trenches at least about $2*L_o$, preferential wetting sidewalls and ends, and a neutral wetting floor, with ends of the trenches aligned;

causing the first copolymer film to form a single array of perpendicularly oriented cylindrical domains of a first polymer block of the block copolymer in a matrix of a second polymer block of the block copolymer within each of said first trenches, wherein the pitch distance between each cylindrical domain within a trench is about L_o, and the pitch distance between the cylindrical domains of adjacent first trenches is about $2*L_o$;

crosslinking the annealed first block copolymer film within each of the first trenches;

forming a second plurality of trenches by removing the material layer such that each of said second trenches is situated between the annealed and crosslinked first copolymer films within the first trenches, each of said second trenches having a width of about L_o, a length of about nL_o, a pitch distance between adjacent first and second trenches of at least about L_o, preferential wetting sidewalls and ends, and a neutral wetting floor, with the ends of the second trenches aligned with the ends of the first trenches;

forming a second film comprising a self-assembling block copolymer within the second plurality of trenches to a thickness of about L_o; and

causing the second copolymer film to form a single array of perpendicularly oriented cylindrical domains of a first polymer block of the block copolymer in a matrix of a second polymer block of the block copolymer within each of said second trenches, wherein the pitch distance between each cylindrical domain within a second trench and between the cylindrical domain of adjacent trenches is about L_o.

19. The method of Claim 18, wherein the sidewalls of the second trenches comprise the material layer, the matrix of the annealed first copolymer film, or a combination of both.

20. The method of Claim 18, wherein forming the second plurality of trenches comprises exposing the matrix of the annealed first copolymer film to define the sidewalls of the second trenches.

21. A method of forming nanoscale microstructures, comprising:

depositing a self-assembling block copolymer within a first plurality of trenches within a material layer to form a first copolymer film having a thickness of about L_o, wherein each trench has a width of at least about L_o, a length of about nL_o, a pitch distance between adjacent trenches of at least about $2*L_o$, preferential wetting sidewalls and ends, and a neutral wetting floor, with ends of the first trenches aligned, the block copolymer comprising about 60:40 to about 80:20 ratio of a first polymer block to a second polymer block and capable of microphase separating upon annealing into cylindrical domains within a matrix;

causing a microphase separation in the first block copolymer film to produce a single array of perpendicularly-oriented cylindrical microstructures composed of the second polymer block in a matrix of the first polymer block within each of the first trenches, wherein adjacent cylindrical microstructures within each trench are separated by a pitch distance of about L_o, and cylindrical microstructures of adjacent first trenches are separated by a pitch distance of about $2*L_o$;

crosslinking the first block copolymer film within each of the first trenches;

forming a second plurality of trenches by removing the material layer between the crosslinked first copolymer films within the first trenches, each of said second trenches having a width of about L_o, a length of about nL_o, a pitch distance between adjacent first and second trenches of at least about L_o, preferential wetting sidewalls and ends, and a neutral wetting floor, with the ends of the second trenches aligned with the ends of the first trenches;

depositing the block copolymer within the second plurality of trenches to form a second copolymer film having a thickness of about L_o; and

causing a microphase separation in the block copolymer to produce a single array of perpendicularly-oriented cylindrical microstructures composed of the first polymer block in a matrix of the second polymer block within each of the second trenches, wherein adjacent cylindrical microstructures within each trench and cylindrical microstructures of adjacent first trenches are separated by a pitch distance of about L_o.

22. A method for fabricating nanoscale microstructures, comprising:

forming a neutral wetting material layer on a substrate;

forming a material layer on the neutral wetting material layer, the material layer defining a plurality of trenches, each trench having a width of about L_o, a length of about nL_o, a pitch distance between adjacent trenches of at least about $2*L_o$, preferential wetting sidewalls, and a floor defined by the neutral wetting material layer, with ends of the trenches aligned;

forming a first film comprising a self-assembling block copolymer within the trenches to a thickness of about L_o;

annealing the first copolymer film to form a single array of perpendicularly oriented cylindrical domains of a first polymer block of the block copolymer in a matrix of a second polymer block of the block copolymer within each trench, wherein the pitch distance between each cylindrical domain within a trench is about L_o, and the pitch distance between the cylindrical domains of adjacent trenches is about $2*L_o$;

crosslinking the first block copolymer film within each of the first trenches;

forming a second plurality of trenches by removing the material layer between the crosslinked first copolymer films within the first trenches, each of said second trenches having a width of about L_o, a length of about nL_o, a pitch distance between adjacent first and second trenches of at least about L_o, preferential wetting sidewalls, and a neutral wetting floor, with the ends of the second trenches aligned with the ends of the first trenches;

forming a second copolymer film comprising a self-assembling block copolymer within the second plurality of trenches to a thickness of about L_o; and

causing a microphase separation in the second copolymer film to produce a single array of perpendicularly-oriented cylindrical microstructures composed of a first polymer block in a matrix of a second polymer block within each of the second trenches, wherein adjacent cylindrical microstructures within each trench and cylindrical microstructures of adjacent first trenches are separated by a pitch distance of about L_o.

23. A method for fabricating nanoscale microstructures, comprising:

forming a layer of a neutral wetting material on a preferential wetting substrate;

masking the neutral wetting material layer to provide a series of masked and unmasked sections, each unmasked section having a width at or about L_o, and each masked section having a width at or about nL_o;

removing the unmasked sections of the neutral wetting layer to expose sections of the preferential wetting substrate;

removing the mask to expose sections of the neutral wetting layer;

forming a material layer over the sections of the substrate and the neutral wetting layer;

forming a plurality of trenches in the material layer to expose the sections of the substrate and the neutral wetting layer, each trench having a width of about L_o, a length of about $m*(n+1)*L_o$ where *m* is the number of sections of the preferentially wetting substrate and n is the number of perpendicularly oriented cylinders, and *m* and *n* are independently 1-50, a pitch distance between adjacent trenches of at least about $2*L_o$, and preferential wetting sidewalls and ends, with the ends of the trenches aligned;

forming a self-assembling block copolymer film comprising an about 60:40 to about 80:20 ratio of a first polymer block to a second polymer block within the trenches to a thickness of about L_o; and

causing the block copolymer film to form a single array of cylindrical domains of the second polymer block of the block copolymer in a matrix of the first polymer block of the block copolymer within each trench, wherein each trench contains *m* rows of *n* cylindrical domains at a pitch distance of about L_o with the cylindrical domains of adjacent trenches at a pitch distance of about $2*L_o$, and the cylindrical domains on the sections of the neutral wetting layer in a perpendicular orientation to the substrate, and the cylindrical domains on the sections of the preferential wetting layer in a parallel orientation to the substrate.

24. A method of forming nanoscale microstructures, comprising:

forming a layer of a neutral wetting material on a preferential wetting substrate;

masking the neutral wetting layer to provide a series of masked and unmasked sections, each unmasked section having a width at or about L_o, and each masked section having a width at or about nL_o;

removing the unmasked sections of the neutral wetting layer to expose sections of the preferential wetting substrate;

removing the mask to expose sections of the neutral wetting layer;

forming a material layer over the sections of the substrate and the neutral wetting layer;

forming a plurality of trenches in the material layer to expose the sections of the substrate and the neutral wetting layer, each trench having a width of about L_o, a length of about $m*(n+1)*L_o$ where *m* is the number of sections of the preferentially wetting substrate and *n* is the number of perpendicularly oriented cylinders, and *m* and *n* are independently 1-50, a pitch distance between adjacent trenches of at least about $2*L_o$, and preferential wetting sidewalls and ends, with the ends of the trenches aligned;

forming a self-assembling block copolymer film comprising an about 60:40 to about 80:20 ratio of a first polymer block to a second polymer block within the trenches to a thickness of about L_o, the block copolymer capable of microphase separating upon annealing into cylindrical domains within a matrix; and

causing a microphase separation in the block copolymer to produce a single array of cylinders in a polymer matrix within each of the trenches, wherein the cylinders on the sections of the neutral wetting layer are in a perpendicular orientation to the substrate, the cylinders on the sections of the preferential wetting layer are in a parallel orientation to the substrate, each trench contains *m* rows of *n* cylinders, and the cylinders within each trench are at a pitch distance of about L_o and the cylinders in adjacent trenches are at a pitch distance of about $2*L_o$.

25. A polymeric film on a substrate, the film comprising: an annealed copolymer film within adjacently spaced apart trenches, ends of the trenches being aligned; the film comprising a rectangular array of perpendicularly oriented cylindrical domains of a first block of the copolymer within a matrix of a second block of the copolymer, the cylindrical domains within each trench in a single array at a pitch distance of about L_o and aligned with the cylindrical domains in adjacent trenches at a pitch distance of about $2*L_o$.

26. A polymeric film on a substrate, the film comprising: an annealed copolymer film within adjacently spaced apart trenches, ends of the trenches being aligned, the film comprising a rectangular array of perpendicularly oriented cylindrical domains of a first block of the copolymer within a matrix of a second block of the copolymer, the cylindrical domains in one dimension at a pitch distance of about L_o and aligned with cylindrical domains in a second dimension at a pitch distance of about $2*L_o$.

27. A polymeric film on a substrate, the film comprising: an annealed copolymer film within a trench having opposing ends and sidewalls and an unpatterned neutral wetting floor, the film comprising a square array of perpendicularly oriented cylindrical domains of a first block of the copolymer within a matrix of a second block of the copolymer, the cylindrical domains in a single array at a pitch distance of about L_o and aligned with adjacent cylindrical domains at a pitch distance of about L_o.

28. A polymeric film on a substrate, the film comprising: an annealed copolymer film within a trench having opposing ends and sidewalls and an unpatterned neutral wetting floor, the film comprising a square array of perpendicularly oriented cylindrical domains of a first block of the copolymer within a matrix of a second block of the copolymer, the cylindrical domains in one dimension in a single row at a pitch distance of about L_o and aligned with cylindrical domains in a second dimension at a pitch distance of about L_o.

29. A polymeric film on a substrate, the film comprising: an annealed copolymer film within adjacently spaced apart trenches, ends of the trenches being aligned; the film comprising a rectangular array of cylindrical domains of a first block of the copolymer within a matrix of a second block of the copolymer, the cylindrical domains within each trench in a single array at a pitch distance of about L_o and aligned with the cylindrical domains in adjacent trenches at a pitch distance of about $2*L_o$, wherein the single array within each trench comprises *n* perpendicular oriented cylinders between two parallel-oriented cylinders.

30. A polymeric film on a substrate, the film comprising: an annealed copolymer film comprising a rectangular array of cylindrical domains of a first block of the copolymer within

a matrix of a second block of the copolymer, the cylindrical domains in one dimension comprising *n* perpendicular oriented cylinders between two parallel-oriented cylinders in a single row at a pitch distance of about L_o, said cylindrical domains aligned with cylindrical domains in a second dimension at a pitch distance of about $2*L_o$.

31. The method of Claim 1, comprising annealing the block copolymer film to form the single array of perpendicularly oriented cylindrical domains of the first polymer block in the matrix of the second polymer block.

32. The method of Claim 1, comprising causing a microphase separation in the block copolymer to form the single array of perpendicularly-oriented cylindrical domains of the first polymer block in the matrix of the second polymer block.

33. The method of Claim 1, further comprising, prior to forming the film within the trenches,

forming a neutral wetting material layer on a substrate;

forming a material layer on the neutral wetting material layer; and

forming the plurality of trenches in the material layer.

34. The method of Claim 1, further comprising, after causing the copolymer film to form a single array of perpendicularly oriented cylindrical domains of the first polymer block in the matrix of the second polymer block,

crosslinking the copolymer film within each of the trenches to form a first crosslinked copolymer film;

forming a second plurality of trenches by removing a material layer such that each of said second trenches is situated between the annealed and crosslinked copolymer films, each of said second trenches having a width of about L_o, a length of about nL_o, a pitch distance of at least about L_o between adjacent trenches, preferential wetting sidewalls and ends, and a neutral wetting floor, with the ends of the trenches aligned;

forming a second film comprising a self-assembling block copolymer within the second plurality of trenches to a thickness of about L_o; and

causing the second film to form a single array of perpendicularly oriented cylindrical domains of a first polymer block of the block copolymer in a matrix of a second polymer block of the block copolymer within each of said second trenches, wherein the pitch distance between each cylindrical domain within a second trench and the pitch distance between the cylindrical domains of adjacent trenches is about L_o.

35. The method of Claim 1, further comprising, prior to forming the film,

forming a layer of a neutral wetting material on a preferential wetting substrate;

masking the neutral wetting layer to provide a series of masked and unmasked sections, each unmasked section having a width at or about L_o, and each masked section having a width at or about nL_o;

removing the unmasked sections of the neutral wetting layer to expose sections of the preferential wetting substrate;

removing the mask to expose sections of the neutral wetting layer;

forming a material layer over the sections of the substrate and the neutral wetting layer;

forming the plurality of trenches in the material layer to expose the sections of the substrate and the neutral wetting layer, each trench having a width of about L_o and a length of about $m*(n+1)*L_o$ where m is the number of sections of the preferentially wetting substrate and n is the number of perpendicularly oriented cylinders, and m and n are independently 1-50.

36. The method of Claim 35, wherein the block copolymer film forms a single array of cylindrical domains of the first polymer block of the block copolymer in a matrix of the second polymer block of the block copolymer within each trench, and the cylindrical domains on the sections of the neutral wetting layer are in a perpendicular orientation to the substrate, and the cylindrical domains on the sections of the preferential wetting layer are in a parallel orientation to the substrate.