

METHOD TO PRODUCE NANOMETER-SIZED FEATURES WITH DIRECTED ASSEMBLY OF BLOCK COPOLYMERS

TECHNICAL FIELD

[0001] Embodiments of the invention relate to methods, a stamp and a system for patterning a substrate by use of self-assembling block copolymers, and devices resulting from those methods.

BACKGROUND OF THE INVENTION

[0002] Lithography is a key process in the fabrication of semiconductor integrated circuits. Photolithography typically involves projecting an image through a reticle or mask onto a thin film of photoresist or other material that covers a semiconductor wafer or other substrate, and developing the film to remove exposed or unexposed portions of the resist to produce a pattern in subsequent processing steps. In semiconductor processing, the continual shrink in feature sizes and the increasing development of nanoscale mechanical, electrical, chemical and biological devices requires systems to produce nanoscale features. However, with conventional photolithography using light, the minimum feature size and spacing between patterns is generally on the order of the wavelength of the radiation used to expose the film. This limits the ability to produce sub-lithographic features of about 60 nm using conventional lithography.

[0003] Microcontact printing has been developed to create sublithographic features in semiconductor devices. This technique generally involves stamping or pressing a soft template or stamp bearing small scale topographic features onto a receptor substrate to form a pattern on the substrate. The features on the template are typically prepared by photolithography or electron (e-beam) lithography. For example, FIG. 1 illustrates a conventional soft template or stamp 10 formed, for example, from polydimethylsiloxane, with defined features 12 structured with a stamping surface 14 and sidewalls 16. The stamping surface 14 defines the dimension (d) of the pattern to be stamped onto a substrate. As shown in FIG. 2, the features 12 of the stamp are wetted with an ink 18 that is physisorbed or chemisorbed onto the stamping surface 14 and the sidewalls 16 of the features 12. As

depicted in FIG. 3, the inked stamp is brought into contact with the receptor substrate 20 (e.g., silicon wafer) and the ink 18 is transferred to regions of the substrate 20 where the ink forms self-assembled monolayers (SAMs) 22 (FIG. 4).

[0004] However, resolution of small features is problematic because of inconsistent printing due to capillary forces that pull ink sorbed to surfaces of the features 12 adjacent to the stamping surface 14 (e.g., the sidewalls 18) onto the substrate (e.g., areas 24). Such wicking of the ink material onto the substrate also alters the intended dimension (d) of the stamped features (SAMs) 22, as defined by the stamping surfaces 14 of the stamp/template. In addition, the size and dimension of the stamped features 22 on the receptor substrate are limited to the dimensions (d) of the lithographically-formed features 12 defined on the stamp.

[0005] Other processes such as e-beam lithography and extreme ultraviolet (EUV) lithography have been used in attempts to form sub-lithographic features. However, the high costs associated with such lithographic tools have hindered their use.

[0006] Self-assembled block copolymer films have been prepared by patterning the surface of a substrate with chemical stripes (chemical templating), each stripe being preferentially wetted by the alternate blocks of a block copolymer. A block copolymer film with lamellar morphology, a periodicity matching the stripe pattern and both blocks being neutral wetting at the air interface (e.g., PS-PMMA) that is cast on the patterned substrate and thermally annealed will self-assemble so that the domains orient themselves above the preferred stripes and perpendicular to the surface. However, the process has no advantage over EUV lithography or other sub-lithographic patterning techniques since one of these patterning techniques must be used to form the substrate template pattern, and with the use of expensive patterning tools, the low-cost benefits of using block copolymers are lost.

[0007] It would be useful to provide a method and system for preparing sub-lithographic features that overcome existing problems.

BRIEF DESCRIPTION OF THE DRAWINGS

[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] **FIG. 1** illustrating an elevational, cross-sectional view of a conventional stamp used in a microcontact printing application.

[0010] **FIG. 2** illustrates a diagrammatic view of the stamp of **FIG. 1**, with ink physisorbed or chemisorbed onto the surface of the stamp, and a receptor substrate to be contacted by the inked stamp. **FIG. 3** illustrates the inked stamp of **FIG. 2**, brought into contact with the receptor substrate, according to a conventional microcontact printing process. **FIG. 4** illustrates a subsequent processing step with the formation of SAMs from the transferred ink on the receptor substrate.

[0011] **FIG. 5** illustrates a diagrammatic top plan view of a portion of a substrate of a stamp at a preliminary processing stage according to an embodiment of the present disclosure, showing the substrate with trenches. **FIGS. 5A-5B** are elevational, cross-sectional views of the substrate depicted in **FIG. 5** taken along lines 5A-5A and 5B-5B, respectively.

[0012] **FIG. 6** is top plan view of a portion of a substrate according to another embodiment showing the substrate with trenches for forming a stamp with a hexagonal close-packed array of perpendicular cylinders.

[0013] **FIGS. 7-8** illustrate diagrammatic top plan views of the stamp of **FIG. 5** at various stages of the fabrication of a self-assembled block copolymer film according to an embodiment of the present disclosure. **FIGS. 7A-8A** illustrate elevational, cross-sectional views of embodiments of a portion of the substrate depicted in **FIGS. 7-8** taken, respectively, along lines 7A-7A and lines 8A-8A. **FIG. 7B** is a cross-sectional view of the substrate depicted in **FIG. 7** taken along lines 7B-7B.

[0014] FIG. 9 is a top plan view of the stamp of FIG. 6 at a subsequent stage of fabrication showing a self-assembled polymer film composed of a hexagonal array of cylinders within the trenches.

[0015] FIG. 10 is a top plan view of the stamp of FIG. 5 at a subsequent stage of fabrication according to another embodiment of the invention, showing a self-assembled polymer film composed of a single row of cylinders with the trenches. FIG. 10A is a cross-sectional view of the substrate depicted in FIG. 10 taken along lines 10A-10A.

[0016] FIG. 11 is a top plan view of the stamp of FIG. 5 at a subsequent stage of fabrication according to another embodiment of the invention, showing a self-assembled polymer film composed of a parallel row of half-cylinders with the trenches. FIG. 11A is a cross-sectional view of the substrate depicted in FIG. 10 taken along lines 11A-11A.

[0017] FIG. 12 illustrates a diagrammatic top plan view of a portion of a stamp at a preliminary processing stage according to another embodiment of the disclosure, showing a chemically differentiated stamping surface. FIG. 12A is an elevational, cross-sectional view of the substrate depicted in FIG. 12 taken along lines 12A-12A.

[0018] FIGS. 13-14 illustrate diagrammatic top plan views of the stamp of FIG. 12 at subsequent processing stages. FIGS. 13A-14A illustrate elevational, cross-sectional views of a portion of the substrate depicted in FIGS. 13-14 taken, respectively, along lines 13A-13A and lines 14A-14A, respectively. FIGS. 13B-14B are cross-sectional views of the substrate of FIGS. 13-14 taken, respectively, along lines 13B-13B and lines 14B-14B, respectively. .

[0019] FIGS. 15-18 illustrate subsequent steps in the use of the stamp of FIGS 8-8A in a contact printing process to form a pattern on a substrate according to an embodiment of the invention. FIG. 18A is a cross-sectional view of the substrate shown in FIG. 18, taken along lines 18A-18A.

[0020] FIGS. 19-20 illustrate an embodiment of the use of a chemically differentiated surface of the substrate shown in FIG. 18A for the selective deposit and formation of a self-assembled block copolymer film, shown in a cross-sectional view. FIGS. 21-22 illustrate

the use of the self-assembled block copolymer film of FIG. 20 after removal of one of the polymer blocks, as a mask to etch the substrate and filling of the etched opening.

[0021] FIG. 23 illustrates another embodiment of the use of the stamped pattern of an ink material shown in FIG. 18A to guide deposition of a material onto exposed portions of the substrate to form a chemically differentiated surface, shown in a cross-sectional view.

FIG. 24 illustrates the use of the deposited material of the structure shown in FIG. 23 as a mask to etch the underlying substrate.

[0022] FIG. 25 illustrates yet another embodiment of the use of the stamped pattern of an ink material shown in FIG. 18A as a seed material for selective deposition of an additional material to increase the thickness and/or hardness of the ink elements on the substrate, shown in a cross-sectional view. FIG. 26 illustrates the use of the ink pattern with added material shown in FIG. 25 as a mask to etch openings in the underlying substrate.

[0023] FIGS. 27-32 illustrate steps in another embodiment of a method according to the invention to chemically pattern a substrate, shown in a cross-sectional view. FIGS. 31-32 illustrate the removal of non-crosslinked polymer material and the use of the inked pattern to direct self-assembly of a block copolymer material.

[0024] FIG. 33 illustrates an elevational, cross-sectional view of an embodiment of a substrate bearing a neutral wetting layer at a preliminary processing step. FIG. 34 illustrates the substrate of FIG. 33 at a subsequent processing step.

[0025] FIGS. 35-39 illustrate an embodiment of a process according to the invention for forming a chemically patterned master template for forming a stamp for use in inducing self-assembly of a lamellar-phase block copolymer material on a substrate. FIG. 35 illustrates a perspective view of a base substrate at a preliminary processing stage bearing a hydrophilic material on the surface. FIGS. 36-39 illustrate the substrate of FIG. 35 at subsequent processing stages to form a patterned master template. FIGS. 37A-39A illustrate top plan views and FIGS. 37B-39B illustrate elevational, cross-sectional views of the substrates shown in FIGS. 37-39, respectively.

[0026] FIGS. 40-43 illustrate another embodiment of a process for forming a chemically patterned master template for use in forming a stamp for directing self-assembly of a lamellar-phase block copolymer material. FIG. 40 illustrates a perspective view of a base substrate at a preliminary processing stage bearing a hydrophobic material on the surface. FIGS. 41-43 illustrate the substrate of FIG. 40 at subsequent processing stages to form a patterned master template. FIGS. 41A-43A illustrate top plan views and FIGS. 41B-43B illustrate elevational, cross-sectional views of the substrates shown in FIGS. 41-43, respectively.

[0027] FIGS. 44-47 illustrate an embodiment according to the invention for forming a stamp on a master template as illustrated in FIG. 39. FIG. 44 illustrates a perspective view of a master template with a material for forming the stamp in a preliminary processing stage. FIG. 45 illustrates the master template/stamp material complex at a subsequent processing step. FIGS. 44A-45A illustrate top plan views and FIGS. 44B-45B illustrate elevational, cross-sectional views of the master template/stamp material complex shown in FIGS. 44-45, respectively. FIGS. 46-47 illustrate elevational, cross-sectional views of the master template/stamp material complex of FIG. 45 at subsequent processing steps showing the removal of the chemically patterned stamp from master template. FIG. 47A illustrates a perspective view of the stamp of FIG. 47, showing the chemically pattern surface of the stamp.

[0028] FIGS. 48-52 illustrate an embodiment of the invention for using the stamp illustrated in FIGS. 47-47A for directing ordering of a lamellar-phase block copolymer material. FIGS. 48-49 illustrate elevational, cross-sectional views of the stamp brought into contact with the block copolymer material on a substrate. FIG. 50 illustrates an elevational, cross-sectional view of the annealing of the block copolymer material in contact with the stamp. FIG. 50A illustrates a top plan view of the surface of the annealed block copolymer material of FIG. 50. FIGS. 51-52 illustrate the removal of the chemically patterned stamp from the annealed and self-assembled block copolymer material of FIG. 50, shown in an elevational, cross-sectional view.

[0029] FIGS. 53-55 illustrate the use of the self-assembled lamellar-phase block copolymer material of FIG. 52 to mask and etch an underlying substrate. FIG. 53 illustrates an

elevational, cross-sectional view of the block copolymer material of FIG. 52 at a subsequent processing step to selectively remove polymer domains to form a mask with openings to the substrate. **FIGS. 54-55** illustrate the substrate shown in FIG. 53 at subsequent processing stages to form and fill openings in the substrate. **FIGS. 53A-55A** are top plan views of the substrate shown in FIGS. 53-55, respectively.

[0030] **FIGS. 56-58** illustrate another embodiment of a process for forming a chemically patterned master template and stamp for directing self-assembly of a cylinder-phase block copolymer material. **FIG. 56** illustrates a perspective view of a master template having a surface bearing dots composed of a hydrophilic material amidst a hydrophobic material. **FIG. 56A** is a top plan view and **FIG. 56B** is an elevational, cross-sectional view of the master template shown in FIG. 56.

[0031] **FIG. 57** illustrates an embodiment of a stamp formed from the master template of FIG. 56 in an elevational, cross-sectional view. **FIG. 57A** is a top plan view of the surface of the stamp of FIG. 57.

[0032] **FIG. 58** illustrates an embodiment of the use of the stamp of FIG. 57 to direct ordering of a cylindrical-phase block copolymer material in an elevational, cross-sectional view. **FIG. 58A** illustrates a top plan view of the surface of the annealed and ordered block copolymer material of FIG. 58.

[0033] **FIG. 59** illustrates an elevational, cross-sectional view of the use of the self-assembled cylindrical-phase block copolymer material of FIGS. 58-58A to mask and etch an underlying substrate. **FIG. 60** illustrates the substrate shown in FIG. 59 at a subsequent processing stage to fill the cylindrical openings in the substrate. **FIG. 60A** is a top plan view of the substrate shown in FIG. 60.

[0034] **FIG. 61** illustrates geometries for an integrated circuit layout that can be prepared using embodiments of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0035] 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.

[0036] 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.

[0037] " L_0 " 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 or a blend of a block copolymer with one or more of its constituent homopolymers.

[0038] The term "chemical affinity" means the tendency of molecules to associate with each other based upon chemical forces between the molecules. The term "physiosorbed" means the physical adsorption of a molecule (e.g., ink material) to a surface, for example, through weak intermolecular interactions such as Van der Waals forces. The term "chemisorbed" means the chemical adsorption of a molecule (e.g., ink material) to a surface, for example, through chemically bonding such as through hydrogen bonds, ionic bonds, dithiol linkages, electrostatic bonds or other "weak" chemical bond.

[0039] In embodiments of the invention, a stamp or template is prepared by guided self-assembly of block copolymers, with both polymer domains at the air interface. Block copolymer films spontaneously assemble into periodic structures by microphase separation of the constituent polymer blocks after annealing, forming ordered domains at nanometer-scale dimensions. One of the polymer blocks has affinity for and is swelled by absorption of an ink chemical and a second polymer domain has substantially no affinity for the ink chemical and remains unchanged. The chemical ink can then be transferred from the stamp to a receptor

substrate where the ink forms SAMs. The resolution of the imprinted SAMs exceed other microcontact techniques using self-assembled polymer films, and processing costs using the technique is significantly less than using electron beam lithography or EUV photolithography, which have comparable resolution.

[0040] The two-dimensional (2-D) inked pattern that is formed on the receptor substrate can then be used, for example, as a template or pattern for self-assembled ordering of a block copolymer film that is cast onto the patterned receptor substrate. Following self assembly on the receptor substrate, one block of the copolymer can then be selectively removed and the remaining patterned film used as an etch mask for patterning nanosized features into the underlying substrate.

[0041] Methods for fabricating a stamp composed of a self-assembled block copolymer thin film that defines nanometer-scale cylindrical and linear array patterns according to embodiments of the invention are illustrated in **FIGS. 5-14**.

[0042] In some embodiments, the stamp is prepared under processing conditions that use a graphoepitaxy techniques utilizing the sidewalls of trenches as constraints to induce orientation and registration of a film of a self-assembling diblock copolymer to form an ordered array pattern registered to the trench sidewalls. Graphoepitaxial techniques can be used to order cylindrical-phase diblock copolymers in one dimension, for example, parallel lines of half-cylinders, hexagonal close-packed arrays of perpendicular cylinders, or a single row of perpendicular cylinders within lithographically defined trenches. A desired pattern of cylinders on the stamp can be prepared by providing trenches having walls that are selective to one polymer block of a block copolymer and a floor composed either of a material that is block-sensitive or preferentially wetting to one of the blocks of the block copolymer in trenches where lines of parallel half-cylinders are desired, or a material that is neutral wetting to both blocks in trenches where an array of perpendicular cylinders are desired.

[0043] Additionally, in some embodiments, the trench floors can be chemically differentiated to provide a wetting pattern to control orientation of the microphase separated and self-assembling cylindrical domains in a second dimension, for example, parallel lines of half-cylinders or perpendicular-oriented cylinders. The trench floors are structured or

composed of surface materials to provide a neutral wetting surface or preferential wetting surface to impose ordering on a block copolymer film that is then cast on top of the substrate and annealed to produce desired arrays of nanoscaled lines and/or cylinders.

[0044] As illustrated in FIGS. 5-5B, a base substrate 28 is provided, which can be silicon, silicon oxide, silicon nitride, silicon oxynitride, silicon oxycarbide, among other materials. In some embodiments, a neutral wetting material 30 is formed over the base substrate 28. A material layer 32 to be etched can then be formed over the neutral wetting material 30 and etched to form trenches 34. Portions of the material layer 32 form a spacer 36 between the trenches. The trenches 34 are structured with opposing sidewalls 38, opposing ends 40, a floor 42, a width (w_t), a length (l_t) and a depth (D_t).

[0045] As illustrated in FIG. 6, in embodiments for forming a stamp 26' with a hexagonal close-packed array of perpendicular cylinders, the ends 40' of the trenches 34' are angled to the sidewalls 38', for example, at an about 60° angle, and in some embodiments, the trench ends are slightly rounded. In other embodiments, the material layer 32 can be formed on the base substrate 28, etched to form the trenches 34, and then a neutral wetting material (e.g., random copolymer) 30 can be applied to the trench floors 42 and crosslinked. Non-crosslinked random copolymer material outside the trenches (e.g., on the spacers 36) can be subsequently removed.

[0046] The trenches can be formed using a lithographic tool having an exposure system capable of patterning at the scale of L_0 (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.

[0047] 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.

[0048] The boundary conditions of the trench sidewalls 38 in both the x- and y-axis impose a structure wherein each trench contains " n " number of features (e.g., cylinders, lamellae, etc.). Factors in forming a single array or layer of nanostructures within the trenches include the width and depth of the trench, the formulation of the block copolymer to achieve the desired pitch (L_0), and the thickness (t) of the copolymer film. The length (l) of the trenches is at or about nL_0 where n is an integer multiple of L_0 , typically within a range of about $n*10$ - $n*100$ nm (with n being the number of features or structures (i.e., cylinders)). The depth (D_t) of the trenches 34 is about equal to L_0 ($D_t \sim L_0$) such that the cast block copolymer material 44 of about L_0 will fill the trenches, and is generally over a range of about 10-100 nm. The trenches 34 are constructed with a width (w_t) such that a block copolymer (or blend) will self assemble upon annealing into a single layer of n elements (e.g., cylinders, lamellae, etc.) spanning the width (w_t) of the trench, with the center-to-center distance of adjacent identical elements being at or about L_0 . The width of the spacer 34 between adjacent trenches can vary and is generally about L_0 to about nL_0 . In some embodiments, the trench dimension is about 100-1,500 nm wide (w_t) and about 100-25,000 nm in length (l), with a depth (D_t) of about 10-100 nm.

[0049] To form a single layer of n lamellae from a lamellar-phase block copolymer (inherent pitch value of L_0), which span the width registered to the sidewalls 38 for the length of the trench 34, the width (w_t) of the trenches can be a multiple of the inherent pitch value (L_0) of the polymer, being equal to or about nL_0 (" $n*L_0$ ") and typically ranging from about $n*10$ to about $n*100$ nm (with n being the number of features or structures). For forming a 1-D array of perpendicular-oriented cylinders with a center-to-center pitch of at or about L_0 (e.g., a width of about 65-75 nm for a L_0 value of about 36-42 nm), the trenches 32 can be constructed with a width (w_t) of about $2*L_0$ or less, e.g., about $1.0*L_0$ to about $2*L_0$ (e.g.,

about $1.75 \cdot L_0$). For forming parallel lines of half-cylinders or a periodic, hexagonal close-pack or honeycomb array of perpendicular cylinders, the trenches **32**, **32'** can be constructed with a width (w_t) at or about an integer multiple of the L_0 value or nL_0 where $n = 3, 4, 5$, etc. (e.g., a width of about 120-2,000 nm for an L_0 value of about 36-42 nm).

[0050] For example, a block copolymer having a 35-nm pitch (L_0 value) deposited into a 75-nm wide trench having a neutral wetting floor will, upon annealing, result in a zigzag pattern of 35-nm diameter perpendicular cylinders that are offset by a half distance for the length (l_b) of the trench, rather than a single line of perpendicular cylinders aligned with the sidewalls 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 the perpendicular cylinders within the center of the trench.

[0051] A block copolymer material of about L_0 is deposited to about fill the trenches **34** and, upon annealing, the block copolymer film will self-assemble into morphologies to form an array of elements that are oriented in response to the wetting properties of the trench surfaces. 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). The trench sidewalls **38** and ends **40** are structured to be preferential wetting by one block of the block copolymer to induce registration of elements (e.g., cylinders, half-cylinders, lamellae, etc.) as the polymer blocks self-assemble. Upon annealing, the preferred block of the block copolymer will segregate to the sidewalls and edges of the trench to assemble into a thin (e.g., $\frac{1}{4}$ pitch) interface (wetting) layer, and will self-assemble to form elements according to the wetting surface of the trench floor **42**.

[0052] For example, in response to neutral wetting properties of the trench floor surface material (e.g., crosslinked neutral wetting random copolymer mat) and preferential wetting sidewalls and ends, an annealed cylinder-phase block copolymer film will self-assemble to form cylinders in a perpendicular orientation to the trench floors in the center of a polymer matrix, and a lamellar-phase block copolymer film will self-assemble into a lamellar array of alternating polymer-rich blocks (e.g., PS and PMMA) that extend across the width and for the

length of the trench and are oriented perpendicular to the trench floor and parallel to the sidewalls. In a trench having a preferential wetting floor, sidewalls and ends, an annealed cylinder-phase block copolymer film will self-assemble to form lines of half-cylinders in a polymer matrix extending the length of the trench and parallel to the trench floor.

[0053] The structuring of the trench sidewalls **38** and ends **40** to be preferential wetting causes one of the blocks of the copolymer material to form a thin wetting layer on those surfaces. To provide preferential wetting surfaces, for example, in the use of a PS-*b*-PMMA block copolymer, the material layer **32** 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 such as methacrylate-based resists, among other materials, which exhibit preferential wetting toward the PMMA block. In the use of a cylinder-phase copolymer material, the material will self assemble to form a thin (e.g., ¼ pitch) interface layer of PMMA and PMMA cylinders or half-cylinders (e.g., ½ pitch) in a PS matrix. In the use of a lamellar-phase block copolymer material, the material will assemble into alternating PMMA and PS lamellae (e.g., ½ pitch) within each trench, with PMMA at the sidewall interface (e.g., ¼ pitch).

[0054] In other embodiments, a preferential wetting material such as a polymethylmethacrylate (PMMA) polymer modified with an –OH containing moiety (e.g., hydroxyethylmethacrylate) can be applied onto the surfaces of the trenches, for example, by spin coating and then heating (e.g., to about 170°C) to allow the terminal OH groups to end-graft to oxide sidewalls **38** and ends **40** 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.

[0055] The structuring of the trench floors **42** to be neutral wetting (equal affinity for both blocks of the copolymer) allows both blocks of the copolymer material to wet the floor of the trench. A neutral wetting material **30** can be provided by applying a neutral wetting polymer (e.g., a neutral wetting random copolymer) onto the base substrate **28**, forming the material layer **32** and then etching the trenches to expose the underlying neutral wetting material, as illustrated in **FIGS. 5-5B**. A neutral wetting random copolymer can also be applied after

forming the trenches, for example, as a blanket coat by casting or spin-coating into the trenches and thermally processing to flow the material into the bottom of the trenches by capillary action, which results in a layer (mat) 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 layer. Non-crosslinked random copolymer material outside the trenches (e.g., on the spacers 36) can be subsequently removed.

[0056] For example, in the use of a poly(styrene-block-methyl methacrylate) block copolymer (PS-b-PMMA), a thin film of a photo-crosslinkable random PS:PMMA copolymer (PS-r-PMMA) which exhibits non-preferential or neutral wetting toward PS and PMMA can be cast onto the base substrate 28 (e.g., by spin coating). The polymer material can be fixed in place by grafting (on an oxide substrate) or by thermally or photolytically crosslinking (any surface) to form a mat that is neutral wetting to PS and PMMA and insoluble due to the crosslinking.

[0057] 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% PS) can be selectively grafted to a base substrate 28 (e.g., an oxide) as a layer 30 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.

[0058] 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% PMMA, about (58-x)% PS and x% (e.g., about 2-3%) of either polybenzocyclobutene or poly(para-azidomethylstyrene)). An azidomethylstyrene-functionalized random copolymer can be UV photo-crosslinked (e.g., 1-5 MW/cm² 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 **30**. 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).

[0059] In another embodiment in which the base substrate **28** is silicon (with native oxide), another neutral wetting surface for PS-*b*-PMMA can be provided by hydrogen-terminated silicon. For example, the floors **42** of trenches **34** can be etched, for example, with a hydrogen plasma, to remove the oxide material and form hydrogen-terminated silicon **30**, which is neutral wetting with equal affinity for both blocks of a block copolymer material such as PS-*b*-PMMA. 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 (NH₄F), by HF vapor treatment, or by a hydrogen plasma treatment (e.g., atomic hydrogen). An H-terminated silicon substrate can be further processed by grafting a random copolymer such as PS-*r*-PMMA selectively onto the substrate resulting in a neutral wetting surface, for example, 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 the surface to produce an about 10-15 nm thick film.

[0060] In other embodiments, to induce formation of parallel half-cylinders in the trenches, the trenches are structured with a floor surface that is preferential wetting by one of the polymer blocks of a block copolymer. Annealing of a cylindrical-phase block copolymer material having an inherent pitch value of about L_0 will result in "*n*" rows or lines of half-cylinders (parallel to the sidewalls and trench floor) extending the length (l_t) and spanning the width (w_t) of the trenches.

[0061] Preferential wetting floors **42** can be provided by a silicon material with an overlying layer **30** of native oxide, or by forming a layer **30** of oxide (e.g., silicon oxide, SiO_x), silicon nitride, silicon oxycarbide, ITO, silicon oxynitride, resist material such as such as methacrylate-based resists, etc., over the base substrate **28**.

[0062] Referring now to **FIGS. 7-7B**, a film of a self-assembling block copolymer material **44** 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 into the trenches 34 and onto the trench floors 42, and processed such that the copolymer material will then self-assemble. The block copolymer material can be deposited by spin casting or 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.

[0063] Capillary forces pull excess of the block copolymer material 44 (e.g., greater than a monolayer) into the trenches 34. In a trench having a depth (D_t) at or about the L_0 value of the copolymer material, the block copolymer is deposited to fill the trench such that the film thickness (t_f) of the deposited block copolymer is generally at or about L_0 and the film will self assemble to form a single layer of elements (e.g., cylinders lamellae, etc.) across the width (w_t) of the trench, the elements having a diameter/width at or about $0.5 L_0$ (e.g., about 20 nm). For example, a typical thickness (t_f) of a lamellar-phase PS-b-PMMA block copolymer film 44 is about $\pm 20\%$ of the L_0 value of the copolymer (e.g., about 10-100 nm) to form alternating polymer-rich lamellar blocks having a width of about $0.5 L_0$ (e.g., 5-50 nm) within each trench. In the use of a solvent anneal, the film can be much thicker than L_0 , e.g., up to about +1000% of the L_0 value. The thickness of the film 44 can be measured, for example, by ellipsometry techniques. As shown, a thin film 44a of the block copolymer material can be deposited onto the spacers 36 of the material layer 32; this film will form a monolayer of elements with no apparent structure from a top-down perspective (e.g., lamellae in a parallel orientation).

[0064] The block copolymer material is fabricated such that each of the self-assembled polymer domains has a different solubility for a given ink chemical. The ink chemical is applied as an organic solution, either neat (undissolved) or combined with a solvent that will be selectively absorbed into and cause one of the polymer domains to swell and become impregnated with the ink chemical material. In some embodiments, the ink but not the solvent will be selectively absorbed into one of the polymer domains.

[0065] In some embodiments, the block copolymer can be chemically modified to include a functional group having chemical affinity for the ink material, for example, a thiol or amine

group. For example, one of the blocks can inherently contain a thiol or amine functional group, for example, polyvinylpyridine.

[0066] The film morphology, including the domain sizes and periods (L_0) 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 lamellar, cylindrical, or spherical morphologies, among others.

[0067] 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 generally between about 60:40 and 80:20, the diblock copolymer assembles into periodic cylindrical domains 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.

[0068] An example of a lamellae-forming PS-b-PMMA diblock copolymer ($L_0 = 32$ nm) to form about 16 nm wide lamellae is composed of a weight ratio of about 50:50 (PS:PMMA) and total molecular weight (M_n) of about 51 kg/mol. An example of a cylinder-forming PS-b-PMMA copolymer material ($L_0 = 35$ nm) to form about 20 nm diameter cylindrical PMMA domains in a matrix of PS is composed of about 70% PS and 30% PMMA with a total molecular weight (M_n) of 67 kg/mol.

[0069] Although PS-b-PMMA diblock copolymers are used in the illustrative embodiments, 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, polyethyleneoxide-polystyrene, polyethyleneoxide-polymethylmethacrylate, polystyrene-polyvinylpyridine, polystyrene-polyisoprene (PS-b-PI), polystyrene-polybutadiene, polybutadiene-polyvinylpyridine, polyisoprene-polymethylmethacrylate, and polystyrene-poly lactide, among others. Examples of triblock copolymers include poly(styrene-block methyl methacrylate-block-ethylene oxide).

[0070] 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_0 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_0 value of the polymer can also be modified by adjusting the molecular weight of the block copolymer.

[0071] The block copolymer film 44 is then annealed to cause the polymer blocks to phase separate and self assemble according to the preferential and neutral wetting of the trench surfaces to form a self-assembled polymer film. The resulting morphology of the annealed film 28 (e.g., perpendicular orientation of lamellae) can be examined, for example, using atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM).

[0072] In some embodiments, the deposited block copolymer film 44 can be solvent annealed. In embodiments of a solvent anneal, the film can be swollen by exposure to a vapor of a "good" solvent for both blocks, and the vapor can then be removed. Vapors of a solvent such as benzene, chloroform or a chloroform/octane mixture, for example, can be exposed to the film 44 to slowly swell both blocks (PS, PMMA) of the film. The solvent and solvent vapors are then allowed to slowly evaporate to dry the film, resulting in self-assembled polymer domains.

[0073] The block copolymer film 44 can also be thermally annealed at the annealing temperature (e.g., about 150-250°C) in an atmosphere that is saturated or nearly saturated (but not supersaturated) with a solvent in which both blocks are soluble. The solvent-saturated vapor maintains a neutral air interface in conjunction with the surface interface with a neutral wetting floor 34. The existence of both neutral wetting air and surface interfaces induces the formation of perpendicular features throughout the film.

[0074] Referring to FIGS. 8-8A, upon annealing a lamellar-phase block copolymer film 44 (e.g., PS-*b*-PMMA of about L_0) within a trench 34 with preferential wetting sidewalls 38 and

a neutral wetting trench floor 42 (exhibits neutral or non-preferential wetting toward both blocks, e.g., a random graft copolymer), the polymer material will self-assemble into a film 46 composed of alternating polymer-rich blocks 48, 50 (e.g., PS and PMMA). The lamellar blocks 48, 50 are oriented perpendicular to the trench floor 42 and parallel to the sidewalls 38, extending the length of the trench 34 and spanning the width (w_t) at an average pitch value at or about L_0 . The constraints provided by the width (w_t) of the trenches and the character of the copolymer composition combined with preferential or neutral wetting surfaces within the trenches result, upon annealing, in a single layer of n lamellae 48, 50 across the width (w_t) of the trench. The number " n " or pitches of lamellar blocks within a trench is according to the width (w_t) of the trench and the molecular weight (MW) of the block copolymer. For example, depositing and annealing an about 50:50 PS:PMMA block copolymer film (e.g., $M_n = 51$ kg/mol; $L_0 = 32$ nm) in an about 160 nm wide trench will subdivide the trench into about 5 lamellar pitches. The stamping surface of the stamp 26 is thus defined by a lamellar array of polymer domains that define a linear pattern of lamellar blocks, each about 14-18 nm wide and several microns in length (e.g., about 10-4000 μm), and a center-to-center pitch of about 32 nm. A smaller pitch can be dialed in by using lower molecular weight diblock copolymers

[0075] In embodiments in which a film of a cylindrical-phase block copolymer is deposited into trenches with preferential wetting sidewalls and a neutral wetting trench floor, upon annealing, the cylinder-phase copolymer film will self-assemble into a film composed of perpendicular-oriented cylinders of one of the polymer blocks (e.g., PMMA) within a polymer matrix 54' of the other polymer block (e.g., PS) registered to the sidewalls of the trench.

[0076] FIG. 9 illustrates an embodiment of a stamp 26' composed of an annealed cylinder-phase copolymer film 46' in the formation of an array of hexagonal close-packed array of perpendicularly-oriented cylinders 52' within a polymer matrix 54'. The sidewalls 38' and angled ends 40' of the trenches 34' are used as constraints to induce orientation and registration of cylindrical copolymer domains to achieve the hexagonal cylindrical array registered to the trench sidewalls. The width (w_t) of the trenches 34' is at or about $L_0 \cdot \cos(\pi/6)$ or $L_0 \cdot 0.866$, which defines the number of rows of cylinders, and the trench length (l_t) is at or about mL_0 , which defines the number of cylinders per row. The ends 40' of

the trenches are angled to the sidewalls 38', for example, at an about 60° angle, and in some embodiments can be slightly rounded. A cylindrical-phase diblock copolymer material having an inherent pitch at or about L_0 (or blend with homopolymers) and a thickness (t) of about L_0 will self assemble upon annealing to form a hexagonal array of cylindrical domains 52' of the minor (preferred) polymer block (i.e., like domains such as PMMA) that are oriented perpendicular to the neutral wetting floor 42' of the trench 34' within a matrix 54' of the major polymer block (e.g., PS). The minor (preferred) polymer block (e.g., PMMA) will segregate to the preferential wetting sidewalls 38' and ends 40' to form a wetting layer 52a'. The hexagonal array contains n single rows of cylinders according to the width (w_t) of the trench with the cylinders 52' in each row being offset from the cylinders in the adjacent rows. Each row contains a number of cylinders, generally m cylinders, which number can vary according to the length (l_t) of the trench and the shape of the trench end (e.g., rounded, angled, etc.) with some rows having greater or less than m cylinders. The cylinders 52' are generally spaced apart at a pitch distance (p_1) at or about L_0 between each cylinder in the same row and an adjacent row (center-to-center distance), and at a pitch distance (p_2) at or about $L_0 \cdot \cos(\pi/6)$ or $0.866 L_0$ being the distance between two parallel lines where one line bisects the cylinders in a given row and the other line bisects the cylinders in an adjacent row. The stamping surface of the stamp 26' is thus defined by an array of polymer domains that define a hexagonal or honeycomb pattern of perpendicular-oriented cylinders 52', each about 20-22 nm in diameter with a center-to-center pitch of about 42 nm.

[0077] In another embodiment using a cylindrical-phase copolymer material, the trench dimensions can be modified to use the trench sidewalls and ends as constraints to induce orientation and registration of cylindrical copolymer domains in a single row parallel to the trench sidewalls. The trenches are structured to have a width (w_t) that is at or about $1.0-1.75 \cdot$ the L_0 value of the block copolymer material, a neutral wetting floor, and sidewalls and ends that are preferential wetting by the minority (preferred) block (e.g., the PMMA block) of the diblock copolymer (e.g., PS-b-PMMA). A cylindrical-phase diblock copolymer (or blend with homopolymers) having an inherent pitch at or about L_0 can be deposited into the trenches to a thickness (t_t) of about the L_0 value of the copolymer material (as in FIGS. 7-7A). As illustrated in FIGS. 10-10A, the annealed block copolymer film self-assembles to form film 46". The constraints provided by the width (w_t) of trench 34" and the

character of the block copolymer composition combined with a neutral wetting trench floor 42" and preferential wetting sidewalls 38" results in a one-dimensional (1-D) array or single row of perpendicularly-oriented cylindrical domains 52" of the minority (preferred) polymer block (e.g., PMMA) within a matrix 54" of the major polymer block (e.g., PS), with the preferred block segregating to the sidewalls 38" of the trench to form a wetting layer 52a". In some embodiments, the cylinders have a diameter at or about $0.5 L_0$ (e.g., about 20 nm), the number n of cylinders in the row is according to the length of the trench, and the center-to-center distance (pitch distance) (p) between each like domain (cylinder) is at or about L_0 (e.g., about 40 nm). The resulting stamping surface of the stamp 26" is defined by an array of polymer domains that define a single row of perpendicular-oriented cylinders 52", each about 20-22 nm in diameter with a center-to-center pitch of about 42 nm.

[0078] Referring now to FIGS. 11-11A, in yet another embodiment using a cylindrical-phase copolymer material, the trenches 34'" can be structured with by preferential wetting surfaces 38, 40, 42 to induce formation of half-cylinder copolymer domains 56'" in a polymer matrix 54'" that are in a parallel orientation to the trench floors 42'" and registered to the sidewalls 38'". A preferentially wetting floor 42'" can be provided, for example, by a layer 58'" of oxide, silicon nitride, silicon oxycarbide, among others. The stamping surface of the stamp 26'" is defined by an array of polymer domains that define lines of half-cylinders, each about 20-22 nm wide and several microns in length (e.g., about 10-4000 μm), and a center-to-center pitch of about 42 nm.

[0079] In another embodiment of the invention, graphoepitaxy (topographic features, e.g., sidewalls, ends, etc.) is used to influence the formation of arrays in one dimension, and the trench floors provide a wetting pattern that can be used to chemically control formation of the arrays in a second dimension. For example, as illustrated in FIGS. 12-12A, a neutral wetting material 30'" (e.g., random copolymer) can formed on the base substrate 28'" and crosslinked in select regions 60'", such as by photo-exposure through a reticle or a patterned mask (e.g., photoresist). As shown, the non-crosslinked regions of the neutral wetting material 30'" have been removed (e.g., by wet processing using a solvent) to expose the sections 62'" of the underlying base substrate 28'", resulting in a pattern of discrete regions

60''' of the crosslinked neutral-wetting material 30''' (random copolymer) and sections 62''' of the exposed preferential-wetting base substrate 28'''.

[0080] As depicted in FIGS. 13-13B, the material layer 32''' can then be formed and trenches 34''' etched to expose the sections 60''' of the neutral wetting material 30''' and sections 62''' of the exposed base substrate 10''' on the trench floors 18''' as a series of stripes oriented perpendicular to the trench sidewalls 38'''. The trench floors 42''' are thus defined by alternating preferential wetting sections 62''' (base substrate 28''') and neutral wetting sections 60''' (a mat of the crosslinked random copolymer 30'''). In some embodiments, each of the sections can have a width (w_{r1}) at or about L_o , and in other embodiments, the neutral wetting sections 60''' can have a width (w_{r2}) at or about nL_o and the preferential wetting sections 62''' have a width at or about L_o . The trench sidewalls 38''' and ends 40''' (e.g., of oxide) are preferential wetting to the minority (preferred) block of the block copolymer.

[0081] A cylindrical-phase block copolymer film (e.g., pitch L_o) can then be cast or spin coated into the trenches 34''' to a film thickness (t) of about L_o and annealed. As illustrated in FIGS. 14-14B, the differing wetting patterns on the trench floor 42''' imposes ordering on the cylindrical-phase block copolymer film as it is annealed, resulting in a 1-D array of alternating perpendicular-oriented cylinders 52''' and parallel-oriented half-cylinders 56''' for the length (nL_o) of each trench.

[0082] After the copolymer film is annealed and ordered, the film can then be treated to crosslink the polymer segments (e.g., the PS segments) to fix and enhance the strength of the self-assembled polymer blocks. The polymers can be structured to inherently crosslink (e.g., upon exposure to ultraviolet (UV) radiation, including deep ultraviolet (DUV) radiation), or one or both of the polymer blocks of the copolymer material can be formulated to contain a crosslinking agent.

[0083] Optionally, the unstructured thin film 44a of the block copolymer material outside the trenches (e.g., lamellae in a parallel orientation on spacer 36 in FIG. 7A) can then be removed, as illustrated in FIGS. 8-8A. In embodiments in which the ink chemical would be absorbed by the film 44a, the film would be removed.

[0084] For example, the trench regions can be selectively exposed through a reticle (not shown) to crosslink only the annealed and self-assembled film 46 within the trenches 34, 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 44a on the spacers 36, leaving the registered self-assembled film within the trench and exposing the surface of material layer 32 on the spacers 36 above/outside the trenches. In another embodiment, the annealed film 46 can be crosslinked globally, a photoresist material can be applied to pattern and expose the areas of the film 44a over the spacers 36 outside the trench regions, and the exposed portions of the copolymer film can be removed, for example by an oxygen (O₂) plasma treatment.

[0085] The resulting stamp is structured with a stamping surface 64 composed of an ordered array of polymer domains (e.g., 48, 50) in the desired pattern for stamping onto a receptor substrate. The stamp can then be inked and brought into contact with the receptor substrate to produce the pattern on the substrate.

[0077] The ink chemical material is selected such that it will be absorbed selectively into a polymer domain of the self-assembled polymer film by Van der Waals forces or other non-covalent force or bond (e.g., hydrogen bond, etc.) and will form a self-assembled monolayer (SAM) on the receptor substrate. The ink chemical can include one or more functional groups that chemically react with the receptor substrate. The chemical affinity between the ink material and the receptor substrate is greater than the chemical affinity between the ink material and the polymer domain in which it is absorbed.

[0078] In embodiments of the invention, the ink chemical can have amino, thiol, alcohol or alkyne functional groups. Examples of ink chemicals include thiols such as 2-aminoethanethiol, aminothiophenol, cysteine, homocysteine, leucinethiol, 2-butylaminoethanethiol, 2-cylcohexylaminoethanethiol, etc.; mercaptoalcohols such as mercaptoethanols (e.g., 2-mercaptoethanol (HS-CH₂CH₂OH)), mercaptopropanols (e.g., 2-mercaptoopropanol) and mercaptobutanols (e.g., 4-mercapto-1-butanol, 2-mercaptobutanol); and acetylenics with hydrocarbon tails or other functional groups such as alcohols, thiols, amines, halides, etc., e.g., carboxylates such as propiolic acid, 4-butyric acid, 5-pentynoic acid, and the like.

[0079] The ink chemical material is in the form of an organic solution such that it will diffuse into and be selectively absorbed by one of the polymer domains causing the polymer domain to swell. The ink chemical material can be in the form of a neat (undiluted) solution or combined with an organic solvent that will promote diffusion of the material selectively into the selected polymer domain. Examples of solvents that can be utilized include methanol, ethanol, isopropanol, ethylene glycol, propylene glycol and acetic acid. Typically, the concentration of the ink chemical material in solution is about 1-10k mM.

[0080] In another embodiment, the ink chemical material can be provided in a vaporous form, which can provide a higher level of control with respect to the amount of ink material that is absorbed into the stamp. The stamp would be exposed to a vapor of the ink chemical for a sufficient time period for absorption of an adequate quantity of the ink chemical by the polymer domain.

[0081] FIGS. 15-18 illustrate an embodiment of a stamping process utilizing a stamp 26 according to the invention, as depicted in FIGS. 8-8A.

[0082] Referring to FIG. 15, a stamping process can be conducted by applying (arrows ↓) a solution of the ink chemical material (either neat or in a solvent) 66 onto the stamping surface 64 or, in other embodiments, by exposing the stamping surface to a vapor of the ink chemical. The contact of the ink chemical solution with the stamping surface of the stamp is for a time effective to enable the ink material to diffuse into and be selectively absorbed by the targeted polymer domain.

[0083] Upon contact of the stamp with the ink chemical, the polymer domain 50 with affinity for the ink chemical solution (e.g., PS domain) is swelled by absorption of the ink chemical solution, as illustrated in FIG. 16. The other polymer domain 48 with substantially no affinity for the ink chemical (e.g., PMMA domain) remains unchanged. This results in the stamping surface 64 of the stamp 26 having a relatively corrugated surface that defines the lines of the swollen polymer domains 50.

[0084] As illustrated in FIG. 17, a receptor substrate 68 is then brought into contact (arrows ↓) with the swollen and ink-containing polymer domains 50 situated on the stamping

surface 64 of the stamp 26 to effect transfer of the ink material 66 onto the receptor substrate, resulting in a pattern 70 on the receptor substrate, as shown in FIGS. 18-18A. The ink chemical material 66 is transferred from the stamp 26 by chemical bonding of one or more functional groups of the ink material with a functional group(s) on the surface of the receptor substrate 68.

[0085] Examples of the receptor substrate 68 include silicon oxide, silicon wafers, silicon-on-insulator ("SOI") substrates, silicon-on-sapphire ("SOS") substrates, and other semiconductor substrates such as silicon-germanium, germanium, gallium arsenide and indium phosphide, chalcogenide-class of materials, magnetic materials (e.g., Ni, Fe, Co, Cu, Ir, Mn, Pt, Tu, etc.), and other substrates used in disk drives or optical storage devices. Optionally, the receptor substrate 68 can be modified to incorporate functional groups that enhance chemical bonding and transfer of the ink material from the stamp/template (e.g., stamp 26), as indicated in Table 1 (below). Substrates modified with a glycidoxo functionality will be reactive to inks having amine or thiol functional groups. Substrates modified with an isocyanate functionality will be reactive to inks having alcohol or amino functional groups. Substrates modified with chlorosilyl groups will be reactive to inks with amino, alcohol or thiol functional groups. Alkylazido -modified substrates will be reactive to inks with alkyne functional groups. For example, a silicon oxide substrate can be modified with azide groups to facilitate binding of an acetylenic carboxylate ink.

[0086] Table 1 (below) provides examples of ink chemical materials that can be used for selective absorption by one of the polymer block domains (i.e., PMMA) of a stamp according to the invention, and embodiments of receptor substrate modifications that can be used in combination with the ink chemical material to effect transfer of the ink onto the receptor substrate to form SAMs in a stamped pattern.

Ink Material	Receptor Substrate modification
Thiols, such as: 2-aminoethanethiol aminothiophenol cysteine homocysteine leucinethiol 2-butylaminoethanethiol 2-cylcohexylaminoethanethiol	Glycidoxymodified substrates such as SiO₂ grafted with a glycidoxypentyl(trialkoxym) silane (e.g., glycidoxypentyl trimethoxysilane) Isocyanatomodified substrates such as SiO₂ grafted with a isocyanatopentyl(trialkoxym) silane (e.g., isocyanatopentyl triethoxysilane, isocyanatopentyl trimethoxysilane, etc.) Chlorosilyl-modified substrates such as chlorine-terminated silicon (Si-Cl) (e.g., from H-terminated silicon exposed to Cl₂ gas)
Mercaptoalcohols, such as: mercaptoethanols mercaptopropanols mercaptobutanols	Isocyanatomodified substrates such as SiO₂ grafted with a isocyanatopentyl(trialkoxym) silane (e.g., isocyanatopentyl triethoxysilane, isocyanatopentyl trimethoxysilane, etc.) Chlorosilyl-modified substrates such as chlorine-terminated silicon (Si-Cl)
Acetylenics with hydrocarbon tails or other functional groups such as alcohols, thiols, amines, halides, etc., such as: propionic acid (or acetylene monocarboxylic acid) butynoic acid pentynoic acid	Alkylazido-modified substrates such as SiO₂ grafted with 6-azidosulfonylhexyl (triethoxym)silane, or with a 11-azidoundecyl group (e.g., formed from 11-bromoundecyl(triethoxym)silane reacted with sodium azide).

[0087] An alkylazido-modified receptor substrate 68 can be prepared, for example, as a silicon dioxide (SiO₂) substrate grafted with 6-azidosulfonylhexyl (triethoxym)silane or with a 11-azidoundecyl group monolayers that can be formed by grafting 11-bromoundecyl (triethoxym)silane to a SiO₂ substrate then derivatizing with sodium azide, as described, for example, by Rozkiewicz et al; *Angew. Chem. Int. Ed. Eng.*, 2006, 45, 5292-5296. A chlorosilyl-modified receptor substrate 68 can be prepared, for example, as chlorine-terminated silicon (Si-Cl) by chlorination of hydrogen-terminated silicon surfaces by

exposure to chlorine gas (Cl_2) (e.g., at 80°C or exposure to a tungsten lamp), as described, for example, by Zhu et al; *Langmuir*, 2006, 16, 6766-6772.

[0088] The temperature during the stamping process generally ranges from about room temperature (20°C) to near the boiling point of the ink chemical solution. Contact of the stamp 26 with the receptor substrate 68 is for a time effective to enable chemical bonds to form between functional groups on the receptor substrate and the ink chemical material 66, generally about 1 minute to about 4 hours, and typically about 1-15 minutes.

[0089] The receptor substrate and the ink material may react to form a urea or urethane linkage through a mercapto alcohol, a disulfide linkage through a thiol (R-SH) functional group, a bond involving acid/base groups, or an amine linkage through an amine/epoxide reaction of a triazole image through reaction between an azide and alkyne. Diffusion (or other transfer mechanism) of the ink material from the polymer domains of the stamp onto the receptor substrate (where the ink reacts) can create a concentration gradient, which then draws additional ink onto the surface of the receptor substrate from the inked polymer domains.

[0090] Upon completion of the ink transfer to the receptor substrate, the stamp is then removed leaving the ink chemical material 66 as a pattern 70 on portions of the receptor substrate 68 corresponding to the inked polymer domains 50 on the stamping surface 64 of the stamp 26 and exposed portions 72 of the substrate, as shown in FIGS. 18-18A. In some embodiments, the ink chemical material is processed to form a self-assembled monolayer (SAM) on the surface of the receptor substrate 68. The stamp 26 may then be re-inked, if needed, for further stamping of the same or another receptor substrate.

[0091] The ink pattern 70 on the receptor substrate 68 has identical or substantially identical resolution to the pattern of the inked polymer domains on the stamping surface 64 of the stamp 26. The patterned stamp 26 can be used to produce features (pattern 70) on the receptor substrate that are sub-lithographic, for example, a thickness of about 1-10 angstroms, and lateral width (w_p) that corresponds to the dimension (width (w_{pd})) of the pattern of the "inked" polymer domains on the stamping surface 64 of the stamp 26 (FIG. 17).

[0092] In the embodiment illustrated in **FIGS. 18-18A**, the ink (e.g., SAM) pattern **70** formed using the stamp **26** having a stamping surface **64** composed of a lamellar array of polymer domains defines a linear pattern of fine, parallel lines of nanometer-scale to sublithographic dimensions about 5-50 nm wide and several microns in length (e.g., about 10-4000 μm), and a center-to-center pitch of about 10-100 nm. Stamp **26'''** (**FIGS. 11-11A**), for example, also provides a stamping surface having parallel lines of polymer domains. In other embodiments, the stamp can have a stamping surface composed of a cylindrical array of polymer domains as described, for example, with respect to stamps **26'** and **26''** (**FIGS. 9-10**).

[0093] After applying the ink pattern on the receptor substrate, further processing may be conducted as desired.

[0094] For example, the inked pattern **70** of the stamped regions or elements **66** shown in **FIG. 18A**, can be used to guide the formation of etch masks to pattern portions of the underlying receptor substrate **68**.

[0095] In one embodiment, the inked pattern **70** of elements **66** can be formed as a chemically differentiated surface in a pattern of hydrophobic and hydrophilic materials (or neutral and preferential-wetting materials), which can be used as a template to guide and chemically control the self-assembly of a block copolymer to match the template pattern of elements on the receptor substrate. For example, as depicted in **FIGS. 18-18A**, using a template such as stamp **26** (**FIG. 16**), an ink material that will form a SAM composed of a hydrophobic material such as octadecylthiol (ODT) can be transferred as a pattern **70** of elements **66** (e.g., parallel lines) onto a receptor substrate **68** that has an epoxide surface. Unstamped regions **72** of the substrate adjacent to the line elements **66** can be made hydrophilic by reacting the exposed substrate with a material such as 11-hydroxyundecylthiol. The pattern of hydrophobic material line elements **66** and the hydrophilic substrate regions **72** on the substrate can then be used as a template for guided self-assembly of a block copolymer material.

[0096] Referring to **FIG. 19**, a block copolymer material having domains that are selectively wetting to the template (seed layer) formed by the hydrophobic line elements **66** and the hydrophilic substrate regions **72**, can be deposited as a film **74** onto the substrate. The

copolymer film 74 can then be annealed to form a self-assembled polymer film 76 with lamellae 78, 80 registered to the hydrophobic and hydrophilic regions 66, 72 of the template below, as illustrated in FIG. 20. Then, as shown in FIG. 21, one of the polymer domains (e.g., lamellae 80) of the self-assembled film 76 can be selectively removed and the resulting film 82 can be used as a mask to etch (arrows ↓↓) the underlying substrate 68, for example, by a non-selective RIE etching process, to delineate a series of openings 84 (shown in phantom). Further processing can then be performed as desired, such as filling the openings 84 with a material 86 as shown in FIG. 22, for example, with a dielectric material to separate active areas, or with a conductive material such as a metal or other conductive material to form nanowire channel arrays for transistor channels, semiconductor capacitors, and other structures that can extend to an active area or element in the substrate or an underlayer. Further processing can then be performed as desired. The self-assembly of block copolymers to an underlying chemical pattern is rapid relative to other methods of "top-down" or graphoepitaxy ordering and registration.

[0097] In other embodiments, the inked pattern of elements 66 can be used as a template for selective deposition of a hydrophobic or hydrophilic material onto either the inked elements 66 or the unstamped areas 72 of the substrate.

[0098] For example, referring to FIG. 23, the inked pattern of elements 66' can be used as an "anti-seed" guide or template for the global application and selective deposition of a material 74' that is chemically different from the stamped regions (elements) 66' onto adjacent exposed regions 72' of the substrate 68'. For example, elements 66' composed of a hydrophobic ink material (e.g., octadecyl thiol) can be stamped onto the substrate 68', and a hydrophilic material 74' (e.g., an oxide) can be selectively applied to the non-stamped substrate areas 72', for example, by a vapor deposition, resulting in the structure shown in FIG. 23. The resulting film 82' can be used as a mask to etch (arrows ↓↓) the underlying substrate 68' to form openings 84' (shown in phantom), as depicted in FIG. 24.

[0099] In another embodiment, as shown in FIG. 25, elements 66'' can be used as a seed material for the selective deposition of additional material 74'' to increase the thickness and/or hardness of the elements 66'' and produce a hard mask for etching the substrate 68''. For

example, elements 66" can be formed from acetylenic hydrocarbons or esters of acetylenic carboxylates with hydrocarbon conjugates (e.g., hexylpropynoate ester), with subsequent selective deposition of an inorganic material 74" such as silicon oxide to increase the thickness and/or hardness of the elements 66". In another example, a material 74" such as silicon nitride can be selectively deposited onto the elements 66" by ALD methods to form a hardmask 82" composed, for example, of a series of lines according to the pattern of the elements 66". In other embodiments, elements 66" can be formed as a seed layer from an ink material having a functional group on its tail end (e.g., ink chemical with a bromine functional group) that will selectively initiate polymer growth, and an atom transfer radical polymerization (ATRP) can then be conducted to add additional polymer material 74" to increase the thickness and/or hardness of the elements 66" and produce a hard mask for etching openings 84". The hardmask 82" can be then used, for example, to mask the etch of the underlying substrate 68" (e.g., film stack, etc.) to form openings 84", as shown in FIG. 26.

[00100] Another embodiment of the invention illustrated in FIGS. 27-32, utilizes chemical patterning of a substrate to direct self-assembly of a block copolymer. In some embodiments, the process utilizes a stamp/template 88 that is formed with transparent sections 90, non-transparent sections 92, and a stamping surface 94. The transparent sections 90 are composed of a material that is substantially transparent to UV or DUV radiation in order to allow light to pass therethrough, for example, glass (e.g., quartz (SiO₂)), calcium fluoride (CaF₂), diamond, or a transparent plastic or polymeric material, and the non-transparent (opaque) sections 92 can be composed, for example, of an elastomeric polymer material such as poly(dimethylsiloxane) (PDMS).

[00101] As shown in FIG. 27, the stamping surface 94 can be coated with a thin film 96 of a polymerizable neutral wetting material which exhibits non-preferential or neutral wetting toward the blocks of a block copolymer, such as a random block copolymer (e.g., PS-r-PMMA). The template 88 can then be pressed (arrow ↓) onto a receptor substrate 68 (e.g., a preferential wetting material such as silicon (with native oxide), oxide, etc.) as shown in FIG. 28 to transfer the polymer material 96 onto the substrate 68. Then, as illustrated in FIG. 29, a radiation source (e.g., UV or DUV radiation) can then be transmitted (arrows ↓↓)

through the transparent sections **90** of the stamp/template **88** to photolytically crosslink discrete sections **98** of the polymer material **96** on the substrate **68**. The template **88** can then be removed from contact with the receptor substrate **68**, leaving the crosslinked polymer sections **98** and non-crosslinked polymer material **100**, as depicted in **FIG. 30**.

[00102] Further processing can then be conducted as desired. For example, as shown in **FIG. 31**, the non-crosslinked polymer material **100** can be removed, for example, by wet processing by a chemical dissolution process using a solvent to expose sections **102** of the receptor substrate **68**, resulting in discrete neutral wetting sections **98** composed of the crosslinked polymer material (e.g., crosslinked random copolymer) and preferential wetting sections **102** composed of the exposed receptor substrate (e.g., oxide). A block copolymer material can then be cast or spin coated onto the chemically differentiated surface and annealed to form a self-assembled block copolymer layer **104**. As illustrated in **FIG. 32**, the annealed block copolymer film **104** will register to the differing wetting patterns (**98/102**) on the receptor substrate **68**, for example, to form lamellae **106**, **108** as shown. The resulting film **104** can be further processed, for example, to selectively remove one of the polymer blocks to produce a hard mask for use in a dry etch to transfer the pattern into the underlying substrate material.

[00103] Patterning a substrate using conventional lithographic techniques has been hampered by difficulties such as high costs and/or incompatibility with high throughput production methods. With embodiments of the present invention, a stamp can be prepared using conventional lithography (to form the trenches) but, because the stamp can be used repeatedly to pattern multiple substrates, the production cost per stamped substrate is reduced. In addition, the use of the stamped pattern (e.g., SAM ink pattern **70**) for chemically controlling the formation of a self-assembled block copolymer film, can subsequently provide an etch mask on a nanoscale level that 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.

[00104] In another embodiment of the invention illustrated in **FIGS. 33-60**, the ordering of a self-assembling block copolymer material (e.g., film) is induced and directed by overlaying a

topographically flat stamp that is chemically patterned on its surface. The chemically patterned stamp overlaid on a BCP film cast onto a substrate that has been globally modified to be equally wetting to both blocks of the BCP will direct self-assembly of the BCP film to match the pattern on the stamp. The present embodiment of the invention achieves a pattern transfer to a block copolymer (BCP) without leaving a physically formed impression in the substrate and without a transfer of material to the substrate or the BCP material.

[00105] FIG. 33 illustrates a substrate (generally 110) to be patterned. The substrate 110 can be composed of a base material 112, which can be, for example, silicon, silicon oxide, silicon nitride, silicon oxynitride, silicon oxycarbide, among other material. As shown, a non-preferential or neutral wetting material 114 (equal affinity for blocks of the copolymer) is formed over the base material.

[00106] The neutral wetting material 114 can be formed, for example, by blanket coating a random copolymer material onto the base material 112 by casting or spin-coating, and fixing the polymer material in place by grafting (on an oxide substrate) or by thermally or photolytically crosslinking (any surface). For example, a material that neutral wetting to a PS-b-PMMA block copolymer can be formed from a thin film of a photo-crosslinkable random PS:PMMA copolymer, for example, PS-r-PMMA (60% PS) grafted to an oxide substrate.

[00107] As previously described, a neutral wetting layer can also be formed on a base material 112 such as an oxide by grafting and heating a random copolymer of polystyrene (PS) and polymethacrylate (PMMA) with a few % (e.g., less than or equal to about 5%) hydroxyl group(s) (e.g., 2-hydroxyethyl methacrylate (P(S-r-MMA-r-HEMA)) on the base material. In another embodiment, a surface that is neutral wetting to PS-b-PMMA can also be prepared by spin coating and crosslinking 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)) on the base material.

[00108] In yet another embodiment, a base material 112 of silicon (with native oxide) can be treated by a fluoride ion etch (e.g., with aqueous HF, buffered HF or NH_4F , HF vapor

treatment, etc.) or a hydrogen plasma etch as previously described, to form hydrogen-terminated silicon, which is neutral wetting to a block copolymer material such as PS-b-PMMA. An H-terminated silicon material **114** can be further processed by grafting of a random copolymer such as PS-r-PMMA onto the material **114** (e.g., *in situ* free radical polymerization of styrene and methyl methacrylate with a di-olefinic linker).

[00109] Referring now to **FIG. 34**, a lamellar- or cylindrical-phase block copolymer material **116** is then cast as a film onto the neutral wetting material **114** on the substrate **110**. The block copolymer material has 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). The block copolymer material can be deposited by spin casting or 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. The thickness (t) of the block copolymer material **116** is at or about L_0 .

[00110] The block copolymer material **116** is then induced to self assemble by contact with a stamp, which, according to the invention, is topographically flat and chemically patterned on its surface.

[00111] **FIGS. 35-39** illustrate an embodiment of a process for forming a master template for forming a stamp for use in inducing self-assembly of a block copolymer material on a substrate. The master template (generally **118**), which is topographically flat, is prepared by forming a pattern of chemically differentiated areas on the surface of a base substrate **120**. The base substrate **120** can be composed, for example, of silicon dioxide or gold.

[00112] Referring to **FIG. 35**, in one embodiment, a hydrophilic material **122** on the base substrate **120** can be micropatterned to form the chemical master template **118**. The hydrophilic material **122** can be, for example, silicon (with native oxide), oxide (e.g., silicon oxide, SiO_x), indium tin oxide (ITO), silicon nitride, silicon oxycarbide, silicon oxynitride. In another embodiment, the hydrophilic material **122** can be composed of a metal, for example, gold, silver, copper, palladium or platinum, on the base substrate **122** and an overlying SAM of an alkane thiol such as hydroxyundecylthiol (HUT), or other hydrophilic alkane thiol. The

hydrophilic material **122** can be formed on the base substrate **120** as a monolayer (SAM) of about 0.5-5 nm thick.

[00113] As shown in **FIG. 36**, a layer of resist material **124** can be formed on the hydrophilic material **122**, and then developed in a desired pattern and removed (**FIGS. 37-37B**) to expose portions of the hydrophilic material **122**. The resist material can be patterned using a lithographic tool having an exposure system capable of patterning at the scale of at or about L_0 (10-100 nm). The material for the resist is selected based on the required sensitivity and compatibility with the exposure system that is used. Such exposure systems include, for example, extreme ultraviolet (EUV) lithography, electron beam (e-beam) lithography, immersion lithography, and proximity X-rays as known and used in the art. The pattern formed in the resist material **124** can be composed, for example, of a series of linear openings (stripes) **126**, as shown in **FIGS. 37-37B**.

[00114] Referring now to **FIGS. 38-38B**, a hydrophobic material **128** can then be deposited onto the exposed sections of the hydrophilic material **122** using the resist **124** as a mask. The hydrophobic material **128** can be, for example, an alkyl trialkoxysilane such as methyltrimethoxysilane, methyltriethoxysilane, methyltriisopropoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, n-propyltrimethoxysilane and n-propyltriethoxysilane; an alkylthiolate such as dodecanethiol or octadecanethiol (ODT); among others. The hydrophobic material **128** can be deposited as a monolayer (e.g., self-assembled monolayer (SAM)) of about 0.5-5 nm thick.

[00115] As illustrated in **FIGS. 39-39B**, the resist **124** can then be stripped to expose the previously masked portions of the hydrophilic material **122**. The resulting master template **118** now bears a chemically patterned surface **130** composed of lines of the hydrophobic material **128** (e.g., alkyl trialkoxysilane) adjacent to lines of the hydrophilic material **122** (e.g., oxide). For example, a master template **118** can be prepared with a surface patterned with hydrophobic SAM **128** of octadecanethiol (ODT) adjacent to a hydrophilic SAM **122** of 11-hydroxyundecane-1-thiol (HUT), as described by van Poll et al., *Angew. Chem. Int. Ed.*: 46, 6634-6637 (2007).

[00116] The hydrophilic 122 and hydrophobic 128 material elements on the surface of the master template 118 are dimensioned with a width (w_1) that matches or substantially matches the inherent self-assembled structure (e.g., L_0 value) of the block copolymer material (BCP) 116 that is deposited on the substrate 110 (FIG. 34) in those sections of the polymer material 116 where self-assembly into perpendicular-oriented structures (e.g., lamellae, cylinders) is desired. In areas of the polymer material 116 where a lack of formation of perpendicular-oriented elements is desired, a hydrophobic region 128a (FIG. 39) (or hydrophilic region) can be formed with dimensions (i.e., width (w_2)) that are greater than the L_0 value of the BCP material 116.

[00117] Referring to FIG. 40, in another embodiment of forming a chemical master 118', a hydrophobic material 128' (e.g., an alkyl trialkoxysilane) can be blanket deposited onto a base substrate 120' such as silicon or silicon oxide, for example. The hydrophobic material 128' can then be patterned and removed using a resist 124' as a mask as shown in FIGS. 41-41B, to expose portions of the base substrate 120'. Then, as depicted in FIGS. 42-42B, the exposed base substrate can then be selectively oxidized to form a hydrophilic monolayer (SAM) 122', or in other embodiments, a hydrophilic material (e.g., oxide, SiN, alkane thiol, etc.) can be deposited onto the exposed base substrate 120'. Then, as illustrated in FIGS. 43-43B, the resist 124' can be stripped, with the surface 130' of the master template 118' now bearing a pattern of lines of the hydrophobic material 128' adjacent to lines of the hydrophilic material 122'.

[00118] Using the master template 118 (e.g., FIG. 39) as a guide, a stamp (generally 132) is then formed with hydrophilic and hydrophobic elements in a mirror image of the pattern of elements on the master template surface. The chemically differentiated surface of the stamp 132 can then be used to direct self assembly of the block copolymer material 116 on the substrate 110 (FIG. 33).

[00119] Referring to FIGS. 44-44B, in some embodiments, a soft, flexible or rubbery material 134 such as a polydimethylsiloxane (PDMS) elastomer or other elastomeric, cross-linkable polymer material (e.g., silicones, polyurethanes, etc.) is deposited onto the chemically patterned surface 130 of the master template 118 to form a stamp 132. The

unmodified surface of a PDMS material is hydrophobic. To modify the surface of the stamp, the polymer material can be prepared as a mixture of the elastomeric polymer with different functional small molecules, e.g., a hydrophilic molecule **136a** and a hydrophobic molecule **136b**. As illustrated in **FIGS 45-45B**, preferential wetting by molecules **136a**, **136b** over the polymer material **134** against the master template **118** (arrow $\downarrow$) directs the migration and preferential accumulation (self-assembly) of the small molecules **136a**, **136b** at the surface **138** of the polymer stamp **132** in response to the hydrophilic **122** and hydrophobic **128** regions or elements on the functionalized surface **130** of the master template **118**. During curing, a crosslinking agent of the polymer material **134** reacts with the small molecules **136a**, **136b** and with functional groups of the polymer to "freeze" the pattern of small hydrophilic and hydrophobic molecules **136a**, **136b** into the polymer (e.g., PDMS elastomer) stamp **132** against the hydrophilic **122** and hydrophobic **128** surfaces, respectfully, of the master template **118**. The resulting stamp **132** has a flat surface **138** that bears a pattern of sub-micrometer features of different chemical functionalities (hydrophilic **136a** and hydrophobic **136b**) that replicates the pattern of hydrophilic (**122**) and hydrophobic (**128**) elements on the master template **118**.

[00120] For example, a PDMS elastomer material, such as Sylgard-184 (Dow-Corning), can be prepared as a mixture of PDMS and small functional hydrophobic and hydrophilic molecules (e.g., vinyl-terminated molecules with different head groups), as described by van Poll et al., *Angew. Chem. Int. Ed.*: 46, 6634-6637 (2007). Examples of small hydrophobic molecules include perfluorinated alkenes (e.g., 1*H*,1*H*,2*H*-perfluorodecene), vinyl esters (e.g., alky 2-bromo-2-methyl propionic acid ester), and hydrocarbon alkenes (e.g., 11-undecene), among others. Examples of small hydrophilic molecules include oligo(ethylene glycol) methacrylate (OEGMA), undec-11-enyl hexaethylene glycol monomethyl ether (PEG₆ derivative), and vinylic (mono- or divinyl) poly(ethylene glycol), among others. The PDMS can be mixed, for example, with equimolar amounts of a small amount of the small molecules, generally less than about 5 wt-% (e.g., about 2-3 wt-%). During curing, the molecules will self-assemble according to the functionalized monolayer on the template surface and react with the PDMS backbone by a hydrosilylation reaction during curing.

[00121] Referring now to FIGS. 46 and 47-47A, the now chemically functionalized polymer stamp 132 can then be removed (arrows $\uparrow\uparrow$) from the surface 130 of the master template 118. For example, a solvent such as water (arrows $\downarrow\downarrow$) can be applied or the stamp/template complex soaked in the solvent, which will permeate and swell the stamp body 132 and weaken the interfacial bonds on the hydrophilic areas, and the stamp can then be peeled from the surface of the master template, as shown in FIG. 46.

[00122] As illustrated, the surface 138 of the stamp 132 is chemically differentiated according to the pattern of hydrophilic and hydrophobic elements on the master template 118. The surface of the stamp 132 is composed of hydrophilic lines 136a that are preferential wetting to one domain of the block copolymer (e.g., PMMA) and hydrophobic lines 136b that are preferential wetting to the other block of the block copolymer (e.g., PS). As on the master template, the dimensions (i.e., width (w_1)) of the lines 136a, 136b match or substantially match the dimensions (i.e., w_1) of the hydrophilic lines 122 and hydrophobic lines 128, respectively, on the surface 130 of the master template 118, as well as the L_o value of the block copolymer material (BCP) 116 on the substrate 110 (FIG. 34). The stamp 132 includes a hydrophobic section 136b₁ that has a width (w_2) that corresponds to the dimensions (w_2) of the hydrophobic section 128a on the chemical master 118, which is greater than the BCP L_o value.

[00123] Referring now to FIG. 48, the chemically patterned surface 138 of the stamp 118 is now brought into contact with the surface 140 of the block copolymer material 116 situated on the neutral wetting material 114 on the substrate 110, for example, by pressing the stamp surface 138 onto the block copolymer material (FIG. 49). The rubbery or flexible body of the stamp 132 allows the stamp to conform to the topography of the block copolymer material 116. As depicted in FIG. 50, the block copolymer material 116 is then annealed (arrows $\downarrow\downarrow$) while in contact with the chemically patterned stamp surface to form a self-assembled polymer material 142.

[00124] The chemical pattern of hydrophilic and hydrophobic lines 136a, 136b on the surface of the stamp 132 will direct the self-assembly and perpendicular ordering of the polymer domains of the block copolymer material 116 in regions in which the pitch (w_1) of the

elements **136a**, **136b** on the stamp surface is at or about the inherent pitch or L_o value of the block copolymer material **116**.

[00125] For example, as depicted in **FIGS. 50-50A**, in the use of a lamellar-phase block copolymer (e.g., PS-*b*-PMMA), during the anneal, the PMMA block will align with and preferentially wet the hydrophilic material (lines) **136a** on the surface of the stamp **132** and the PS block will align with and preferentially wet the hydrophobic material (lines) **136b** to form lines of PMMA lamella **144a** and PS lamella **144b**. The neutral wetting material **114** on the substrate **110** ensures that the perpendicular-oriented lamellae extend completely through the self-assembled polymer material **142** from the interface with the neutral wetting material **114** to the surface **138** of the stamp **132** on those lines **136a**, **136b** that have a pitch (w_1) that is at or about the L_o value of the block copolymer material.

[00126] In regions of the substrate **110** where subsequent patterning (using the self-assembled BCP layer as a mask) is not desired, the contact of the block copolymer material with a stamp region (e.g., **136b₁**) which has a width (w_2) that is greater than the L_o value of the block copolymer and is preferential wetting to only one domain of the block copolymer, will result in the formation of parallel-oriented lamellae **144a₁**, **144b₁** for a corresponding width (w_2) within the self-assembly polymer material **142**.

[00127] Referring now to **FIGS. 51-52**, the stamp **132** is then removed from contact ($\uparrow\uparrow$) with the surface of the self-assembled polymer layer **142**. To break the adhesive forces (e.g., Van der Waals forces) and lift the stamp from the polymer surface, in some embodiments, the stamp/solvent complex can be soaked in a solvent (e.g., water, isopropyl alcohol, acetic acid, etc.) that will permeate and swell the body of the stamp **132** (e.g., PDMS) but not the polymer domains **144a**, **144b** of the annealed, self-assembled polymer material **142**. In some embodiments, a solvent can be used that also swells one but not both of the polymer domains of the self-assembled polymer material, e.g., the polymer domain that is subsequently selectively removed (e.g., PMMA lamellae **144a**). After separation and removal of the stamp from the self-assembled polymer material, the stamp **132** can then be re-used for further templating on another area or substrate bearing a BCP material layer.

[00128] The self-assembled polymer material 142 can then be developed to selectively remove one of the polymer domains (e.g., PMMA lamellae 144a) to produce a mask 146 composed of the remaining polymer domain (e.g., PS lamellae 144b) with openings 148 in the desired pattern of lines exposing the substrate 112, as shown in FIGS. 53-53A. The underlying substrate 112 can then be etched (arrows $\downarrow\downarrow$) using the mask 146, as shown in FIGS. 54-54A, to form openings 150 to an underlying active area or element 152. The residual mask 146 (i.e., PS lamellae 144b, 144b₁ and PMMA lamella 144a) can then be removed and the openings 150 filled with a material 154, e.g., a metal or conductive alloy such as Cu, Al, W, Si, and Ti₃N₄, among others, as shown in FIGS. 55-55A to form arrays of parallel conductive lines 154 having a width over a range of about 5-50 nm, to the underlying active area, contact, or conductive line 152. Further processing can be conducted as desired.

[00129] In other embodiments, the block copolymer material 116 can be cylindrical-phase block copolymer (BCP) on a neutral wetting layer 114 (FIG. 34). Referring to FIGS. 56-56B, a master template 118" can be formed with "dots" of a hydrophilic material 122" (e.g., oxide) surrounded by a hydrophobic material 128" (e.g., an alkyl trialkoxysilane). The dots of the hydrophilic material 122" are formed in regions where perpendicular cylinders in the BCP material are desired, and have a diameter (d) and pitch (p) equal to the L_0 value of the cylindrical-phase block copolymer (BCP) material or within about 10% or less than the L_0 value. Other regions (128") of the master template 118" where perpendicular cylinders are not desired are chemically patterned to be hydrophobic.

[00130] As shown in FIGS. 57-57A, a polymer material (e.g., PDMS) composed of hydrophilic 136a" and hydrophobic 136b" components (e.g., molecules) is formed and cured (arrows $\downarrow\downarrow$) on the master template 118". Upon curing, the hydrophilic components 136a" of the stamp material 134" align with the hydrophilic dots 122" and the hydrophobic components 136b" align with the hydrophobic regions 128" on the master template 118". The cured stamp 132" is then removed from the master template 118" and applied to a cylindrical-phase block copolymer material (e.g., 116 in FIG. 34), which is annealed while in contact with the stamp (FIGS. 58-58A (arrow $\downarrow$)).

[00131] Upon annealing, the cylindrical-phase BCP (116), will self-assemble into perpendicular-oriented cylinders 156'' composed of one polymer block (e.g., PMMA) in response to and aligned with the hydrophilic dots 136a'' on the surface 138'' of the stamp 132'', surrounded by a matrix 158'' of the other polymer block (e.g., PS) in response to the hydrophobic areas 136b'' on the stamp surface. In response to areas where the hydrophobic area 136b'' has a width (w'') that is greater than or equal to $1.5 \cdot L_o$, the block copolymer material will self-assemble to form one or more lines of half-cylinders 156a'', which are oriented parallel to and in contact with the neutral wetting layer 114''. The number of lines of half-cylinders 156a'' can vary according to the width (w''), for example, a single line of a parallel half-cylinder will form from a block copolymer ($L_o=50$ nm) where the hydrophobic area 136b'' has a width (w'') of about 70-80 nm. The stamp 132'' is then removed (arrow $\uparrow$) from the surface of the annealed and self-assembled block copolymer material 142''.

[00132] As depicted in FIG. 59, the cylinders 156'' (e.g., PMMA block) can then be selectively removed to form a mask 146'' composed of cylindrical openings 148'' within the matrix 158'' of the other polymer block (e.g., of PS) to expose the base substrate 112''. The substrate 112'' can then be etched using the mask 146'' to form cylindrical openings 150'' (shown in phantom) to active areas 152'' in the substrate 112''. The etched openings 150'' can be filled with an appropriate material 154'' to form contacts to the underlying active areas 152'' (e.g., conductive lines), as depicted in FIGS. 60-60A. The substrate can then be additional processed as needed.

[00133] The present embodiment of the invention of overlying a chemically patterned stamp to direct self-assembly of a BCP film eliminates the need for forming a substrate template pattern, which requires the use of a patterning technique such as EUV lithography or other sub-lithographic patterning techniques to physically or chemically pattern the surface of a substrate, e.g., with chemical stripes (chemical templating), each stripe being preferentially wetted by the alternate blocks of a block copolymer to cause polymer domains to orient themselves above the preferred stripes and perpendicular to the surface. The present embodiment of a chemically patterned stamp provides a low cost and re-usable method to provide registered self-assembled block copolymers with long-range order without the need for patterning a substrate.

[00134] The use of a chemically patterned stamp to direct ordering of a self-assembling block copolymer material does not require patterning of the substrate to form a topographically varied surface as required by graphoepitaxial self-assembly, which significantly reduces costs. Also, only an original master template requires patterning using sub-lithographic tools (e.g., EUV, e-beam, etc.), and at least two levels of amplification result including the fabrication of multiple stamps from a single master template, and the ability to use each stamp multiple times to direct ordering of BCP materials. As a result, the cost of preparing the master template is significantly amortized. In addition, since the stamp is topographically flat, problems of lift-off from a self-assembled polymer film are minimized in conjunction with the surface areas in contact, which provides a significant advantage over nanoimprint lithography. Long-range order and defectivity of a self-assembled block copolymer film is also improved as the stamp templates and directs the proper order in each region of the film. By comparison, graphoepitaxy requires force fields generated from topographic features to impose order from a distance.

[00135] As depicted in **FIG. 61**, the present stamp embodiments can be used to form a variety of geometries for integrated circuit layouts **154**, including periodic conductive lines **156** and contacts **158**, lines with bends **160**, isolated lines and contacts, etc., as needed for the circuit design. Dies comprising the conductive lines and contacts can be incorporated into a circuit module, device or electronic system, including processor systems.

[00136] 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 stamp, comprising a substrate and a self-assembled block copolymer film thereon, the film comprising a first polymer block having an affinity for and swellable by absorption of an ink chemical and a second polymer block having substantially no affinity for and not swellable by said ink chemical.

2. The stamp of Claim 1, wherein the copolymer film comprises perpendicular-oriented cylinders of the first polymer block, parallel-oriented half-cylinders of the first polymer block, or perpendicular-oriented, alternating lamellar domains of the first polymer block and the second polymer block.

3. The stamp of Claim 1, further comprising an ink material selectively absorbed within said first polymer domain without chemically bonding to said first polymer domain.

4. The stamp of Claim 3, wherein the ink material comprises an ink chemical having an amino, thiol, alcohol, azide or alkyne functional group, or a combination thereof.

5. A method of forming a stamp, comprising forming a self-assembled block copolymer film on a stamp substrate, said block copolymer film comprising a first polymer block capable of absorbing an ink chemical to swell said first polymer block and a second polymer block having substantially no affinity for and not swellable by said ink chemical.

6. The method of Claim 5, further comprising:
forming a film comprising the block copolymer in a trench within the stamp substrate, the trench having sidewalls and ends that are preferential wetting to one of the blocks of the block copolymer, and a floor that is preferential wetting to one of the blocks of the block copolymer, neutral wetting to the blocks of the block copolymer, or a combination of preferential wetting and neutral wetting areas; and

causing the block copolymer film to self-assemble to form said self-assembled block copolymer film.

7. The method of Claim 6, wherein the trench floor is neutral wetting, and the self-assembled block copolymer film comprises perpendicularly-oriented cylindrical domains of the first polymer block in a matrix of the second polymer block or alternating lamellar domains of the first polymer block and the second polymer block.

8. The method of Claim 6, wherein the trench floor is preferential wetting, and the self-assembled block copolymer film comprises parallel-oriented half-cylindrical domains of the first polymer block in a matrix of the second polymer block.

9. The method of Claim 6, further comprising, prior to forming the block copolymer film, chemically patterning the floor of the trench to form said combination of preferential wetting and neutral wetting areas,

wherein the block copolymer film comprises a cylindrical-phase block copolymer.

10. The method of Claim 6, further comprising applying an ink material to a surface of the self-assembled block copolymer film wherein the ink material is selectively absorbed into and swells said first polymer block but not the second polymer block.

11. The method of Claim 10, wherein the ink chemical is selected from the group consisting of a thiol, a mercaptoalcohol and an acetylenic with a functional tail group selected from the group consisting of hydrocarbons, alcohols, thiols, amines and halides.

12. A method of forming a pattern on a substrate, comprising:
applying an ink material to a surface of a stamp comprising a self-assembled block copolymer film wherein the ink material is selectively absorbed into and swells a first polymer block but not a second polymer block of the block copolymer film;
contacting the surface of the stamp with the substrate to transfer the ink material onto said substrate to form said pattern.

13. The method of Claim 12, wherein the receptor substrate comprises a glycidoxy-, isocyanato-, alkylazido- or chlorosilyl- functional group; and

the ink material is transferred by chemical bonding of the ink material with the substrate through a linkage selected from the group consisting of a urea linkage, a urethane linkage, a disulfide linkage, an acid-base linkage or an amine linkage.

14. The method of Claim 13, further comprising, selectively depositing a material on the ink material on the substrate to increase the thickness or hardness of the ink material.

15. The method of Claim 14, etching the substrate wherein the material on the ink material masks the substrate.

16. The method of Claim 12, further comprising selectively forming a material on exposed areas of the substrate, said material being chemically different from the ink material.

17. The method of Claim 16, wherein the ink material comprises a hydrophobic material and a hydrophilic material is formed on the substrate, and the method further comprises:

forming a block copolymer material on said hydrophobic ink material and hydrophilic material, and processing said block copolymer material to form a self-assembled block copolymer layer, wherein one polymer block is registered to the hydrophobic ink material and another polymer block is registered to the hydrophilic material; and

selectively removing one block of the self-assembled block copolymer layer to form an etch mask for etching the substrate.

18. A stamp, comprising:

a transparent material section extending from a first surface to a second surface, wherein a radiation source is transmittable through the transparent section; and the first surface having a polymerizable material thereon.

19. The stamp of Claim 18, wherein the polymerizable material is a neutral wetting material.

20. The stamp of Claim 19, wherein the neutral wetting material comprises a random block copolymer.

21. A method of forming a pattern on a substrate, comprising:

applying a polymerizable material to a first surface of a stamp comprising a transparent material section extending from the first surface to a second surface; contacting the stamp with the substrate to apply the polymerizable material; transmitting a radiation source through the transparent section of the stamp to polymerize portions of the polymerizable material; and removing the stamp from the substrate.

22. The method of Claim 21, further comprising, removing non-polymerized material to expose portions of the substrate.

23. The method of Claim 22, wherein the polymerized material comprises a neutral wetting material and the substrate comprises a preferential wetting material, and the method further comprises applying a self-assembling block copolymer material thereover, and annealing the copolymer material to form a self-assembled polymer layer.

24. The method of Claim 23, further comprising selectively removing one block of the self-assembled polymer layer to form an etch mask for etching the substrate.

25. A method of forming a self-assembled block copolymer material, comprising:
contacting a block copolymer material with a stamp comprising a surface comprising an area of hydrophilic material and an area of a hydrophobic material, said hydrophilic and hydrophobic areas having a width at or about the L_o value of the block copolymer material, the block copolymer material situated on a neutral wetting material; and

annealing the block copolymer material to cause self-assembly of the block copolymer material into perpendicular-oriented polymer domains, wherein one polymer block domain preferentially wets the hydrophilic material on the stamp surface and another polymer block domain preferentially wets the hydrophobic material on the stamp surface.

26. The method of Claim 25, further comprising removing the stamp from contact with the block copolymer material.

27. The method of Claim 26, further comprising contacting the stamp with a second block copolymer material.

28. The method of Claim 26, further comprising:
removing one of the polymer block domains of the self-assembled block copolymer material to form a mask comprising the remaining polymer block with openings that expose the substrate; and

etching the substrate through the openings in the mask.

29. The method of Claim 25, further comprising preparing the stamp by:
forming a master template comprising a surface having defined hydrophilic and hydrophobic areas;

depositing an elastomeric polymer material on the surface of the master template, the polymer material comprising hydrophilic and hydrophobic components;

curing the polymeric material to form the stamp having a chemically patterned surface with the hydrophilic components on the surface registered to the hydrophilic areas of the master template and the hydrophobic components on the surface registered to the hydrophobic areas of the master template; and

removing the stamp from the master template.

30. The method of Claim 29, wherein the elastomeric polymer is selected from the group consisting of poly(dimethylsiloxane), silicones and polyurethanes.

31. The method of Claim 30, wherein the hydrophobic component is a molecule selected from the group consisting of perfluorinated alkenes, vinyl esters, and hydrocarbon alkenes.

32. The method of Claim 30, wherein the hydrophilic component is a molecule selected from the group consisting of oligo(ethylene glycol) methacrylate, undec-11-enyl hexaethylene glycol monomethyl ether, and vinylic poly(ethylene glycol).