60 of each trench or opening 40 can be selectively wetted by one block of the block copolymer. Selective wetting results from the difference in interfacial energies between the sidewall surface and each block of the block copolymer. This difference in interfacial energy can be due to the chemical composition of each material (e.g., structures that favor hydrogen bonding).

[35] Referring to Figures 1 and 2, in certain embodiments, a substantially symmetric diblock copolymer 100 having an inherent periodicity of L_o can be deposited within a trench or opening 40 (e.g., the copolymer layer is less than or equal to the depth of trench or opening), wherein floor 50 of trench or opening 40 is neutral-wetting with respect to each block of block copolymer 100, and both sidewalls 60 of trench or opening 40 are selectively wetted by one block of block copolymer 100.

[36] Referring to Figure 3, the deposited copolymer 100 can then be annealed to allow the diblock copolymer to self-assemble and form within each trench a set of alternating lamellae 110 and 120 that are substantially perpendicular to the surface and substantially in register with each trench sidewall. As used herein, "substantially perpendicular" lamellae refers to a set of lamellae that are, on average, perpendicular to the surface. As used herein, lamellae that are "substantially in register" with a trench sidewall refers to lamellae that are parallel to the sidewall (i.e., positioned at a constant distance from the sidewall) over a trench length of at least 10 micrometers. Figures 1 to 3 illustrate an embodiment in which n = 4 (i.e., the width of each trench 40 is $4L_o$), and thus, 4 periods of lamellae are shown. However, as discussed herein above, n can be from 1 to 15, and accordingly from 1 to 15 periods of lamellae would result in these embodiments.

[37] In certain embodiments, lamellae 110 that include a first block of the self-assembled block copolymer can optionally be crosslinked, for example, by exposure to radiation, e.g., ultraviolet (UV) radiation. In some embodiments, the block of the block copolymer being crosslinked can be susceptible to crosslinking without the addition of crosslinking agent. For

example, if the block copolymer is a polystyrene-*b*-polymethylmethacrylate diblock copolymer, the polystyrene block can be crosslinked by exposure to UV radiation. For further examples, one block of the block copolymer can be made thermally crosslinkable by including a small amount (e.g., 0.1 to 5 mole %) of a thermally crosslinkable monomer (e.g., a benzocylobutane-containing monomer) and/or made photochemically crosslinkable by including a small amount (e.g., 0.1 to 5 mole %) of a photochemically crosslinkable monomer (e.g., divinyl benzene) in the block of the copolymer. In certain other examples, one block of the block copolymer can be made thermally and/or photochemically crosslinkable by including a small amount (e.g., 0.1 to 5 mole %) of a thermally and/or photochemically crosslinkable monomer (e.g., para-azidomethylstyrene). Alternatively, or in addition to, in some embodiments, crosslinking agents can be added to the lamellae that are to be crosslinked. A wide variety of crosslinking agents are known in the art and include, for example, the combination of a crosslinker (e.g., 1,3,5-trimethyl-2,4,6-(triacetoxymethyl)benzene) and a thermal acid generator (e.g., cyclohexylmethyl(2-oxocyclohexyl)sulfonium trifluoromethanesulfonate). Crosslinked lamellae can have, for example, improved mechanical properties and lower susceptibility to removal.

[38] Remaining uncrosslinked lamellae 120 can optionally be selectively removed (not illustrated in Figure 3), subsequent to crosslinking in certain embodiments, leaving the crosslinked lamellae 110 on the surface, although removal of uncrosslinked lamellae at this stage can, in certain embodiments, result in filling of such newly formed trenches with a second block copolymer when it is subsequently deposited. A wide variety of methods for removing uncrosslinked lamellae are known in the art including, for example, irradiation (e.g., UV or electron beam), ozone treatment, wet chemical processing methods such as immersion in a solvent, and/or etching methods such as reactive ion etching and ion beam etching. For example, when the block copolymer is a polystyrene-*b*-polymethylmethacrylate diblock copolymer and the lamellae including the polystyrene block are crosslinked, the remaining lamellae including the uncrosslinked

on the substrate surface. For example, if the block copolymer is a polystyrene-*b*-polymethylmethacrylate diblock copolymer, a crosslinkable polystyrene-*r*-polymethylmethacrylate random copolymer can be used as the polymer mat.

[41] In certain embodiments, polymer mat 20 can be crosslinked, for example, by exposure to radiation, e.g., ultraviolet (UV) radiation. In some embodiments, the polymer mat being crosslinked can be susceptible to crosslinking without the addition of crosslinking agent. For example, if the polymer mat is a polystyrene-*r*-polymethylmethacrylate random copolymer, the polystyrene in the random copolymer can be a crosslinking site upon exposure to UV radiation. For further examples, the polymer mat can be made crosslinkable by including a small amount (e.g., 0.1 to 5 mole %) of a thermally crosslinkable monomer (e.g., a benzocylobutane-containing monomer) or a photochemically crosslinkable monomer (e.g., divinyl benzene and/or para-azidomethylstyrene) in the polymer mat. In certain other examples, the polymer mat can be made thermally and/or photochemically crosslinkable by including a small amount (e.g., 0.1 to 5 mole %) of a thermally and/or photochemically crosslinkable monomer (e.g., para-azidomethylstyrene). Alternatively, or in addition to, in some embodiments, crosslinking agents can be added to the polymer mat. A wide variety of crosslinking agents are known in the art and include, for example, the combination of a crosslinker (e.g., 1,3,5-trimethyl-2,4,6-(triacetoxymethyl)benzene) and a thermal acid generator (e.g., cyclohexylmethyl(2-oxocyclohexyl)sulfonium trifluoromethanesulfonate). In certain embodiments, the crosslinked polymer mat can have resistance adequate to withstand further processing steps encountered during the block copolymer self-assembly process.

[42] Alternatively, in certain embodiments, the substrate surface can be modified by preparing a hydrogen-terminated silicon surface. For example, a silicon substrate having thereon a layer of oxide of thickness Y can be etched (e.g., with a plasma etch) to form trenches having a depth of Y' that is less than Y. The remaining oxide, having a thickness Y minus Y', on the

known in the art including, for example, preparing homopolymers with end groups (e.g., hydroxyl groups) and/or including a small amount (e.g., 0.1 to 5 mole %) of a hydroxyl-functional monomer (e.g., 2-hydroxyethylmethacrylate and/or para-hydroxystyrene) in the homopolymer such that the hydroxyl groups can interact (e.g., by forming hydrogen and/or covalent bonds) with the silicon-containing surface.

[48] In certain embodiments, a substrate including a plurality of lithographically derived trenches can be prepared using etching technology. For example, a substrate having a surface including a plurality of weirs can be prepared by the following method. A layer of thickness Y can be deposited on a substrate surface, and the layer can be selectively etched using lithographic techniques to form a topography of weirs and trenches.

[49] Referring to Figure 1, a substrate 10 having a plurality of weirs 30 of height Y, forming a surface topography of weirs 30 and trenches 40 of width nL_o, wherein n can be from 1 to 15. The plurality of trenches 40 (e.g., lithographically derived trenches) can be used as a guide for self-assembly of block copolymers as described herein. Referring to Figure 2, block copolymer 100 having an inherent periodicity of L_o can be deposited to form a layer of thickness less than or equal to Y within the plurality of trenches 40. Referring to Figure 3, block copolymer 100 can then be annealed to allow the block copolymer to self-assemble and form within each trench a set of alternating lamellae 110 and 120 that are substantially perpendicular to the substrate surface and substantially in register with each trench sidewall 60. Lamellae 110 that include a first block of the self-assembled block copolymer can be crosslinked. Referring to Figures 3 and 4, at least a portion of material forming weirs 30 can be removed (e.g., using wet and/or dry etching methods) to form at least one opening 240 having a depth of Y'. Such openings 240 are referred to herein as "self-assembled copolymer" defined openings or trenches.

[50] The self-assembled copolymer defined openings or trenches 240 can then be used as guides for self-assembly of block copolymers as described

What is claimed is:

1. A method of patterning a substrate, comprising:

forming weirs and trenches over a substrate, the weirs individually comprising a self assembled first block copolymer comprising a first set of alternating lamellae;

forming a second block copolymer within the trenches; and

self-assembling the second block copolymer within the trenches to form a second set of alternating lamellae within individual of the trenches.

2. The method of claim 1 wherein the first and second block copolymers are of the same composition.

3. The method of claim 1 wherein the first and second block copolymers are of different compositions.

4. The method of claim 1 wherein the weirs and trenches are formed to have substantially perpendicularly straight sidewalls.

5. The method of claim 1 wherein the second block copolymer is substantially symmetric.

6. The method of claim 1 wherein the second block copolymer prior to self-assembling has a thickness equal to or less than depth of the trenches.

7. The method of claim 6 wherein the second block copolymer prior to self-assembling has a thickness less than depth of the trenches.

8. The method of claim 1 wherein sidewalls of the trenches are selectively wetted by one block of the second block copolymer.

9. The method of claim 1 wherein floors of the trenches are neutral-wetting to each block of the second block copolymer.

10. The method of claim 1 wherein sidewalls of the trenches are selectively wetted by one block of the second block copolymer and floors of the trenches are neutral-wetting to each block of the second block copolymer.

11. The method of claim 1 comprising removing alternating lamellae of the first set and alternating lamellae of the second set to form openings where lamellae were removed.

12. The method of claim 1 comprising:

removing alternating lamellae of the first set and alternating lamellae of the second set to form a mask over the substrate, the mask comprising mask openings where lamellae were removed; and

using the mask with mask openings to etch a pattern of openings into the substrate under the mask.

13. The method of claim 1 comprising:

removing alternating lamellae of the first set and alternating lamellae of the second set to form a mask over the substrate, the mask comprising mask openings where lamellae were removed; and

depositing material into the mask openings.

14. The method of claim 13 wherein the material is conductive.

15. The method of claim 13 wherein the material is non-conductive.

16. The method of claim 1 wherein individual of the trenches have a width of nL_0, wherein "n" is from 1 to 15 and L_0 is an inherent periodicity of the second block copolymer.

17. The method of claim 16 wherein individual of the trenches are of constant width.

18. The method of claim 17 wherein the trenches are of the same constant width.

19. The method of claim 1 wherein the first set of alternating lamellae are of the same elevational thickness.

20. The method of claim 1 wherein the second set of alternating lamellae are of the same elevational thickness.

21. The method of claim 1 wherein the first set of alternating lamellae are of the same elevational thickness and the second set of alternating lamellae are of the same elevational thickness which is different from that of the first set of alternating lamellae.

22. The method of claim 21 wherein the elevational thickness of the second set of alternating lamellae is less than that of the first set of lamellae.

23. A method of patterning a substrate, comprising:

forming first trenches in sacrificial material over a substrate;

forming a first block copolymer within the first trenches;

self-assembling the first block copolymer within the first trenches to form a first set of alternating lamellae within the first trenches;

removing the sacrificial material to form second trenches over the substrate, the second trenches comprising sidewalls which comprise the self-assembled first block copolymer;

forming a second block copolymer within the second trenches; and

self-assembling the second block copolymer within the second trenches to form a second set of alternating lamellae within the second trenches.

60 of each trench or opening 40 can be selectively wetted by one block of the block copolymer. Selective wetting results from the difference in interfacial energies between the sidewall surface and each block of the block copolymer. This difference in interfacial energy can be due to the chemical composition of each material (e.g., structures that favor hydrogen bonding).

[35] Referring to Figures 1 and 2, in certain embodiments, a substantially symmetric diblock copolymer 100 having an inherent periodicity of L_o can be deposited within a trench or opening 40 (e.g., the copolymer layer is less than or equal to the depth of trench or opening), wherein floor 50 of trench or opening 40 is neutral-wetting with respect to each block of block copolymer 100, and both sidewalls 60 of trench or opening 40 are selectively wetted by one block of block copolymer 100.

[36] Referring to Figure 3, the deposited copolymer 100 can then be annealed to allow the diblock copolymer to self-assemble and form within each trench a set of alternating lamellae 110 and 120 that are substantially perpendicular to the surface and substantially in register with each trench sidewall. As used herein, "substantially perpendicular" lamellae refers to a set of lamellae that are, on average, perpendicular to the surface. As used herein, lamellae that are "substantially in register" with a trench sidewall refers to lamellae that are parallel to the sidewall (i.e., positioned at a constant distance from the sidewall) over a trench length of at least 10 micrometers. Figures 1 to 3 illustrate an embodiment in which $n = 4$ (i.e., the width of each trench 40 is $4L_o$), and thus, 4 periods of lamellae are shown. However, as discussed herein above, n can be from 1 to 15, and accordingly from 1 to 15 periods of lamellae would result in these embodiments.

[37] In certain embodiments, lamellae 110 that include a first block of the self-assembled block copolymer can optionally be crosslinked, for example, by exposure to radiation, e.g., ultraviolet (UV) radiation. In some embodiments, the block of the block copolymer being crosslinked can be susceptible to crosslinking without the addition of crosslinking agent. For example, if the block copolymer is

a polystyrene-*b*-polymethylmethacrylate diblock copolymer, the polystyrene block can be crosslinked by exposure to UV radiation. For further examples, one block of the block copolymer can be made thermally crosslinkable by including a small amount (e.g., 0.1 to 5 mole %) of a thermally crosslinkable monomer (e.g., a benzocyclobutane-containing monomer) and/or made photochemically crosslinkable by including a small amount (e.g., 0.1 to 5 mole %) of a photochemically crosslinkable monomer (e.g., divinyl benzene) in the block of the copolymer. In certain other examples, one block of the block copolymer can be made thermally and/or photochemically crosslinkable by including a small amount (e.g., 0.1 to 5 mole %) of a thermally and/or photochemically crosslinkable monomer (e.g., para-azidomethylstyrene). Alternatively, or in addition to, in some embodiments, cross linking agents can be added to the lamellae that are to be crosslinked. A wide variety of crosslinking agents are known in the art and include, for example, the combination of a crosslinker (e.g., 1,3,5-trimethyl-2,4,6-(triacetoxymethyl)-benzene) and a thermal acid generator (e.g., cyclohexyl-methyl(2-oxocyclohexyl)sulfonium trifluoromethanesulfonate). Crosslinked lamellae can have, for example, improved mechanical properties and lower susceptibility to removal.

[38] Remaining uncrosslinked lamellae 120 can optionally be selectively removed (not illustrated in Figure 3), subsequent to crosslinking in certain embodiments, leaving the crosslinked lamellae 110 on the surface, although removal of uncrosslinked lamellae at this stage can, in certain embodiments, result in filling of such newly formed trenches with a second block copolymer when it is subsequently deposited. A wide variety of methods for removing uncrosslinked lamellae are known in the art including, for example, irradiation (e.g., UV or electron beam), ozone treatment, wet chemical processing methods such as immersion in a solvent, and/or etching methods such as reactive ion etching and ion beam etching. For example, when the block copolymer is a polystyrene-*b*-polymethylmethacrylate diblock copolymer and the lamellae including the polystyrene block are crosslinked, the remaining lamellae including the uncrosslinked

on the substrate surface. For example, if the block copolymer is a polystyrene-*b*-polymethylmethacrylate diblock copolymer, a crosslinkable polystyrene-*r*-polymethylmethacrylate random copolymer can be used as the polymer mat.

[41] In certain embodiments, polymer mat 20 can be crosslinked, for example, by exposure to radiation, e.g., ultraviolet (UV) radiation. In some embodiments, the polymer mat being crosslinked can be susceptible to crosslinking without the addition of crosslinking agent. For example, if the polymer mat is a polystyrene-*r*-polymethylmethacrylate random copolymer, the polystyrene in the random copolymer can be a crosslinking site upon exposure to UV radiation. For further examples, the polymer mat can be made crosslinkable by including a small amount (e.g., 0.1 to 5 mole %) of a thermally crosslinkable monomer (e.g., a benzocyclobutane-containing monomer) or a photochemically crosslinkable monomer (e.g., divinyl benzene and/or para-azidomethylstyrene) in the polymer mat. In certain other examples, the polymer mat can be made thermally and/or photochemically crosslinkable by including a small amount (e.g., 0.1 to 5 mole %) of a thermally and/or photochemically crosslinkable monomer (e.g., para-azidomethylstyrene). Alternatively, or in addition to, in some embodiments, crosslinking agents can be added to the polymer mat. A wide variety of crosslinking agents are known in the art and include, for example, the combination of a crosslinker (e.g., 1,3,5-trimethyl-2,4,6-(triacetoxymethyl)benzene) and a thermal acid generator (e.g., cyclohexylmethyl(2-oxocyclohexyl)sulfonium trifluoromethanesulfonate). In certain embodiments, the crosslinked polymer mat can have resistance adequate to withstand further processing steps encountered during the block copolymer self-assembly process.

[42] Alternatively, in certain embodiments, the substrate surface can be modified by preparing a hydrogen-terminated silicon surface. For example, a silicon substrate having thereon a layer of oxide of thickness Y can be etched (e.g., with a plasma etch) to form trenches having a depth of Y' that is less than Y. The remaining oxide, having a thickness Y minus Y', on the

known in the art including, for example, preparing homopolymers with end groups (e.g., hydroxyl groups) and/or including a small amount (e.g., 0.1 to 5 mole %) of a hydroxyl-functional monomer (e.g., 2-hydroxyethylmethacrylate and/or para-hydroxystyrene) in the homopolymer such that the hydroxyl groups can interact (e.g., by forming hydrogen and/or covalent bonds) with the silicon-containing surface.

[48] In certain embodiments, a substrate including a plurality of lithographically derived trenches can be prepared using etching technology. For example, a substrate having a surface including a plurality of weirs can be prepared by the following method. A layer of thickness Y can be deposited on a substrate surface, and the layer can be selectively etched using lithographic techniques to form a topography of weirs and trenches.

[49] Referring to Figure 1, a substrate 10 has a plurality of weirs 30 of height Y, forming a surface topography of weirs 30 and trenches 40 of width nL_o, wherein n can be from 1 to 15. The plurality of trenches 40 (e.g., lithographically derived trenches) can be used as a guide for self-assembly of block copolymers as described herein. Referring to Figure 2, block copolymer 100 having an inherent periodicity of L_o can be deposited to form a layer of thickness less than or equal to Y within the plurality of trenches 40. Referring to Figure 3, block copolymer 100 can then be annealed to allow the block copolymer to self-assemble and form within each trench a set of alternating lamellae 110 and 120 that are substantially perpendicular to the substrate surface and substantially in register with each trench sidewall 60. Lamellae 110 that include a first block of the self-assembled block copolymer can be crosslinked. Referring to Figures 3 and 4, at least a portion of material forming weirs 30 can be removed (e.g., using wet and/or dry etching methods) to form at least one opening 240 having a depth of Y'. Such openings 240 are referred to herein as "self-assembled copolymer" defined openings or trenches.

[50] The self-assembled copolymer defined openings or trenches 240 can then be used as guides for self-assembly of block copolymers as described

What is claimed is:

1. A method of patterning a substrate, comprising:

forming weirs and openings over a substrate, the weirs individually comprising a self-assembled first block copolymer comprising a first set of alternating lamellae; forming a second block copolymer within the openings;

and

self-assembling the second block copolymer within the openings to form a second set of alternating lamellae within individual of the openings.

2. The method of claim 1 wherein the first and second block copolymers are of the same composition.

3. The method of claim 1 wherein the first and second block copolymers are of different compositions.

4. The method of claim 1 wherein the weirs and openings are formed to have substantially perpendicularly straight sidewalls.

5. The method of claim 1 wherein the second block copolymer is substantially symmetric.

6. The method of claim 1 wherein the second block copolymer prior to self-assembling has a thickness equal to or less than depth of the openings.

7. The method of claim 6 wherein the second block copolymer prior to self-assembling has a thickness less than depth of the openings.

8. The method of claim 1 wherein sidewalls of the openings are selectively wetted by one block of the second block copolymer.

9. The method of claim 1 wherein floors of the openings are neutral-wetting to each block of the second block copolymer.

10. The method of claim 1 wherein sidewalls of the openings are selectively wetted by one block of the second block copolymer and floors of the openings are neutral-wetting to each block of the second block copolymer.

11. The method of claim 1 comprising removing alternating lamellae of the first set and alternating lamellae of the second set to form openings where lamellae were removed.

12. The method of claim 1 comprising:

removing alternating lamellae of the first set and alternating lamellae of the second set to form a mask over the substrate, the mask comprising mask openings where lamellae were removed; and

using the mask with mask openings to etch a pattern of openings into the substrate under the mask.

13. The method of claim 1 comprising:

removing alternating lamellae of the first set and alternating lamellae of the second set to form a mask over the substrate, the mask comprising mask openings where lamellae were removed; and

depositing material into the mask openings.

14. The method of claim 13 wherein the material is conductive.

15. The method of claim 13 wherein the material is non-conductive.

16. The method of claim 1 wherein individual of the openings have a width of nL_0, wherein "n" is from 1 to 15 and L_0 is an inherent periodicity of the second block copolymer.

17. The method of claim 16 wherein individual of the openings are of constant width.

18. The method of claim 17 wherein the openings are of the same constant width.

19. The method of claim 1 wherein the first set of alternating lamellae are of the same elevational thickness.

20. The method of claim 1 wherein the second set of alternating lamellae are of the same elevational thickness.

21. The method of claim 1 wherein the first set of alternating lamellae are of the same elevational thickness and the second set of alternating lamellae are of the same elevational thickness which is different from that of the first set of alternating lamellae.

22. The method of claim 21 wherein the elevational thickness of the second set of alternating lamellae is less than that of the first set of lamellae.

23. A method of patterning a substrate, comprising:

forming first openings in sacrificial material over a substrate;

forming a first block copolymer within the first openings; self-assembling the first block copolymer within the first openings to form a first set of alternating lamellae within the first openings;

removing the sacrificial material to form second openings over the substrate, the second openings comprising sidewalls which comprise the self-assembled first block copolymer;

forming a second block copolymer within the second openings; and

self-assembling the second block copolymer within the second openings to form a second set of alternating lamellae within the second openings.