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METHODS OF FORMING A STAMP, METHODS OF PATTERNING A
SUBSTRATE, AND A STAMP AND A PATTERNING SYSTEM FOR SAME

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PRIORITY CLAIM

This application claims the benefit of the filing date of United States Patent Application Serial No. 11/787,928, filed April 18, 2007, for "METHODS OF FORMING A STAMP, METHODS OF PATTERNING A SUBSTRATE, AND A STAMP AND A
10 PATTERNING SYSTEM FOR SAME."

TECHNICAL FIELD

Embodiments of the invention relate to semiconductor fabrication and, more specifically, to methods, a stamp and a system for patterning a substrate.

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BACKGROUND

As the development of nanoscale semiconductor devices and systems increase, new processes and materials are needed to fabricate such semiconductor devices and components. While feature sizes on the semiconductor devices are decreasing, the cost of
20 lithographic tools is increasing exponentially. Further reductions in feature size are often restricted by the lower limit of dimensions that can be achieved using lithographic methods. Semiconductor devices having features of about 60 nanometers (nm) or less, which are referred to herein as "sub-lithographic" features, are difficult to produce using conventional lithography.

25 Microcontact printing is one method for creating sub-lithographic features on semiconductor devices. The technique creates self-assembled monolayers (SAMs) on specific sites on a surface of a substrate of the semiconductor device. In a conventional process, a master mold with topographical features is prepared by photolithography or electron (e-beam) lithography. Referring to FIG. 1A, a stamp substrate 10 having a
30 resist 12 thereon creates a pattern on a surface of the stamp substrate 10. An elastomer casing 14, conventionally formed from polydimethylsiloxane, is deposited over the stamp substrate 10 and resist 12, and cured. The stamp substrate 10 and resist 12 are separated from the cured elastomer casing 14 to form a soft stamp 14' with topographical features. (FIGs. 1B and 1C) The soft stamp 14' includes a pattern that corresponds to the pattern in

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the resist 12, which pattern is to be formed on the semiconductor device. The soft stamp 14' is then wetted with an ink 16 and brought into contact with a receptor substrate 18. (FIG. 1D) The ink is physisorbed on the soft stamp 14' and is transferred to the receptor substrate 18 to form SAMs 20. (FIG. 1F) Theoretically, the SAMs 20 are formed only in regions where the ink 16 contacts the receptor substrate 18. However, the physisorbed nature of the ink 16 leads to poor resolution of the stamped features on the receptor substrate 18 as ink 16 not in contact with the receptor substrate 18 wicks down the soft stamp 14' due to capillary action. Another disadvantage is that the stamped features are no smaller than the lithographically defined features of the soft stamp 14'.

Attempts have been made to prepare sub-lithographic features on semiconductor devices by other methods known in the art. For example, e-beam lithography and extreme ultraviolet (EUV) lithography have been used in attempts to prepare such sub-lithographic features. However, widespread use of such methods has been hampered by difficulties including, for example, high costs and/or incompatibility with high throughput production methods. Accordingly, improved methods and systems for preparing sub-lithographic features on semiconductor devices are desired, as are stamps for achieving same.

BRIEF DESCRIPTION OF DRAWINGS

FIGs. 1A – 1C are cross-sectional views of a soft stamp during various stages of fabrication according to conventional process techniques;

FIGs. 1D – 1F are cross-sectional views of a soft stamp during microcontact printing according to conventional process techniques;

FIG. 2 is a flow chart of an embodiment of fabricating and using a stamp of the present invention;

FIG. 3 is a cross-sectional view of an embodiment of a stamp of the present invention with an ink material chemisorbed to the stamp;

FIG. 4 is a cross-sectional view of a stamp-ink material-receptor substrate complex according to an embodiment of the present invention;

FIGs. 5 – 18 are cross-sectional views of embodiments of stamp structures or intermediate stamp structures of the present invention during various stages of fabrication;

FIG. 19 is a cross-sectional view of an embodiment of a stamp of the present invention including self-assembled block copolymer domains; and

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FIGs. 20A, 20B and 20C are cross-sectional views of an embodiment of a receptor substrate including self-assembled monolayers thereon.

MODES FOR CARRYING OUT THE INVENTION

5 The following description with reference to the drawings describes embodiments of devices and methods according to the invention. Such description is for illustrative purposes only and not for purposes of limiting the same. Other embodiments of the present invention are contemplated and encompassed thereby.

 An embodiment of a method of the present invention for patterning a substrate is disclosed, as are embodiments of a stamp and a patterning system of the present invention. According to one embodiment, a stamp may be prepared or selected such that at least one region of a stamping surface of the stamp has chemical affinity for an ink material, as indicated at 1000 in FIG. 2. As used herein, the term "chemical affinity" means and includes the tendency of a molecule to associate with another molecule based on chemical forces between the molecules. The region of chemical affinity on the stamping surface forms a pattern that mirrors a desired pattern to be formed on a receptor substrate. As used herein, the term "receptor substrate" means and includes semiconductor substrates, silicon wafers, silicon on insulator ("SOI") substrates, silicon on sapphire ("SOS") substrates, epitaxial layers of silicon on a base semiconductor foundation and other semiconductor materials such as silicon-germanium, germanium, gallium arsenide and indium phosphide. In one embodiment, the receptor substrate includes silicon dioxide. However, a wide variety of materials may be used as the receptor substrate, such as any electrically conductive, electrically nonconductive, or electrically semiconductive material forming a solid phase at room temperature, as long as the receptor substrate and the ink material are capable of chemically bonding.

 The stamping surface includes at least a first region having chemical affinity for the ink material. Other regions of the stamping surface may lack chemical affinity for the ink material or may have a different chemical affinity for the ink material, such as substantially less chemical affinity. The region of chemical affinity provides the stamping surface with at least one region of chemical differentiation, which has different chemical properties than the other regions of the stamping surface. The region of chemical differentiation enables the stamping surface to chemically react with at least a portion of the ink material. The region of chemical differentiation may be formed by depositing a

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material having chemical affinity for the ink material on the stamp, or by modifying the deposited material or the stamping surface to include moieties or functional groups having chemical affinity for the ink material. The region of chemical differentiation on the stamping surface may include, for example, gold, thiol functional groups or amine functional groups.

As illustrated in FIG. 3, an embodiment of stamp 300 may include the regions of chemical differentiation 52 and the stamp substrate 50. The stamping surface of the stamp 300 may be substantially planar with at least one region of chemical differentiation 52 thereon, with the remainder of the stamping surface lacking chemical affinity for the ink material. Alternatively, the stamping surface may include topographical features wherein peak tips of the topographical features have chemical affinity for the ink material. As such, the peak tips correspond to the regions of chemical differentiation 52. The peak tips may be formed from a different material than the other portions of the stamp 300. Regardless of whether the stamping surface is substantially planar or includes topographical features, in one embodiment, the regions of chemical differentiation 52 include a region of gold. In another embodiment, the regions of chemical differentiation 52 include a region formed from another inorganic material, such as silicon dioxide, modified with thiol or amine functional groups. In another embodiment, the regions of chemical differentiation 52 include domains of a self-assembled block copolymer. The block copolymer surface may be modified to include, for example, gold, thiol or amine functional groups. The ink material (I-X-Y) is also shown in FIG. 3, attached to the stamp 300 through the regions of chemical differentiation 52. Additional details of the ink material and of fabricating the stamp 300 are described herein.

As indicated at 1020 of FIG. 2, the ink material is selected such that the chemical affinity between the stamping surface and the ink material is less than the chemical affinity between the ink material and the receptor substrate. The ink material may be any material to be deposited on the receptor substrate and capable of forming a pattern, such as a SAM, on the receptor substrate. By way of non-limiting example, the ink material may be a small molecule with the ability to function as a SAM. The ink material may include at least one functional group that chemically reacts with the region of chemical differentiation 52 on the stamping surface. The ink material may also include at least one functional group that chemically reacts with the receptor substrate. The ink material may

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be mono-functional, bi-functional or more. In one embodiment, the ink material has two or more functional groups on opposite ends of the ink material, providing orthogonal reactivity. As used herein, the term "orthogonal reactivity" means and includes at least one functional group on the ink material that reacts in a first manner and at least one
5 functional group on the ink material that is inert or reacts in a second, different manner under the same conditions.

The ink material may have a composition of I-X-Y, where "I" includes a first functional group capable of binding to the region of chemical differentiation 52, "X" is a spacer or linker molecule and "Y" includes a second functional group capable of binding
10 to the receptor substrate. Any portion of I and Y may include the functional group capable of bonding to the stamping surface or the receptor substrate. For instance, a terminal portion of I or a terminal portion of Y may include the desired functional group, or an interior portion of I or an interior portion of Y may include the desired functional group. Additional ink materials other than those described herein may be used as long as portions
15 "I" and "Y" are present in such a manner that they do not interfere with each other's respective binding or with the creation of the pattern on the receptor substrate.

The spacer (X) of the ink material may be selected to provide a particular thickness of the resultant pattern on the receptor substrate. Any spacer that does not disrupt binding of the ink material to the region of chemical differentiation 52 and receptor substrate is
20 suitable. The spacer may be a polar, nonpolar, positively charged, negatively charged, or uncharged molecule. By way of non-limiting example, a saturated or unsaturated, linear or branched alkyl, aryl, or other hydrocarbon spacer may be used, as well as corresponding halogenated hydrocarbons, especially fluorinated hydrocarbons. By way of non-limiting example, the ink material may be 2-aminoethanethiol, aminothiophenol,
25 cysteine, homocysteine, leucinethiol, 2-butylaminoethanethiol, 2-cyclohexylaminoethanethiol, a mercapto alcohol, *e.g.*, 2-mercaptoethanol (HS-CH₂CH₂OH) or 4-mercapto-1-butanol, acetylenic thiol, an aliphatic or aromatic thiol, lactic acid, hydroxybutyric acid, hydroxyisocaproic acid, hydroxyisophthalic acid, 8-hydroxy-7-iodo-5-quinolinesulfonic acid, hydroxymandelic acid, hydroxymethanesulfinic
30 acid, a hydroxybenzoic acid, hydroxynaphthalenesulfonic acid, hydroxypentadecanoic acid, hydroxyundecanoic acid, an acetylenic carboxylate or sulfonate, *e.g.*, propiolic acid, 4-butynoic acid, or 5-pentynoic acid, or combinations thereof.

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As indicated at 1030 and 1040 of FIG. 2, the stamping surface is wetted with the ink material. Physisorbed ink material is removed from the stamping surface while chemisorbed ink material remains on the regions of chemical differentiation 52. As used herein, the term "physisorbed" and grammatical equivalents thereof means and includes the physical adsorption of a molecule, such as the ink material, to a surface, such as the stamping surface. The physisorbed ink material may be adhered to the stamping surface through weak intermolecular interactions, such as Van der Waals forces. As used herein, the term "chemisorbed" and grammatical equivalents thereof means and includes the chemical adsorption of a molecule, such as the ink material, to a surface, such as the stamping surface. The chemisorbed ink material may be chemically bonded to the stamping surface, such as through hydrogen bonds, ionic bonds, dithiol linkages, electrostatic bonds or any other so-called "weak" chemical bond. For example, the stamp may be washed under conditions which remove the physisorbed ink material, but do not remove the chemisorbed ink material due to the chemical affinity of the ink material for the regions of chemical differentiation 52.

For hydrogen bonds, electrostatic or acid/base interaction, the wash is preferably a non-polar organic solvent that has at least some ability to solvate the ink material. Polar solvents tend to disrupt the chemisorbed ink. A wash may be performed for approximately 0.1 to 1 minute at a temperature up to the boiling point of the solvent or ink material. In some embodiments, the ink material may be removed by heating the ink material-stamp complex so as to boil off the physisorbed ink. Alternatively, the ink material-stamp complex may be exposed to a high vacuum so as to pull off physisorbed ink without removing the chemisorbed ink material. FIG. 3 depicts an embodiment of a stamp 300 having chemisorbed ink material (I-X-Y) on the regions of chemical differentiation 52. Thus, the ink material is only in contact with the regions of chemical differentiation 52.

The stamping surface may be wetted with the ink material under conditions which enable the ink material to react chemically with the regions of chemical differentiation 52. The ink material may be coated onto the stamping surface by any convenient method. By way of non-limiting example, the ink material may be directly contacted with the stamping surface or the ink material may be absorbed onto a piece of paper and the stamping surface may be pressed against the piece of paper. Alternately, a cotton swab or the like may be used to transfer ink material to the stamping surface. Ink material may be

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rapidly transferred to the stamping surface. For example, contacting the stamping surface with ink material for a period of time of approximately 6 to 600 seconds is sufficient to enable the ink material to chemisorb to the region of chemical differentiation 52.

However, contact may be maintained for substantially longer periods of time to ensure
5 that the ink material reacts with the region of chemical differentiation 52. The “Y” portion of the ink material may react with the stamping surface, forming hydrogen bonds, ionic bonds, dithiol linkages, electrostatic bonds, or any other so-called “weak” chemical bond. In one embodiment, the stamp includes gold regions of chemical differentiation 52 thereon and reacts with the ink material having at least one sulfur-containing functional
10 group, such as a thiol functional group.

Depending on the nature of the bonds that form between the stamping surface and ink material, the ink material may be applied to the stamping surface using a non-aqueous medium. For example, if the ink material and stamping surface interact via acid/base interaction, exposure to a polar solvent may interfere with the ink material binding to the
15 stamping surface. In other embodiments, the ink material may be dissolved in a solvent for transfer to the stamping surface. The ink material may be transferred to the stamping surface in a solvent at a concentration of less than 0.001 mM, preferably from about 1 to about 10k mM. Any solvent within which the ink material is substantially soluble, and which allows the ink material to chemically bind to the stamping surface, may be used.

20 The stamping surface may, optionally, be exposed to more than one ink material where the second ink material may be chemically distinct from the first ink material. The exposure to the second ink material may be substantially simultaneous with the introduction of the first ink material or may be separate. As described in more detail herein, the second ink material may chemically react with second regions of chemical
25 differentiation that are distinct from the regions of chemical differentiation 52 that bind to the first ink material.

As indicated at 1050 of FIG. 2 and illustrated in FIG. 4, the stamp 300 having the ink material chemisorbed to the region of chemical differentiation 52 is brought into contact with the receptor substrate 200, forming a stamping surface-ink material-receptor
30 substrate complex 400. As described in detail below, the receptor substrate 200 may, optionally, include an additional material layer thereon to improve wettability of the receptor substrate. Upon contact, the Y portion of the ink material may form a chemical bond with the receptor substrate 200. The bonds between the ink material and the receptor

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substrate 200 may be covalent, ionic or polar bonds. The chemical bonds between the stamping surface and the ink material may have a weaker bond strength than those between the ink material and the receptor substrate 200. The stamp 300 may be contacted with the receptor substrate 200 under appropriate conditions to transfer the ink material from the stamping surface to desired regions on the receptor substrate 200. The temperature during ink material transfer to the receptor substrate may be selected to maximize the rate of binding without cleaving the ink material-receptor substrate or ink material-stamping surface bonds. Thus, the ink material-receptor substrate bonds may form prior to cleaving the ink material-stamping surface bonds. Selection of the appropriate range of temperatures is within the skill of one in the art and depends upon the particular ink material and receptor substrate. Generally, suitable temperatures will range from room temperature to near boiling point of the ink material. The stamping surface and the receptor surface 200 may be contacted under conditions which enable chemical bonds to form between the receptor substrate 200 and the ink material. In one embodiment, the stamping surface -ink material-receptor substrate complex remains intact for approximately 1 to 240 minutes. For example, 15 minutes may be adequate for microcontact printing using Huisgens-1,3-dipolar cycloaddition reaction.

As indicated at 1060 of FIG. 2, the stamping surface-ink material-receptor substrate complex 400 may be exposed to conditions which eliminate or disrupt the chemical affinity between the regions of chemical differentiation 52 on the stamping surface and the ink material, while the chemical affinity between the ink material and the receptor substrate 200 may be substantially unaffected by the conditions. The bonds between the stamp 300 and the ink material may be cleaved thermally, oxidatively, electrochemically, or by exposure to a polar, protic solvent. By way of non-limiting example, if the regions of chemical differentiation 52 include gold or thiol groups, the bonds between the stamp 300 and the ink material may be cleaved thermally, oxidatively, or electrochemically. If, however, the regions of chemical differentiation 52 include acid/base groups, the bonds between the stamp 300 and the ink material may be cleaved by exposure to a polar, protic solvent.

In one embodiment, if the stamping surface includes topographical features, which correspond to the regions of chemical differentiation 52, an aqueous solution is introduced into channels between the topographical features to cleave the bonds between the stamp 300 and the ink material. By way of non-limiting example, referring to FIG. 4, the

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aqueous solution may be introduced into voids 130' to break the bonds between the ink material and the stamp 300. In another embodiment, the bonds between the ink material and the regions of chemical differentiation 52 are cleaved by applying heat to the stamping surface-ink material-receptor substrate complex 400. In one embodiment, the bonds between the ink material and the regions of chemical differentiation 52 are cleaved by contacting the stamping surface-ink material-receptor substrate complex 400 with a solution having a high ionic strength. In another embodiment, the bonds between the ink material and the regions of chemical differentiation 52 are cleaved by contacting the stamping surface-ink material-receptor substrate complex 400 with a solution having a high ionic strength and applying heat. The bonds between the ink material and the regions of chemical differentiation 52 may be cleaved without cleaving most of the bonds between the ink material and the receptor substrate 200. The stamp 300 may be removed from the receptor substrate 200, leaving ink material (which may form, for example, SAMs) on portions of the receptor substrate 200 in contact with the regions of chemical differentiation 52 of the stamping surface. The stamp 300 may then be prepared and re-inked for further receptor substrate stamping.

By way of non-limiting example, if the stamp 300 has gold regions of chemical differentiation 52 and the ink material includes thiol functional groups, the stamp 300 may be exposed to hydrogen peroxide or bleach to oxidize the thiol functional groups to sulfonic acid, cleaving the ink material from the gold regions of chemical differentiation 52. Since the gold-thiol bonds are relatively weak (20 Kcal/mol-35 Kcal/mol) as compared to potential C-N, C-O, Si-O or Si-N bonds between the ink material and the receptor substrate 200, the gold-thiol bonds may be cleaved without disrupting the ink material/receptor substrate bonds. Other methods of cleaving the gold-thiol bond include thermal cleavage and electrochemical cleavage.

By way of non-limiting example, if the stamp 300 has regions of chemical differentiation 52 that include thiol functional groups (*e.g.*, mercaptopropyl(trialkoxysilanes), the disulfide bonds between the stamp 300 and the ink material may be cleaved by reductive conditions including (1) exposure to metallic zinc; (2) electrochemical reduction or (3) exposure to other thiols (*e.g.*, thiol-disulfide rearrangement discussed herein). Dithiothreitol is a particularly useful reagent for reducing disulfides to thiols in this manner.

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By way of non-limiting example, if the stamp 300 includes amine regions of chemical differentiation 52 (e.g., aminoalkyl(trialkoxysilanes) and the ink contains carboxyl or other acid group, the acid-base interaction may be broken by exposure to a polar, protic solvent (e.g., water, methanol, ethanol, formic acid, hydrogen fluoride, ammonia or combinations thereof). In this situation, applying the ink material to the stamp 300 and contacting the stamp 300 and the receptor substrate 200 may occur in the absence of a polar, protic solvent. A polar aprotic solvent (e.g., dimethyl sulfoxide, dimethylformamide, or hexamethylphosphorotriamide) may be present during the stamping, if miscible with polar, protic solvents that disrupt the stamp-ink material bond which is dried after the stamping.

Table 1 is a non-limiting, exemplary list of materials that may be used in combination as the regions of chemical differentiation 52, the receptor substrate 200 and the ink material. The ink material may react with the regions of chemical differentiation 52 and the receptor substrate 200 to form the stamping surface-ink material-receptor substrate complex 400.

Table 1: Materials for the Regions of Chemical Differentiation, Inks, and Receptor Substrates

Regions of Chemical Differentiation	Ink Material	Receptor Substrate
Gold	2-aminoethanethiol, aminothiophenol, cysteine, homocysteine, leucinethiol, 2-butylaminoethanethiol, or 2-cyclohexylaminoethanethiol	SiO ₂ grafted with a glycidoxypentyl(trialkoxysilane
Gold	To form urea linkers: 2-aminoethanethiol, aminothiophenol, cysteine, homocysteine, leucinethiol, 2-butylaminoethanethiol, or 2-cyclohexylaminoethanethiol to form urethane linkers: any mercapto alcohol, e.g. 2-mercaptoethanol (HS-CH ₂ CH ₂ OH) or 4-mercapto-1-butanol	SiO ₂ grafted with an isocyanatopentyl(trialkoxysilane
Gold	Any acetylenic thiol	SiO ₂ grafted with 6-azidosulfonyl-hexyl(triethoxysilane or SiO ₂ grafted with 11-bromoundecyl (triethoxysilane and further reacted with sodium azide

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Gold	2-aminoethanethiol, aminothiophenol, cysteine, homocysteine, leucinethiol, 2-butylaminoethanethiol, 2-cyclohexylaminoethanethiol, any mercapto alcohol, e.g. 2-mercaptoethanol (HS-CH ₂ CH ₂ OH) or 4-mercapto-1-butanol	Si-Cl from H-terminated silicon
Gold	Any aliphatic or aromatic thiol	SiO ₂ grafted with 6-azidosulfonyl-hexyl(triethoxy)silane or SiO ₂ grafted with 11-bromoundecyl (triethoxy) silane and further reacted with sodium azide
Thiol Group	2-aminoethanethiol, aminothiophenol, cysteine, homocysteine, leucinethiol, 2-butylaminoethanethiol, or 2-cyclohexylaminoethanethiol	SiO ₂ grafted with a glycidoxypentyl(trialkoxysilane)
Thiol Group	To form urea linkers: 2-aminoethanethiol, aminothiophenol, cysteine, homocysteine, leucinethiol, 2-butylaminoethanethiol, or 2-cyclohexylaminoethanethiol To form urethane linkers: any mercapto alcohol, e.g. 2-mercaptoethanol (HS-CH ₂ CH ₂ OH) or 4-mercapto-1-butanol	SiO ₂ grafted with an isocyanatopentyl(trialkoxysilane)
Thiol Group	Any acetylenic thiol e.g., N (2-mercaptoethyl) propiolamide	SiO ₂ grafted with 6-azidosulfonyl-hexyl(triethoxy)silane or SiO ₂ grafted with 11-bromoundecyl (triethoxy) silane and further reacted with sodium azide
Thiol Group	2-aminoethanethiol, aminothiophenol, cysteine, homocysteine, leucinethiol, 2-butylaminoethanethiol, 2-cyclohexylaminoethanethiol or any mercapto alcohol, e.g. 2-mercaptoethanol (HS-CH ₂ CH ₂ OH) or 4-mercapto-1-butanol	Si-Cl from H-terminated silicon
Thiol Group	Any aliphatic or aromatic thiol	SiO ₂ grafted with 6-azidosulfonyl-hexyl(triethoxy)silane or SiO ₂ grafted with 11-bromoundecyl (triethoxy) silane and further reacted with sodium azide

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Amine Group	lactic acid, hydroxybutyric acid, hydroxyisocaproic acid, hydroxyisophthallic acid, 8-hydroxy-7-iodo-5-quinolinesulfonic acid, hydroxymandelic acid, hydroxymethanesulfinic acid, hydroxybenzoic acids, hydroxynaphthalenesulfonic acid, hydroxypentadecanoic acid, or hydroxyundecanoic acid	SiO ₂ grafted with an isocyanatopropyl(trialkoxysilane
Amine Group	any acetylenic carboxylate or sulfonate, e.g. propiolic acid, 4-butynoic acid, 5-pentynoic acid, etc.	SiO ₂ grafted with 6-azidosulfonyl-hexyl(triethoxy)silane or SiO ₂ grafted with 11-bromoundecyl (triethoxy) silane and further reacted with sodium azide
Amine Group	lactic acid, hydroxybutyric acid, hydroxyisocaproic acid, hydroxyisophthallic acid, 8-hydroxy-7-iodo-5-quinolinesulfonic acid, hydroxymandelic acid, hydroxymethanesulfinic acid, hydroxybenzoic acids, hydroxynaphthalenesulfonic acid, hydroxypentadecanoic acid, or hydroxyundecanoic acid	Si-Cl from H-terminated silicon
Amine Group	Any aliphatic or aromatic thiol	SiO ₂ grafted with 6-azidosulfonyl-hexyl(triethoxy)silane or SiO ₂ grafted with 11-bromoundecyl (triethoxy) silane and further reacted with sodium azide

Although Table 1 identifies certain ink materials having orthogonal reactivity, many functional groups in the ink materials are suitable for use with materials with which they are not categorized in Table 1. Any and all such combinations are within the scope of the present invention. The ink material/stamping surface and ink material/receptor substrate combination may be selected based on conventional understanding of chemical interactions and bond strengths. The stamp 300 may be formed by any conventional method that produces the desired pattern on the stamping surface, which pattern mirrors the pattern to be formed on the receptor substrate 200. The pattern on the stamping surface is defined by the regions of chemical differentiation 52, which have chemical affinity for the ink material. By way of non-limiting example, the pattern on the stamp 300 may be formed by conventional techniques, such as by using a mold or by

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photolithography or e-beam lithography. The pattern on the stamp 300 may also be formed using block copolymers. In one embodiment, the stamp 300 is created lithographically, such as by using, for example, photoresist materials or e-beam resist materials. Referring to FIG. 5, a film 70 may be deposited on the stamp substrate 50. The

5 film 70 may provide the regions of chemical differentiation 52 by using a material for film 70 that has chemical affinity for the ink material. Alternatively, the material used to form the film 70 may be chemically modified to include functional groups having chemical affinity for the ink material. By way of non-limiting example, the film 70 may be formed from gold, an inorganic material, such as silicon dioxide, or a block copolymer.

10 A resist layer 180 may be deposited over the film 70 and patterned by conventional photolithographic or e-beam lithographic techniques, forming openings 72. Photoresist materials, e-beam resist materials and lithographic techniques are well known in the art and, therefore, forming the pattern in the resist layer 180 is not discussed in detail herein. The resist material may be a positive or negative resist and may be an organic or an

15 inorganic material including, but not limited to, polystyrene based resists, poly(meth)acrylate based resists, silsesquioxane materials ("SSQ") and combinations thereof. The resist layer 180 may be formed over the film 70 by a conventional coating technique including, but not limited to, dip coating, bar coating, spin coating, roll coating, spray coating, and flow coating depending on the material used in the resist layer 180.

20 The pattern in the resist layer 180 may be transferred to the film 70 using resist layer 180 as a mask, as known in the art. As shown in FIG. 6, the film 70 may be etched to produce the stamping surface 70' on the stamp substrate 50. While the stamp 300 is illustrated in FIG. 6 as including topographical features, the stamp 300 may be substantially planar. If the material used as film 70 has affinity for the ink material, such as gold, the stamping

25 surface 70' may correspond to regions of chemical differentiation 52. However, if the material used as film 70 does not have affinity for the ink material, the stamping surface 70' may be modified to include a layer of gold or to include functional groups, such as thiol or amine groups, that have affinity for the ink material. The modified stamping surface 70' may correspond to the regions of chemical differentiation 52. By

30 way of non-limiting example, if silicon dioxide or block copolymers are used as the material of film 70, the film 70 may be modified with a layer of gold or with thiol or amine groups to provide the regions of chemical differentiation 52.

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In one embodiment, the regions of chemical differentiation 52 are formed from gold. In other words, gold may be used as the material of film 70 or gold is used to coat another material used as film 70. In one embodiment, E-beam lithography may be used to create the stamp 300 by depositing a resist layer 180 over the stamp substrate 50. The pattern produced in the resist layer 180 may be transferred to the stamp substrate 50 as known in the art. A film 70'' including a chromium layer (75 nm) followed by a layer of gold (5 nm) is deposited over the resist layer 180. Any metals deposited under the gold layer, such as the chromium layer, may have little or no affinity for thiol groups. The chromium layer may be used as an adhesive layer for the gold. Referring to FIGs. 7 and 8, the resist layer 180 and overlying metal (film 70'') may then be removed, such as by ultrasonication for 20 minutes in toluene. The resulting stamp 300'''' having gold regions of chemical differentiation 52 thereon (corresponding to the stamping surface 70') may be dried, for example, in a nitrogen stream. Since gold has affinity for thiol groups, the stamp 300 may be used with an ink material having thiol functional groups to pattern the receptor substrate 200. The formation of SAMs of ink material or gold regions of chemical differentiation 52 may enable complete or substantially complete patterns of ink material to be formed on the receptor substrate 200, such that a better transfer of the ink material to the receptor substrate 200 may occur relative to the stamps that do not form complete SAMs.

In another embodiment, the film 70 is formed from an inorganic material including, or modified to include, exposed thiol or amine functional groups thereon. By way of non-limiting example, the film 70 may be formed from silicon dioxide and coated with a mercaptopropyl(trialkoxysilane) compound (e.g., CAS Nos. 14814-09-6, 4420-74-0, available from Gelest Inc., Morrisville, PA). The coating of the mercaptopropyl(trialkoxysilane) compound may provide exposed thiol groups on the stamp 300, which correspond to the regions of chemical differentiation 52. To form such a stamping surface, a silicon dioxide film may be deposited on the stamp substrate 50 and patterned by conventional techniques to form topographic features. In other words, silicon dioxide may be the material used for film 70. By way of non-limiting example, the silicon oxide film may be patterned by (1) conventional photolithography (i.e., down to 60 nm) of photoresist followed by dry etch; (2) e-beam lithography (down to ~30 nm) of e-beam resist followed by dry etch; (3) graphoepitaxial self-assembly of a block copolymer and removal of one domain to form an etch mask followed by dry etch as further described

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herein; or (4) pitch multiplication. The silicon oxide film may be a thin coating on the stamp substrate 50. For example, the silicon oxide film may be between about 1-10 nm thick. In one embodiment, the majority of the etch occurs into a separate material that does not react with mercaptopropyl(trialkoxysilane, such as silicon. This material forms the non-reactive areas around the regions of chemical differentiation 52. The patterned silicon oxide film may then be exposed to the mercaptopropyl(trialkoxysilane compound so as to form a thiol-containing layer on the surface of the silicon dioxide. In one embodiment, a thiosilane monolayer may be deposited on the silicon oxide film prior to patterning such that the thiosilane monolayer survives the etching process (*e.g.*, the thiosilane monolayer is covered by the resist during patterning) and such that the thiol groups are exclusively on the stamp tips and not on the sides of the topographical features. For example, if the thiosilane monolayer is deposited over a patterned substrate, the thiosilane monolayer will likely be deposited on the sidewalls of any topographical features of the stamp and the ink material may be deposited on the sidewalls of the topographical features. However, if the thiosilane monolayer is deposited prior to patterning, the thiosilane monolayer, and thus the thiol groups, will be exclusively on the stamp tips.

By way of non-limiting example, the film 70 may be formed from silicon oxide and coated with an aminoalkyl(trialkoxysilane compound (available from Gelest, Inc., Morrisville, PA). The coating of the aminoalkyl(trialkoxysilane compound may provide exposed amine groups on the stamp 300, which correspond to the regions of chemical differentiation 52. The method of creating the stamp 300 coated with the aminoalkyl(trialkoxysilane compound may follow the general method described above with respect to the stamp 300 coated with the mercaptopropyl(trialkoxysilane compound. The patterned silicon oxide film may be exposed to the aminoalkyl(trialkoxysilane compound to form an amine layer of the silicon oxide film surface. In one embodiment, an aminosilane monolayer is formed on the silicon oxide film prior to patterning such that the aminosilane monolayer survives the etching process to create regions of chemical affinity including amine groups exclusively on the stamp tips and not on the sides of the topographical features.

In another embodiment, the film 70 is formed from a block copolymer. The film 70 formed from the block copolymer may be modified with gold or at least one of thiol and amine functional groups to provide the stamping surface 70', which corresponds

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to the regions of chemical differentiation 52. In one embodiment, one of the blocks inherently contains a thiol or amine functional group, for example, polyvinylpyridine. When the film 70 on the stamp 300 is formed from a block copolymer, a first block of the block copolymer may be selected, or modified to include, at least one functional group
5 that reacts with a first ink material, while the second block may be inert or, optionally, may include at least one functional group that reacts with a second functional group of a second ink material. Alternatively, or in addition to, the second block may be removed prior to contacting the stamping surface with the ink material. When block copolymers are used for film 70, one domain of the block domain may be selectively removed to form
10 openings 72 as discussed herein. Alternatively, a planar device may be formed wherein one domain lacks affinity for the ink material. Films 70 formed from the block copolymer may self assemble into periodic structures by microphase separation of the constituent blocks after annealing. Following self-assembly, one block of the block copolymer may be selectively removed, producing a patterned film formed from the remaining block. The
15 patterned film may be used as an etch mask for patterning features onto the underlying substrate. Alternatively, one block of the block copolymer may have chemical affinity for the first ink material while the other block(s) may have chemical affinity for the second ink material. In one embodiment, the stamp is made from a PS-PMMA block copolymer, the ink material is alkynethiol-gold nanoparticles and the receptor substrate is 11-
20 azidoundecyl(trialkoxysilane) on SiO₂. The alkynethiol gold nanoparticles will selectively absorb to the PS domains of the PS-PMMA block copolymer film by selective wetting of the PS over PMMA by the alkyne tails on the nanoparticles.

Block copolymers are polymers that include at least one long sequence (i.e., "block") of the same monmeric unit(s) covalently bound to at least one long sequence
25 (i.e., "block") of unlike type *e.g.*, including differing monmeric unit(s). Block copolymers are conventionally named using the word "-block-" or "-b-" to separate each monmeric unit, while random copolymers are conventionally named using the term "-random-" or an "-r-" to separate each monmeric unit. A wide variety of block copolymers are contemplated herein including diblock copolymers (copolymers having
30 two blocks), triblock copolymers (copolymers having three blocks), multiblock copolymers (copolymers having more than three blocks), and combinations thereof.

If a diblock copolymer is used as the material of film 70, each block of the block copolymer may differ from other blocks not only in terms of the structure of the

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monomeric units that form that block, but also in other properties including, for example, physical properties (*e.g.*, mechanical strength, surface tension, wettability, and/or solubility) and chemical properties (*e.g.*, solubility, chemical reactivity, susceptibility to removal techniques and/or susceptibility to cross-linking reactions). Film morphology, including the size and shape of the microphase separated domains may be controlled by the molecular weight and volume fraction of the blocks in the diblock copolymer. By way of non-limiting example, the ratio of each block of a diblock copolymer is between about 40:60 and about 60:40 to create lamellar domains or alternating stripes of the blocks. Domain sizes of the blocks may be between about 5 nm and about 50 nm. The block copolymer used in creating the stamp 300' may be selected based on their chemical affinity toward the ink material.

By way of non-limiting example, the blocks of the block copolymer may be polybutadiene-polybutylmethacrylate, polybutadiene-polydimethylsiloxane, poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA), polybutadiene-polymethylmethacrylate, polybutadiene-polyvinylpyridine, polybutylmethacrylate-polybutylacrylate, polybutylmethacrylate-polyvinylpyridine, polybutadiene-polyvinylpyridine, polyethyleneoxide-polyisoprene, polyethyleneoxide-polybutadiene, polyethyleneoxide-polystyrene, polyethylene-polyvinylpyridine, polyisoprene-polymethylmethacrylate, polyisoprene-polyvinylpyridine, polybutylacrylate-polymethylmethacrylate, polybutylacrylate-polyvinylpyridine, polyhexylacrylate-polyvinylpyridine, polyisobutylene-polybutylmethacrylate, polyisobutylene-polydimethoxysiloxane, polyisobutylene-polymethylmethacrylate, polyisobutylene-polyvinylpyridine, polyethylene-polymethylmethacrylate, polymethylmethacrylate-polybutylacrylate, polymethylmethacrylate-polybutylmethacrylate, polystyrene-polybutadiene, polystyrene-polybutylacrylate, polystyrene-polybutylmethacrylate, polystyrene-polybutylstyrene, polystyrene-polydimethoxysiloxane, polystyrene-polyvinylpyridine, polyvinylpyridine-polymethylmethacrylate, polystyrene-polyisoprene (PS-*b*-PI), polystyrene-*b*-lactic acid, or polyethyleneoxide-polymethylmethacrylate. As described in detail below, the block copolymer may be a diblock copolymer. However, block copolymers having three (a triblock copolymer) or more (a multiblock copolymer) blocks may also be used. Examples of triblock copolymers include, but are not limited to, poly(styrene-block methyl methacrylate-block-ethylene oxide) and block copolymers having three or more blocks selected from the following: polystyrene, polymethylmethacrylate,

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polyethyleneoxide, polyisoprene, polybutadiene, poly lactic acid, polyvinylpyridine, and combinations thereof.

In one embodiment, the block copolymer is a diblock copolymer. Diblock copolymers may be symmetric (*i.e.*, the volume fraction of the first block is substantially the same as the volume fraction of the second block) or asymmetric (*i.e.*, the volume fraction of the first block is substantially different than the volume fraction of the second block). As used herein, each block of a symmetric diblock copolymer has a volume fraction of from about 0.4 to about 0.6. As used herein, each block of an asymmetric diblock copolymer has a volume fraction less than about 0.4 or greater than about 0.6. In one embodiment, the diblock copolymer is a symmetric diblock copolymer and is used for embodiments in which the diblock copolymer self-assembles to form lamellae (*i.e.*, sheets of material interleaved with another material). Asymmetric diblock copolymers may be used for embodiments in which the diblock copolymer self-assembles to form other morphologies including, for example, spheres, cylinders, gyroids, or combinations thereof. For methods that include a first and a second block copolymer, both the first and the second block copolymers may be symmetric block copolymers.

In one embodiment, the stamp 300 may be created using diblock copolymers, which are applied to the surface of the stamp substrate 50 by any suitable means. Any material which may permit the diblock copolymer to orient in a substantially perpendicular manner may be used for the stamp substrate 50. As used herein, "substantially perpendicular" lamellae refers to a set of lamellae that are, on average, perpendicular to the surface. However, other materials may be used for the stamp substrate 50 if the surface of the stamp substrate 50 is treated with a material that may permit the diblock copolymer to orient substantially perpendicularly thereto. Thus, the stamp substrate 50 is not limited to any particular material.

The diblock copolymer may be applied to the stamp substrate 50 by conventional techniques including, for example, deposition methods, coating methods, transfer methods, and/or other available application methods. The diblock copolymer may be applied by spin coating, dip coating, spray coating, and combinations thereof. In such methods, the diblock copolymer may be dissolved, dispersed, or suspended in a medium (*e.g.*, a solvent). The solution, dispersion, or suspension may be deposited on the stamp substrate 50, and the medium may be optionally removed (*e.g.*, through evaporation at

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ambient or elevated temperature, and at ambient or reduced pressure) during or subsequent to deposition.

Depending on the properties of the blocks (*e.g.*, molecular weight, block weight ratio, film thickness) and the process conditions (*e.g.*, annealing conditions, surface treatment and the like), the blocks of the diblock copolymer may microphase separate on a
5 nanometer-scale length scale, forming a hexagonal array of pores in a thin polymer film. Other phase morphologies of the diblock copolymer include, but are not limited to, a spherical phase, a lamellar phase, etc.

Thus, in one embodiment, at least one region of chemical differentiation is formed
10 on a stamp substrate, the at least one region of chemical differentiation exhibiting chemical affinity for at least one ink material. The at least one region of chemical differentiation may include gold, a compound containing at least one thiol functional group or a compound containing at least one amine functional group. The at least one region of chemical differentiation on the stamp substrate may be formed by depositing a
15 block copolymer on the stamp substrate and self-assembling the block copolymer into at least two domains having a perpendicular orientation to the stamp substrate. At least one of the domains of the self-assembled block copolymer may be optionally removed. At least one of the domains may be coated with gold, a compound containing thiol functional groups, a compound containing amine functional groups, or combinations thereof. The at
20 least one region of chemical differentiation may include topographical features.

Referring to FIG. 9, the stamp substrate 50 is provided having a neutral wetting surface with respect to each block of the diblock copolymer. As such, no block of the block copolymer preferentially wets the surface of the stamp substrate 50. The stamp substrate 50 may be formed from one of the materials previously described. While the
25 stamp substrate 50 is depicted as being substantially planar, the stamp substrate 50 may be patterned prior to deposition of the diblock copolymer. For example, the stamp substrate 50 may include trenches that serve as guides for the formation of self-assembled block copolymers therein. The trenches may be formed using conventional lithographic techniques or using block copolymers, as described in detail herein. In one embodiment,
30 the stamp substrate 50 is chemically patterned to include a series of chemical regions of about the same size of each block in the block copolymer, which serve as guides for the formation of the self-assembled block copolymers therein. A symmetric diblock copolymer may be deposited on the stamp substrate 50, forming film 70". If the stamp

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substrate 50 does not have a neutral wetting surface, a material layer 60 may be formed between the stamp substrate 50 and the film 70", providing the neutral wetting surface. While material layer 60 is shown in FIG. 9, this layer is optional.

In one embodiment, the material layer 60 is hydrogen terminated silicon, which provides the neutral wetting surface for the diblock copolymer polystyrene-b-polymethylmethacrylate. In another embodiment, the material layer 60 includes a random copolymer and may be cross-linked using the same or different methods than used to cross-linking at least one block of the block copolymer. The cross-linked material layer 60 may be used, for example, to render the stamp substrate 50 neutral wetting with respect to each block of the block copolymer, enabling the block copolymer to self-assemble on the stamp substrate 50. For example, if the diblock copolymer is a polystyrene-b-polymethylmethacrylate diblock copolymer, a cross-linkable polystyrene-r-polymethylmethacrylate random copolymer may be used as the material layer 60. The cross-linked material layer 60 is preferably resistant to further processing encountered during the block copolymer self-assembly process.

Once the diblock copolymer is deposited on the stamp substrate 50 (or on the material layer 60), the diblock copolymer may be annealed to break up existing domains and allow the diblock copolymer to self-assemble. The diblock polymer may be annealed by thermal annealing, solvent annealing, or combinations thereof. During the annealing, the diblock polymer may form ordered domains having nanometer-scale dimensions. Thermal annealing may include exposing the diblock copolymer to an elevated temperature (*e.g.*, at or above the glass transition temperature of the diblock copolymer), and lowering the temperature to allow the self-assembled block copolymer to harden. By way of non-limiting example, the diblock polymer may be thermally annealed by heating the diblock copolymer to a temperature of from about 0° C to about 250° C for up to about 24 hours or longer, preferably under a vacuum or inert atmosphere. Solvent annealing may include exposing the diblock copolymer to a solvent until the diblock copolymer swells. At least a portion of the solvent may then be removed, such as through evaporation.

As shown in FIG. 10, each block of the diblock copolymer in the film 70" may self-assemble into a domain during the anneal. Symmetric diblock copolymers self-assemble into lamellar structures in which alternating lamellae each represent a domain including one block of the diblock copolymer. A distance between the middle of a first

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lamella and the middle of the next lamella of the same type is the inherent periodicity (L_0) of the diblock copolymer, which is dependent on the length and/or molecular weight of the polymer chain for each block. Thus, the inherent periodicity of the diblock copolymer may be increased by increasing the length and/or molecular weight of the polymer chain for one or both diblocks of the diblock copolymer. Conversely, the L_0 may be decreased by decreasing the length and/or molecular weight of the polymer chain for one or both block of the diblock copolymer. Diblock copolymers contemplated herein may have an L_0 from about 10 nm to about 100 nm. For methods that use a first and second block copolymer, the L_0 of the first block copolymer may be the same as or different from the L_0 of the second block copolymer.

The diblock copolymer in the film 70" self-assembles during the anneal to form a set of alternating lamellae 110 and 120 that are substantially perpendicular to the stamp substrate 50. The lamellae 110, 120 may have differentiated chemical affinities in that lamellae 110 may have affinity for a first ink material while lamellae 120 may be substantially inert or may have affinity for a second ink material. Each block of the diblock copolymer may be selected to provide the desired chemical affinity for the ink material(s), or one or more of the blocks may be modified with a functional group to provide the desired chemical affinity. The upper surface of the lamellae 110, 120, as shown in the stamp 300' of FIG. 10, may correspond to the regions of chemical differentiation 52. Alternatively, if the lamellae 110, 120 do not have chemical affinity for the ink material(s), the upper surface of one of lamellae 110 or 120 may be modified to include gold; thiol groups or amine groups to provide the regions of chemical differentiation 52.

Alternatively, lamellae 120 may be removed to create a pattern on the stamp 300", as shown in FIG. 11. To remove the lamellae 120, lamellae 110 may be cross-linked, for example, by exposure to radiation, e.g., ultraviolet (UV) radiation. Cross-linked lamellae may have, for example, improved mechanical properties and lower susceptibility to removal during further processing. In some embodiments, the block of the block copolymer that forms lamellae 110 may be susceptible to cross-linking without the addition of a cross-linking agent. For example, if the block copolymer is a polystyrene-b-polymethylmethacrylate diblock copolymer, the polystyrene block may be cross-linked by exposure to UV radiation. Alternatively, the block of the block copolymer that forms

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lamellae 110 may be made cross-linkable by including a small amount (e.g., 1 to 5 mole %) of a thermally cross-linkable monomer (e.g., a benzocyclobutane-containing monomer) or a photochemically cross-linkable monomer (e.g., divinyl benzene or azido-methylstyrene). Alternatively, or in addition to, in some embodiments, the cross-linking agent may be added to the block of the block copolymer that forms lamellae 110. A wide variety of cross-linking agents are known in the art and include, for example, the combination of a cross-linker (e.g., 1,3,5-trimethyl-2,4,6-(triacetoxymethyl)benzene) and a thermal acid generator (e.g., cyclohexylmethyl(2-oxocyclohexyl)sulfonium trifluoromethanesulfonate).

Referring to FIG. 11, the lamellae 120, which are not cross-linked, may be selectively removed, leaving the cross-linked lamellae 110 and voids 130 on the surface of the stamp 300". The voids 130 are defined by sidewalls 150 of the cross-linked lamellae 110. A wide variety of methods for removing uncross-linked 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 diblock copolymer is polystyrene-b-polymethylmethacrylate diblock copolymer and the lamellae including the polystyrene blocks are cross-linked, the lamellae including the uncross-linked polymethylmethacrylate block may be selectively removed, for example, by acetic acid development after a blanket exposure to ultraviolet (UV) radiation. The resulting stamp 300" may be used for printing or may be subjected to further processing, for example, wherein the stamp 300" functions as a mask.

In one embodiment, depicted in FIG. 12, material 170 may be selectively deposited over the cross-linked lamellae 110. The material 170 may have a different etch selectivity than lamellae 110. By way of non-limiting example, the material 170 may be gold that is deposited using a grazing angle deposition. Gold may be sputtered onto the surface at an angle of a few degrees above parallel to the stamping substrate 50. The gold will be deposited above lamellae 100 and to a small extent within voids 130 at the top of the sidewalls. However, the bottom surface 135 of voids 130 will be largely protected from gold deposition by the adjacent lamellae 110 and a stamp 300" including gold regions of chemical differentiation 52 on the cross-linked lamellae 110 may be formed. (FIG. 13).

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The cross-linked lamellae 110 of the stamp 300" may also be used as a mask for further processing. For example, the voids 130 may be filled with a material prior to stamping the receptor substrate 200. Referring to FIG. 12, material 170 may be deposited within the voids 130 and over the cross-linked lamellae 110. The material 170 may have a
5 different etch selectivity than lamellae 110. For example, the material 170 may be an inorganic material, such as silicon dioxide or gold. The material 170 may be planarized, exposing the top surface of lamellae 110. The lamellae 110 may be selectively removed, leaving a pattern of the material 170 on the stamp substrate 50 and voids 135, as shown in FIG. 14. If material 170 does not create regions of chemical differentiation upon stamping
10 substrate 50, an inorganic material such as gold may be deposited on the top surfaces of the material 170 or the top surfaces of the material 170 may be modified prior to selective etching of lamellae 110 to include thiol or amine functional groups, forming regions of chemical differentiation 52 on the material 170.

In another embodiment, the voids 130 of FIG. 11 may form trenches that serve as
15 guides for self-assembly of the block copolymers. However, in the alternative, trenches may be formed by conventional lithography and used as guides for the self-assembly of the block copolymers. Referring to FIG. 15, a second block copolymer 170', which may be the same as or different than the block copolymer used in film 70", may be deposited in the voids 130. In one embodiment, the voids 130 have a bottom surface (an exposed
20 surface of the stamp substrate 50) that is neutral wetting with respect to each block of the second block copolymer 140. However, if the voids 130 do not include a neutral wetting surface, the material layer 60 may, optionally, be deposited therein to render the stamp substrate 50 surface neutral wetting, as previously described. The sidewalls 150 may be wetted by at least one block of the second block copolymer 170' (e.g., one block of the
25 second block copolymer 170' is similar to, or the same as, the cross-linked block of the lamellae 110). The second block copolymer 170' may be annealed, by methods such as those previously described, to allow self-assembly within each void 130 to form a second set of alternating lamellae 142 and 144, as shown in FIG. 16. The lamellae 142, 144 may be oriented substantially perpendicular to the stamp substrate 50 and substantially in
30 register with each sidewall 150, forming stamp 300'''.

Optionally, lamellae 142 may be cross-linked by methods such as those previously described. Referring to FIGs. 16 and 17, uncross-linked lamellae 144 may be removed by methods such as those previously described, forming a pattern of lamellae 142. The

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resulting pattern may be used, for example, as an etch mask to form sub-lithographic openings in the stamp substrate 50. As used herein, the term "sub-lithographic" means and includes having one or more sizes or dimensions that are less than the minimum sizes or dimensions obtainable using conventional lithography. Alternatively, the pattern may form stamp 300'''''. The stamps 300''''', 300'''''' shown in FIGs. 16 and 17 may be used for patterning the receptor substrate 200, provided that two of lamellae 110, 142 and 144, as shown in FIG. 16, have chemical affinity for the desired ink material. For example, with respect to FIG. 16, if each of lamellae 110, 142 and 144 have chemical affinity for the ink material, the ink material may bind to all three regions and no pattern would be transferred to the receptor substrate 200. However, if two of lamellae 110, 142 and 144 have chemical affinity for the ink material, the ink material may bind to these two regions, forming a pattern, which may be transferred to the receptor substrate 200. The lamellae 110, 142 shown in FIG. 17 may have chemical affinity for the same ink material or the lamellae 110, 142 may have chemical affinity for different ink materials.

In one embodiment, the diblock copolymer is used with the stamp of FIG. 6 by depositing the diblock copolymer within openings 72 formed by film 70. The diblock copolymer is annealed, forming alternating lamellae 210, 220 that are substantially perpendicular to the stamp substrate 50. (FIG. 18). The lamellae 210, 220 may provide regions of chemical differentiation in addition to those that are provided by film 70'. Or, if the lamellae in the openings 72 do not include chemical affinity for the ink materials, the upper surface thereof may be modified to include gold, thiol groups or amine groups to provide the additional regions of chemical differentiation. Alternatively, one of the sets of lamellae in the openings 72 may be cross-linked and removed, by methods such as those previously described, forming a desired pattern in the openings 72. In this embodiment, film 70 is a silicon-containing layer such that film 70 has silicon-containing sidewalls 150. The film 70 may be formed from silicon oxide (SiO_2), silicon nitride (Si_3N_4), SSQ, Si, SiOC, SiON or combinations thereof. Optionally, a homopolymer of one block of the diblock copolymer may be grafted to the silicon-containing sidewalls 150 so that openings 72 may be preferentially wetted by the same block of the diblock copolymer. For example, if the diblock copolymer to be self-assembled in the openings 72 is a polystyrene-b-polymethylmethacrylate diblock copolymer, a polystyrene homopolymer may be grafted to the silicon-containing sidewalls 150 so that the openings 72 may be wetted by the polystyrene block of the diblock copolymer. Alternatively, a

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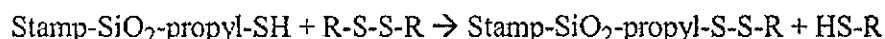
polymethylmethacrylate homopolymer may be grafted to the silicon-containing sidewalls 150 so that openings 72 may be preferentially wetted by the polymethylmethacrylate block of the diblock copolymer. The homopolymers may be grafted by a wide variety of methods known in the art including, for example, preparing
5 homopolymers with end groups (*e.g.*, hydroxyl groups) that may interact (*e.g.*, by forming hydrogen and/or covalent bonds) with the silicon-containing sidewalls.

If the stamp (such as, for example, stamps 300', 300''', 300''''', 300''''''') has chemical affinity for more than one ink material, the first and second blocks of the diblock copolymer in these stamps provide regions of chemical differentiation that react with the
10 first and second ink materials, respectively. The first and second blocks of the diblock copolymer in these stamps form separate domains having sizes and morphologies which correspond to the stamp pattern. The first block of the diblock copolymer is selected, or modified to include, a functional group that reacts with the first ink material and the second block is selected, or modified to include, a functional group that reacts with the
15 second ink material. The diblock copolymer may then be annealed, by methods such as those previously described, producing the two domains. Referring to FIG. 19, the stamp substrate 50 includes thereon a first domain 110' selective to "I" (the first ink material) and a second domain 120' selective to "I*" (the second ink material). The stamp 300', 300''', 300''''', 300''''''' may be used to pattern the receptor substrate 200 with the first and second
20 ink materials. While use of two ink materials is shown with respect to stamps 300', 300''', 300''''', 300''''''', the use of more than two ink materials may be contemplated if the stamp includes more than two distinct regions of chemical differentiation. The first and second ink material may be applied to the stamps during the same printing process or during a separate printing process.

25 By way of non-limiting example, combinations of materials used as the regions of chemical differentiation of the stamp, the ink material and the receptor substrate are described herein. However, the stamp, ink material or receptor substrate may be formed from other materials and may include other combinations of materials, as previously described. For example, the stamp may include gold regions of chemical differentiation and interact with the ink material via a gold-thiol bond. In an embodiment where the
30 stamp includes SiO₂ topographic features coated with a mercaptopropyl(trialkoxysilane compound, the ink material may interact with the stamping surface via disulfide bonds. A disulfide bond is relatively weak (between about 50 Kcal/mol and about 60 Kcal/mol).

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The ink material may include a free thiol (R-SH) functional group, in which case an oxidant, such as bromine, may be used to form the disulfide linkage to the regions of chemical differentiation on the stamp. Alternatively, the ink material may be present in excess in an oxidized dithiol form R-S-S-R, and a thiol-disulfide rearrangement reaction
5 may be used to transfer the ink material to the stamp, according to the following reaction:



When the stamp includes gold regions of chemical differentiation or
10 mercaptopropyl(trialkoxysilane coated regions of chemical differentiation, amines may be present in the ink material and may be employed to bond the receptor substrate and the ink material. The receptor substrate may be a SiO₂ receptor substrate grafted with a glycidoxypentyl(trialkoxysilane compound, (*e.g.* CAS Nos. 2602-34-8 and 2530-83-8 available from Gelest, Inc., Morrisville, PA) and the ink material may include 2-
15 aminoethanethiol, aminothiophenol, cysteine, homocysteine, leucinethiol, 2-butylaminoethanethiol, or 2-cyclohexylaminoethanethiol (all available from Sigma-Aldrich, Inc., St. Louis, MO). In one embodiment, using urethane/urea chemistry, the receptor substrate may be SiO₂ grafted with a isocyanatopropyl(trialkoxysilane compound (available from Gelest, Inc., Morrisville, PA) and the ink material may be 2-
20 aminoethanethiol, aminothiophenol, cysteine, homocysteine, leucinethiol, 2-butylaminoethanethiol, or 2-cyclohexylaminoethanethiol (all available from Sigma-Aldrich, Inc., St. Louis, MO). The receptor substrate and the ink material may react to form urea linkers. Additionally, any mercapto alcohol, *e.g.*, 2-mercaptoethanol (HS-CH₂CH₂OH) or 4-mercapto-1-butanol, may be used to form urethane linkers.
25 In one embodiment, Huisgens-1,3-dipolar cycloaddition may be employed using a SiO₂ receptor substrate grafted with 6-azidosulfonylhexyl (triethoxysilane or 11-azidoundecyl group monolayers formed by grafting 11-bromoundecyl(triethoxysilane (available from Gelest) to SiO₂, then derivatizing with sodium azide (available from Gelest, Inc., Morrisville, PA). The ink material may be an acetylenic thiol and may be
30 prepared, for example, by reaction of 1,4-butanedithiol or 1,2-ethanedithiol with 0.5 eq. of propargyl bromide to yield an acetylenic thiol (single thiol unit) or reacting a aminethanethiol with propidic anhydride to make N-(2-mercaptoethyl) propanolamide.

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Nucleophilic attack on a Si-Cl surface is another chemistry which may be used to bond the receptor substrate and the ink material. The receptor substrate may be Si-Cl, which is formed from H-terminated silicon via Cl₂ gas exposure at 80° C or Cl₂ gas exposure with illumination with a tungsten lamp. The ink material may include 2-aminoethanethiol, aminothiophenol, cysteine, homocysteine, leucinethiol, 2-butylaminoethanethiol, or 2-cyclohexylaminoethanethiol (all available from Sigma-Aldrich, Inc., St. Louis, MO) or any mercapto alcohol, *e.g.*, 2-mercaptoethanol (HS-CH₂CH₂OH) or 4-mercapto-1-butanol.

Another embodiment of the ink material/receptor substrate that may be used with the stamp having gold regions or mercaptopropyl(trialkoxysilane coated regions of chemical differentiation utilizes nitrene insertion. The receptor substrate may be SiO₂ grafted with 6-azidosulfonylhexyl (triethoxy)silane available from Gelest, Inc., Morrisville, PA or SiO₂ grafted with an azidoalkyl as described herein. The ink material may be an aliphatic or aromatic thiol. The azido group on the surface of the receptor substrate may decompose to a nitrene above 110° C and the nitrene may react with proximate functional groups of the ink material.

In one embodiment, the stamp may utilize an acid-based interaction with the ink material and the stamp may be formed of SiO₂ topographic features coated with material to create exposed amine groups, such as an aminoalkyl(trialkoxysilane compound. When urethane bonding is utilized, the receptor substrate may be SiO₂ grafted with an isocyanatopropyl(trialkoxysilane available from Gelest, Inc., Morrisville, PA. The ink material may be, for example, lactic acid, hydroxybutyric acid, hydroxyisocaproic acid, hydroxyisophthalic acid, 8-hydroxy-7-iodo-5-quinolinesulfonic acid, hydroxymandelic acid, hydroxymethanesulfinic acid, hydroxybenzoic acids, hydroxynaphthalenesulfonic acid, hydroxypentadecanoic acid, or hydroxyundecanoic acid.

Huisgens-1,3-dipolar cycloaddition may also be utilized with the stamp having aminoalkyl(trialkoxysilane regions of chemical differentiation thereon. The receptor substrate may be SiO₂ grafted with 6-azidosulfonylhexyl (triethoxy)silane available from Gelest, Inc or derivatized with an azidoalkyl as known in the art. The ink material may be any acetylenic carboxylate or sulfonate, *e.g.*, propiolic acid, 4-butynoic acid, 5-pentynoic acid, etc.

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Using nucleophilic attack on Si-Cl surface, the receptor substrate may be Si-Cl, which is formed as previously described. The ink material may be, by way of non-limiting example, lactic acid, hydroxybutyric acid, hydroxyisocaproic acid, hydroxyisophthallic acid, 8-hydroxy-7-iodo-5-quinolinesulfonic acid, hydroxymandelic acid, hydroxymethanesulfinic acid, hydroxybenzoic acids, hydroxynaphthalenesulfonic acid, hydroxypentadecanoic acid, or hydroxyundecanoic acid.

Nitrene insertion may also be utilized with a stamp having aminoalkyl(trialkoxysilane regions of chemical differentiation thereon. The receptor substrate may be SiO₂ grafted with 6-azidosulfonylhexyl (triethoxysilane available from Gelest, Inc., Morrisville, PA or with an azidoalkyl, and the ink material may be any aliphatic or aromatic thiol moiety.

The stamp (300-300''''') produced by any of the above-mentioned embodiments may be used to pattern the receptor substrate 200, such as by nanocontact chemical printing. By way of non-limiting example, the stamp may be used to print SAMs on a surface of the receptor substrate 200. The pattern on the receptor substrate 200 may have identical, or substantially identical, resolution to the pattern on the stamp. In some embodiments, the pattern on the stamp may be used to produce features on the receptor substrate 200 that are sub-lithographic. By way of non-limiting example, the pattern on the stamp may have a pitch of between about 10 nm and about 100 nm, producing features between about 5 nm and about 50 nm on the receptor substrate 200. In another embodiment, the pattern on the stamp is about 14 nm or less, producing features on the receptor substrate 200 having a size of about 14 nm or less.

As illustrated in FIG. 20A, the pattern formed on the receptor substrate 200 may be a first SAM 210. The ink material deposited on the receptor substrate 200 by the stamp may form the first SAM 210 that corresponds to the pattern on the stamping surface, thus providing a differentiated pattern on the receptor substrate 200. The first SAM 210 may have a thickness of less than about 20 Å (2nm), which is affected by the selection of the ink material and, in particular, the spacer thereof. By way of non-limiting example, the first SAM 210 has a lateral width less than about 60 nm. In one embodiment, the first SAM 210 has a lateral width of about 14 nm. It will be understood that the lateral width of the SAMs corresponds to the feature size of the stamping surface. After the receptor substrate 200 is patterned, further processing may proceed as desired. Conventional techniques, which are not described in detail herein, may be used to produce a

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semiconductor structure that includes the receptor substrate 200 and the first SAM 210. By way of non-limiting example, portions of the receptor substrate 200 adjacent the first SAM 210 may remain free of the ink material that produces the first SAM 210. These exposed portions of the receptor substrate 200 may be subjected to further etching or
5 plating. For example, the first SAM 210 may be used as an etch mask on the receptor substrate 200 or may be used to guide selective deposition on the receptor substrate 200. If desired, the first SAM 210 may also be used to direct vapor deposition. Thus, oxide, for example, may be selectively deposited on portions of the receptor substrate 200 lacking the first SAM 210. Alternatively, or in addition to, material may be deposited exclusively
10 on the first SAM 210 or exclusively on portions of the receptor substrate 200 lacking the first SAM 210.

The receptor substrate 200 may also be treated with a second ink material that is chemically distinct from the first ink material used to form the first SAM 210, creating a second SAM 220 thereon, as shown in FIG. 20B. The second ink material may be one of
15 the ink materials described herein. A block copolymer with domains selective to the first SAM 210 and second SAM 220, respectively, and with domain sizes and morphologies that match stamp pattern may be deposited over the first SAM 210 and the second SAM 220. Deposition and self-assembly of this diblock copolymer may proceed as previously discussed to form a second set of alternating lamellae 310 and 320 that are
20 substantially perpendicular to the surface of the receptor substrate, as shown in FIG. 20C. Further processing may proceed as described herein. For example, one of the lamellae 310, 320 may be removed and used as either an etch mask or a mask to guide deposition of further materials.

Thus, the SAMs 210, 220 patterned on the receptor substrate 200 may be used for
25 guiding selective deposition of materials and for chemical patterning of block copolymers cast onto it, which may in turn serve as etch masks. While the latter application may seem redundant given that the stamp may have been prepared using block copolymers, the advantage is that lithographic definition of features will be required for the stamp, whereas multiple patterned receptor substrates may be prepared from a single stamp without
30 further lithography. For example, patterning a substrate using conventional lithographically and/or sub-lithographic techniques has been hampered by difficulties including, for example, high costs and/or incompatibility with high throughput production methods. Further, the self-assembly of block copolymers to an underlying chemical

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pattern is rapid relative to other methods of "top-down" (*i.e.*, graphoepitaxy) ordering and registration. Thus, even though, in some embodiments, a stamp may be prepared using conventional lithography, because the stamp may be used to pattern multiple substrates, the production cost per substrate is reduced and the rate of formation of block copolymers
5 on the receptor substrate is greatly reduced.

While the invention is susceptible to various modifications as well as additional forms and implementations, specific embodiments have been shown by way of example in the drawings and have been described in detail herein. However, it should be understood that the invention is not limited to the particular embodiments disclosed. Rather, the
10 invention encompasses all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the following appended claims.

CLAIMS

What is claimed is:

1. A method of patterning a substrate, comprising:
chemisorbing an ink material to at least one region of a stamp, the ink material comprising at least one of an acetylenic carboxylate, an acetylenic sulfonate, and an acetylenic thiol; and transferring the chemisorbed ink material to a receptor substrate.
2. The method of claim 1, wherein chemisorbing an ink material to at least one region of a stamp comprises chemisorbing the ink material, comprised of acetylenic thiol, to the stamp surface by dithiol linkages or gold-thiol bonds.
3. The method of claim 1, wherein transferring the chemisorbed ink material to a receptor substrate comprises cleaving bonds between the stamp and the ink material.
4. The method of claim 1, wherein chemisorbing an ink material to at least one region of a stamp comprises chemisorbing the ink material to gold, a compound containing at least one thiol functional group, a compound containing at least one amine functional group or combinations thereof.
5. The method of claim 1, wherein transferring the chemisorbed ink material to a receptor substrate comprises forming a self-assembled monolayer on the receptor substrate.
6. The method of claim 5, further comprising depositing an oxide on a portion of the receptor substrate, the portion of the receptor substrate being free of the self-assembled monolayer, subsequent to transferring the chemisorbed ink material to a receptor substrate.
7. The method of claim 1, wherein transferring the chemisorbed ink material to a receptor substrate comprises transferring the chemisorbed ink material to a receptor substrate comprising silicon dioxide and a compound selected from the group consisting of grafted glycidoxypropyl(trialkoxysilane, grafted azidoalkyl(trialkoxysilane and isocyanatopropyl(trialkoxysilane.
8. The method of claim 1, wherein chemisorbing an ink material to at least one region of a stamp comprises chemisorbing the ink material comprising an acetylenic thiol functional group to a stamp comprising gold or a compound containing at least one thiol functional group.

9. The method of claim 8, wherein transferring the chemisorbed ink material to a receptor substrate comprises transferring the chemisorbed ink material to a receptor substrate comprising silicon dioxide and grafted 6-azidosulfonylhexyl (triethoxy)silane or 11-azidoundecyl(triethoxy)silane.

10. The method of claim 1, wherein transferring the chemisorbed ink material to a receptor substrate comprises transferring the chemisorbed ink material to a receptor substrate comprising Si—Cl from hydrogen-terminated silicon.

11. The method of claim 1, wherein chemisorbing an ink material to at least one region of a stamp comprises chemisorbing the ink material to at least one region of the stamp, the stamp comprising silicon dioxide and an aminoalkyl(trialkoxysilane compound.

12. The method of claim 11, wherein transferring the chemisorbed ink material to a receptor substrate comprises transferring the chemisorbed ink material to a receptor substrate comprising silicon dioxide and grafted isocyanatopropyl(trialkoxysilane.

13. The method of claim 1, wherein chemisorbing an ink material to at least one region of a stamp comprises chemisorbing the ink material selected from the group consisting of an acetylenic carboxylate and an acetylenic sulfonate to a stamp comprising silicon dioxide and a grafted aminoalkyl silane compound.

14. The method of claim 13, wherein transferring the chemisorbed ink material to a receptor substrate comprises transferring the chemisorbed ink material to a receptor substrate comprising silicon dioxide and 6-azidosulfonylhexyl (triethoxy)silane or a grafted azidoalkyl silane.

15. The method of claim 1, wherein chemisorbing an ink material to at least one region of a stamp comprises chemisorbing an ink material to a receptor substrate comprising silicon dioxide and a grafted mercaptoalkyl silane compound.

16. The method of claim 15, wherein transferring the chemisorbed ink material to a receptor substrate comprises transferring the chemisorbed ink material to a receptor substrate comprising silicon dioxide and 6-azidosulfonylhexyl (triethoxy)silane or a grafted azidoalkyl silane.

17. The method of claim 1, further comprising simultaneously chemisorbing the ink material to the at least one region of the stamp and chemisorbing a second ink material to a second region of the stamp, wherein the second region is chemically differentiated from the at least one region.

18. The method of claim 1, wherein transferring the chemisorbed ink material to a receptor substrate comprises forming a patterned self-assembled monolayer on the receptor substrate and further comprising depositing a block copolymer over the patterned self-assembled monolayer and annealing the block copolymer to enable self-assembly of the block copolymer.

19. A method of patterning a substrate, comprising:

contacting at least one region of a stamp with an ink material having a chemical affinity for the at least one region of the stamp, the ink material comprising at least one of an acetylenic carboxylate, an acetylenic sulfonate, and an acetylenic thiol; and

contacting a substrate with the ink material adhered to the region of the stamp, the substrate having a greater chemical affinity for the ink material than the at least one region of the stamp.

20. The method of claim 19, further comprising washing the at least one region of the stamp to remove physisorbed ink material therefrom.

21. The method of claim 19, further comprising removing the stamp, leaving the ink material on portions of the substrate previously contacting the at least one region of the stamp.

22. The method of claim 19, wherein contacting at least one region of a stamp with an ink material comprises contacting at least one region of chemical differentiation on the stamp with the ink material.

23. The method of claim 19, wherein contacting at least one region of a stamp with an ink material comprises contacting at least one topographical feature on the stamp with the ink material.

24. The method of claim 19, wherein contacting a substrate with the ink material adhered to the region of the stamp comprises contacting the substrate with the ink material chemisorbed to the at least one region of the stamp.

25. The method of claim 19, wherein contacting a substrate with the ink material adhered to the at least one region of the stamp comprises covalently bonding the substrate with the ink material adhered to the at least one region of the stamp.

26. A method of patterning a receptor substrate, comprising:

depositing a block copolymer over a stamp substrate;

annealing the block copolymer to form at least two polymer domains overlying the stamp substrate;

chemisorbing an ink material to at least one of the at least two polymer domains overlying the stamp substrate; and transferring the ink material chemisorbed to the at least one of the at least two polymer domains to the receptor substrate.

27. The method of claim 26, wherein chemisorbing an ink material to at least one of the at least two polymer domains overlying the stamp substrate comprises chemisorbing the ink material to at least one pattern defined by a plurality of lamellae formed from the at least one of the at least two polymer domains.

28. The method of claim 26, wherein chemisorbing an ink material to at least one of the at least two polymer domains overlying the stamp substrate comprises chemisorbing an ink material having different functional groups on opposite ends of thereof.

29. The method of claim 26, wherein chemisorbing an ink material to at least one of the at least two polymer domains overlying the stamp substrate comprises chemisorbing the ink material to a first polymer domain of the block copolymer without chemisorbing the ink material to a second polymer domain of the block copolymer, the first polymer domain having a chemical affinity different than the second polymer domain of the block copolymer.

30. The method of claim 26, wherein transferring the ink material chemisorbed to the at least one of the at least two polymer domains to the receptor substrate comprises contacting the ink material chemisorbed to the at least one of the at least two polymer domains with a receptor substrate having a greater chemical affinity for the ink material than the at least one of the at least two polymer domains.

31. The method of claim 30, wherein contacting the ink material chemisorbed to the at least one of the at least two polymer domains with a receptor substrate having a greater chemical affinity for the ink material than the at least one of the at least two polymer domains comprises covalently bonding the ink material chemisorbed to the at least one of the at least two polymer domains to the receptor substrate.

32. A method of patterning a substrate, comprising:

chemisorbing an ink material to at least one region of a stamp; and

transferring the chemisorbed ink material to a pattern on a receptor substrate comprising:

forming a patterned self-assembled monolayer on the receptor substrate;
depositing a block copolymer over the patterned self-assembled monolayer; and
annealing the block copolymer to enable self-assembly of the block copolymer into a pattern.

33. The method of claim 32, wherein chemisorbing an ink material to at least one region of a stamp comprises chemisorbing the ink material to the stamp surface by dithiol linkages or gold-thiol bonds.

34. The method of claim 32, wherein chemisorbing an ink material to at least one region of a stamp comprises chemisorbing the ink material to gold, a compound containing at least one thiol functional group, a compound containing at least one amine functional group or combinations thereof.

35. The method of claim 32, wherein chemisorbing an ink material to at least one region of a stamp comprises chemisorbing the ink material comprising an acetylenic thiol functional group to a stamp comprising gold or a compound containing at least one thiol functional group.

36. The method of claim 32, wherein transferring the chemisorbed ink material to a receptor substrate comprises transferring the chemisorbed ink material to a receptor substrate comprising silicon dioxide and grafted 6-azidosulfonylhexyl(triethoxy)silane or 11-azidoundecyl(triethyloxy)silane.

37. The method of claim 32, wherein chemisorbing an ink material to at least one region of a stamp comprises chemisorbing the ink material selected from the group consisting of an acetylenic carboxylate and an acetylenic sulfonate to a stamp comprising silicon dioxide and a grafted aminoalkyl silane compound.

38. The method of claim 32, wherein transferring the chemisorbed ink material to a receptor substrate comprises transferring the chemisorbed ink material to a receptor substrate comprising silicon dioxide and 6-azidosulfonylhexyl(triethoxy)silane or a grafted azidoalkyl silane.

39. A method of patterning a substrate, comprising:
chemisorbing an ink material to at least one region of a stamp;

transferring the chemisorbed ink material to a first portion of a receptor substrate; and

depositing an oxide on a second portion of the receptor substrate subsequent to transferring the chemisorbed ink material to a first portion of a receptor substrate, the second portion of the receptor substrate being free of the ink material.