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(54) **METHOD OF MANUFACTURING A SEMICONDUCTOR DEVICE AND COMPOSITION INCLUDING FLOATING ADDITIVE**

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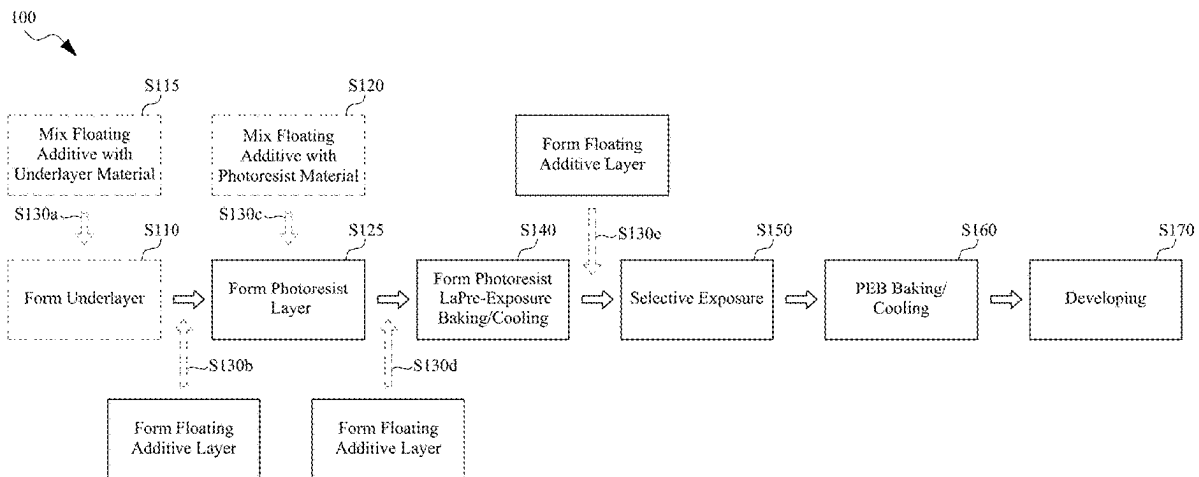
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(57)

ABSTRACT

A method of manufacturing a semiconductor device includes forming a photoresist layer including a photoresist composition over a substrate and forming a floating additive layer comprising a floating additive polymer. The floating additive polymer includes a pendant fluorine substituted organic group and one or more of a pendant acid generating group, a pendant base group, a pendant acid labile group, a pendant chromophore group, a pendant developer solubility promoter group, and a pendant acid diffusion control group. The photoresist layer is selectively exposed to actinic radiation to form a latent pattern. The latent pattern is developed to form a pattern in the photoresist layer.



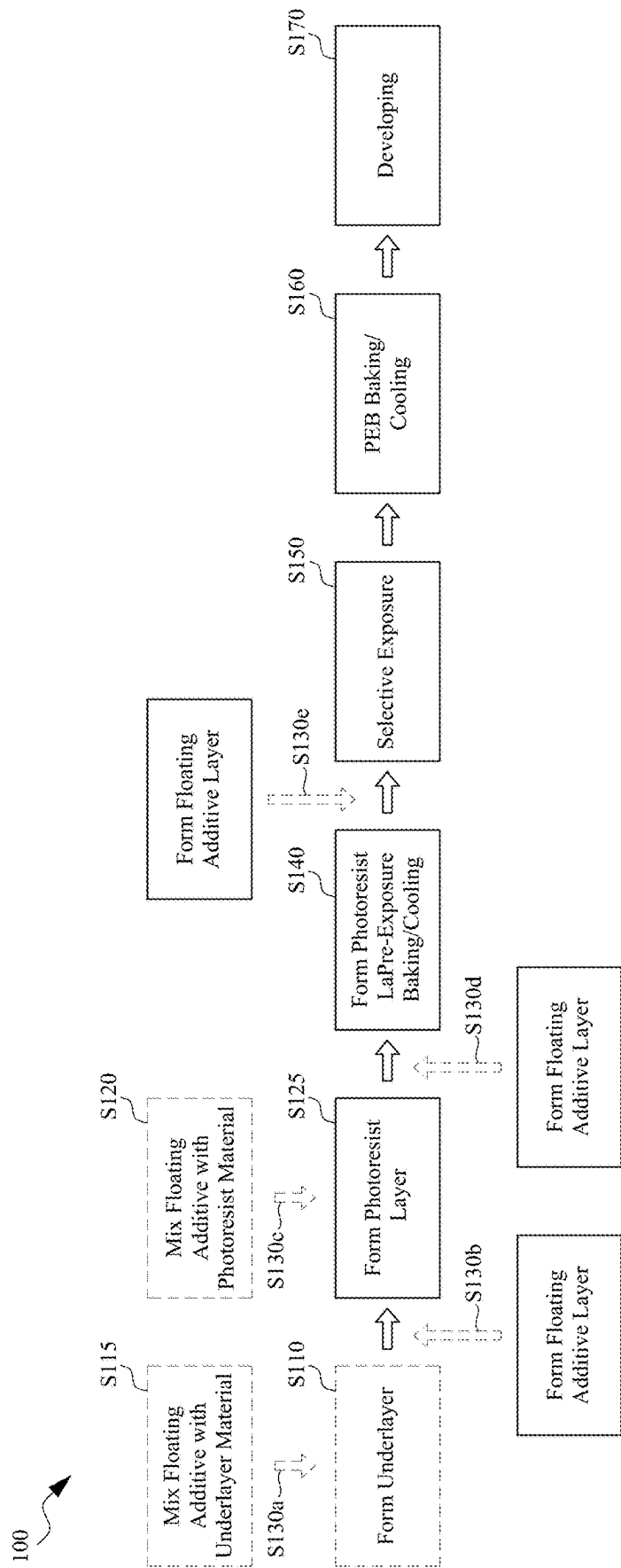


FIG. 1

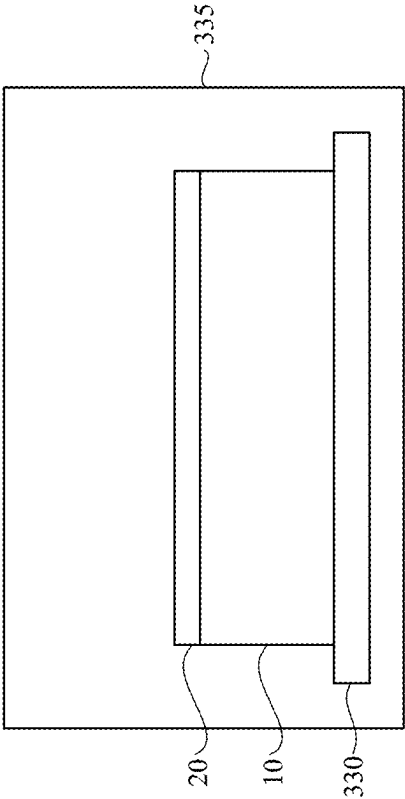


FIG. 2

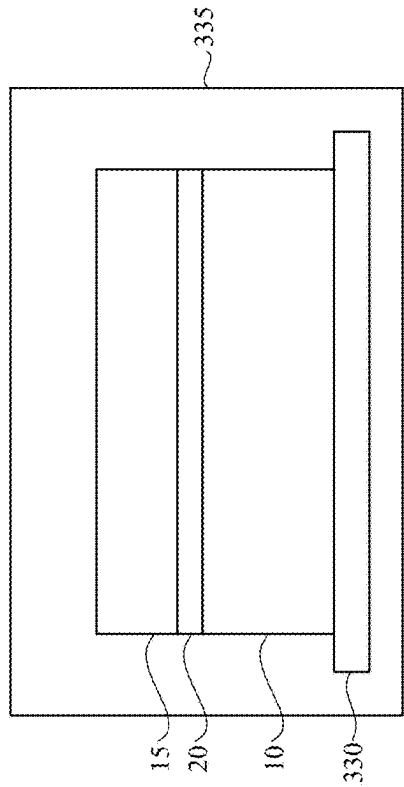


FIG. 3A

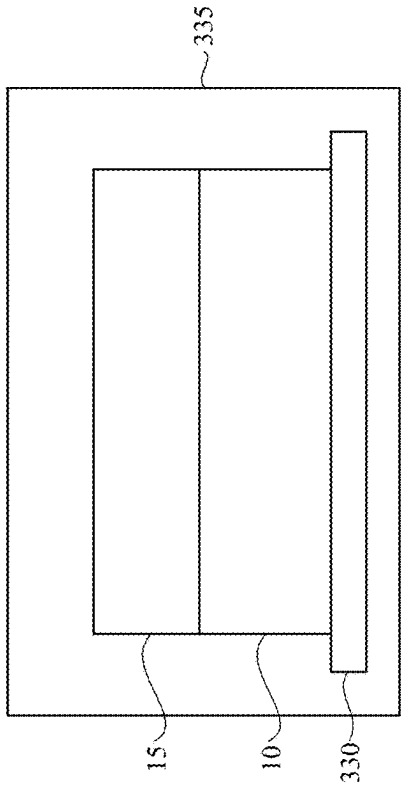


FIG. 3B

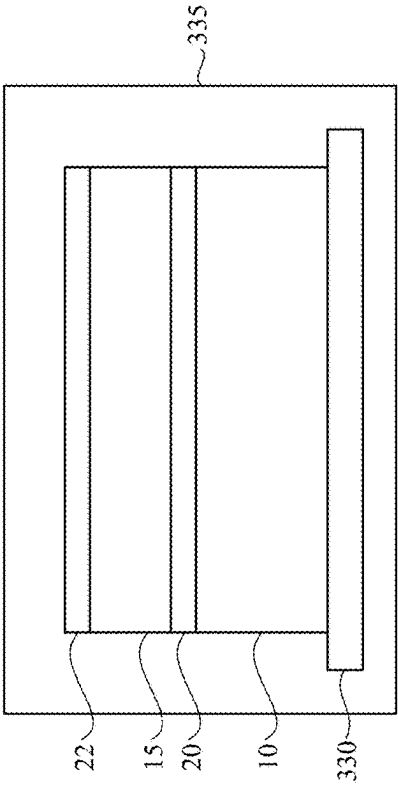


FIG. 4A

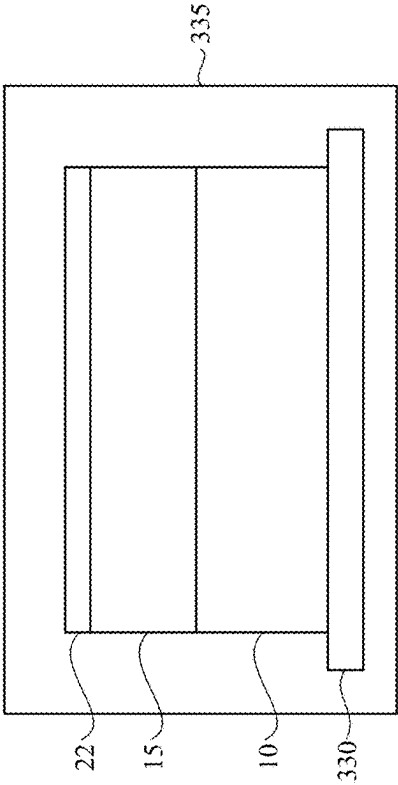


FIG. 4B

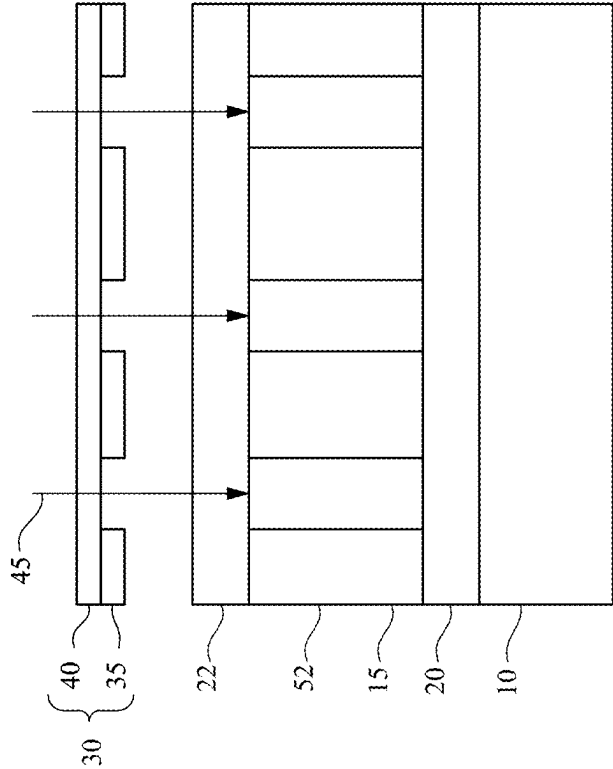


FIG. 5A

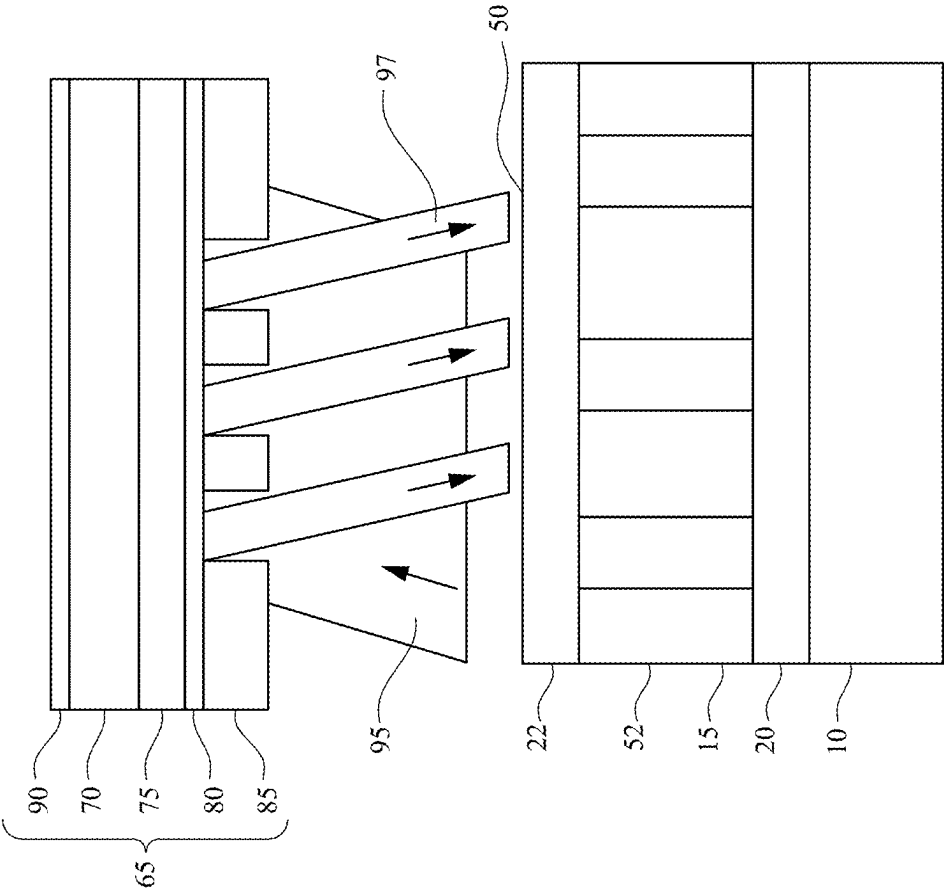
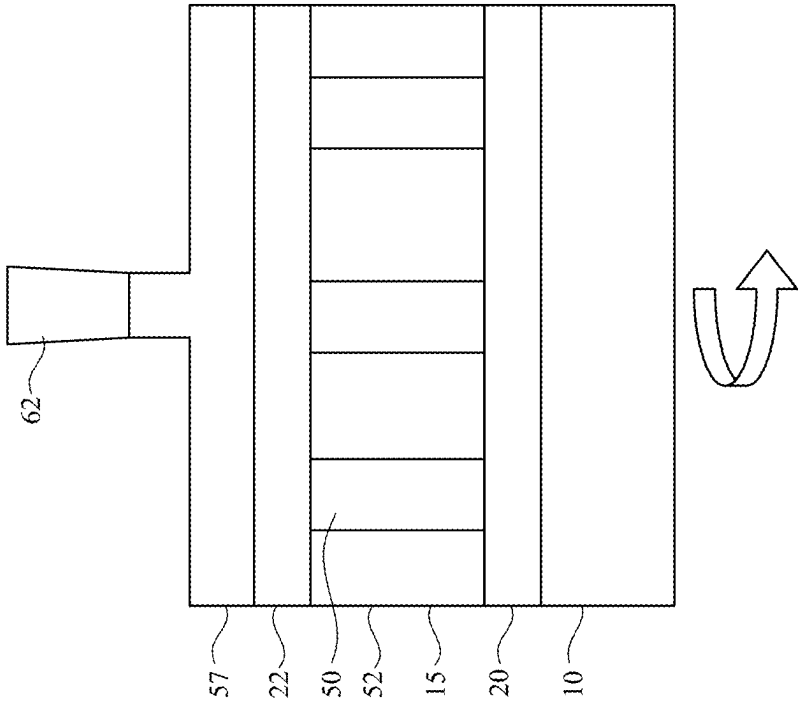


FIG. 5B



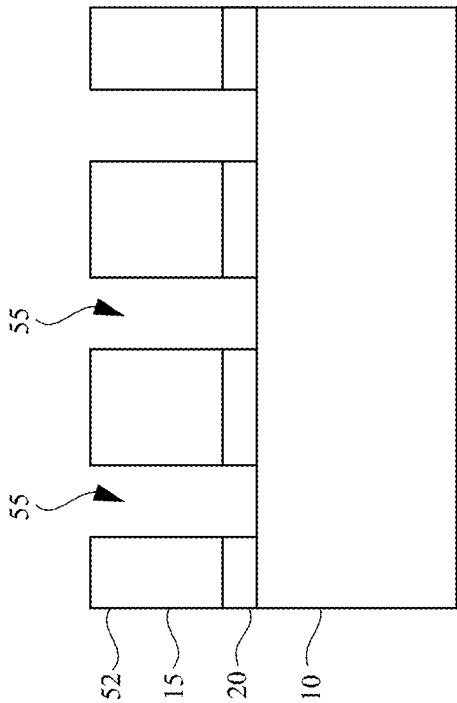


FIG. 7

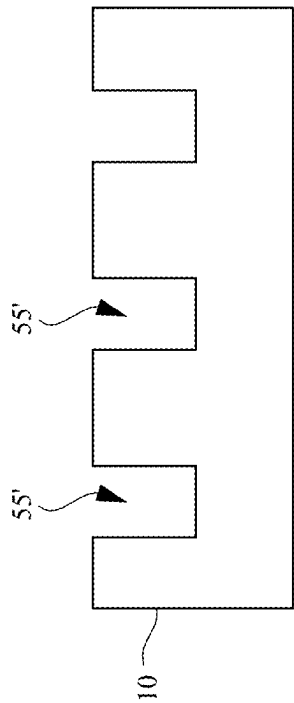
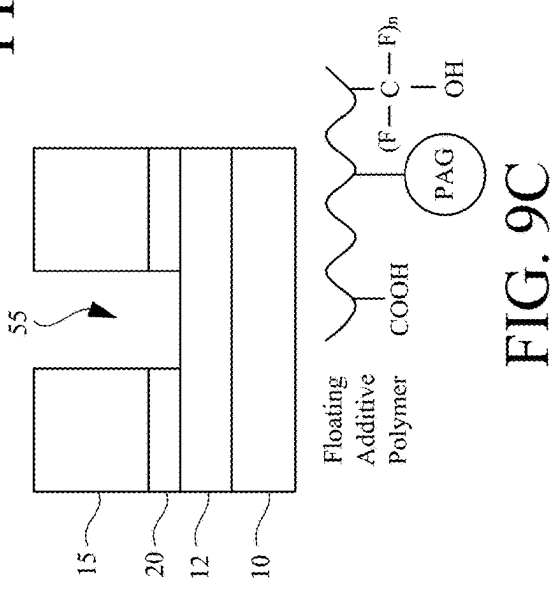
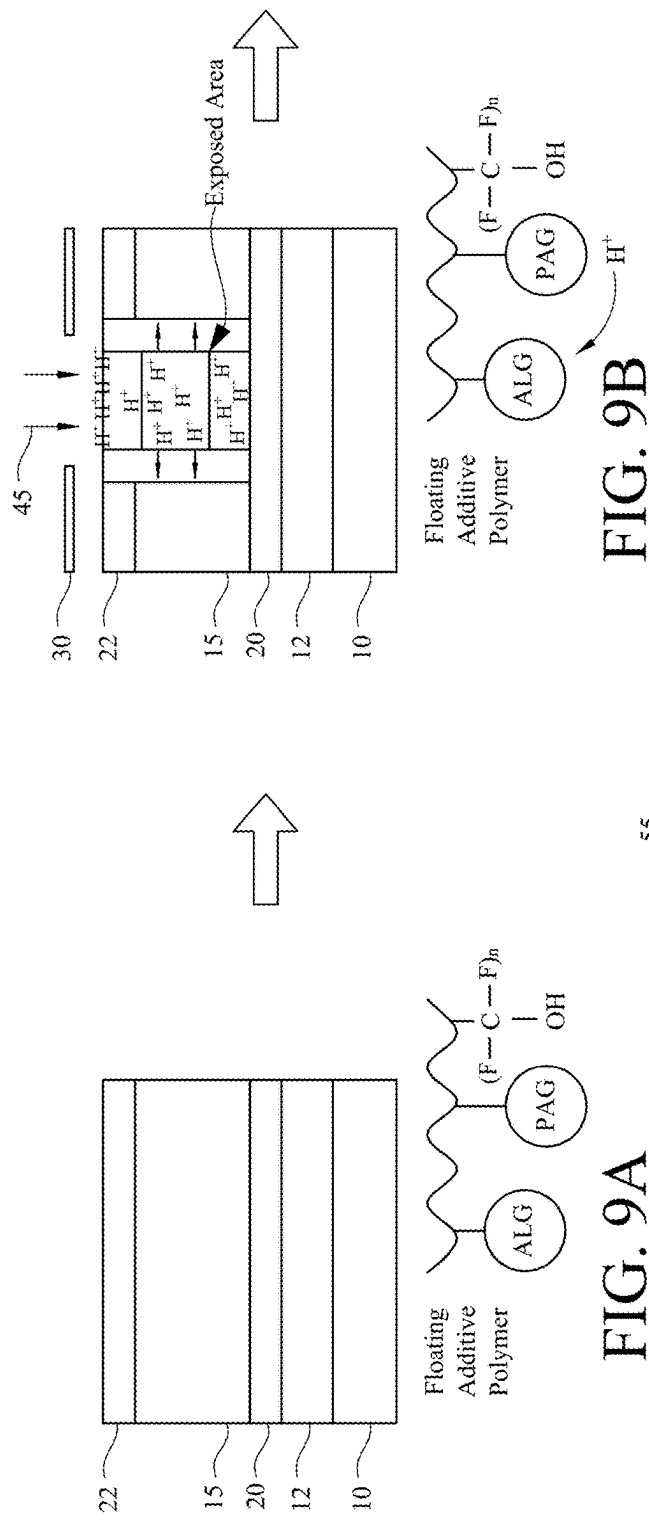
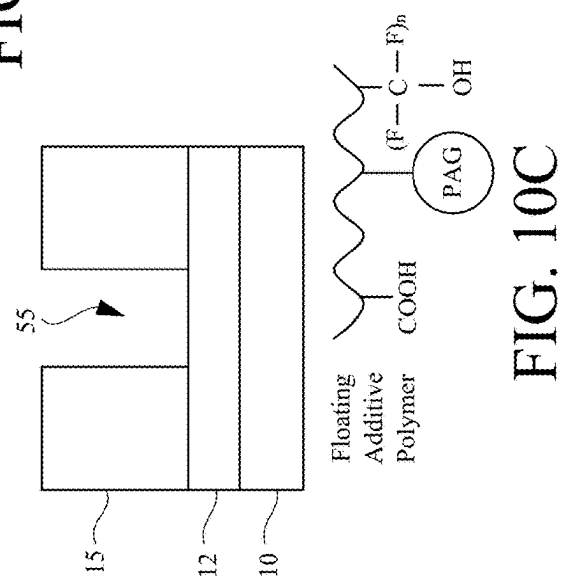
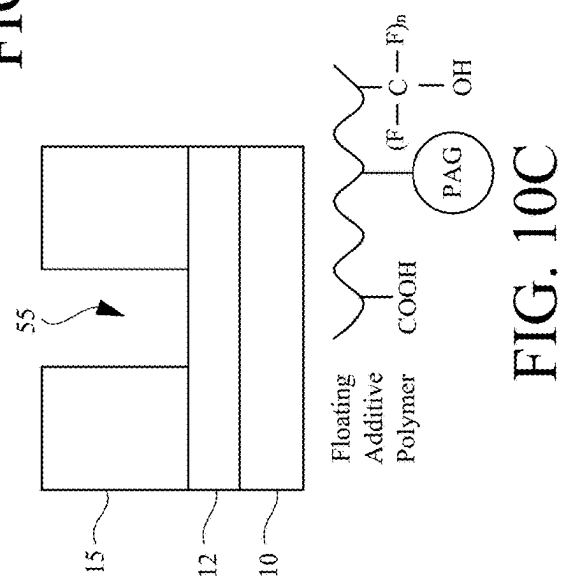
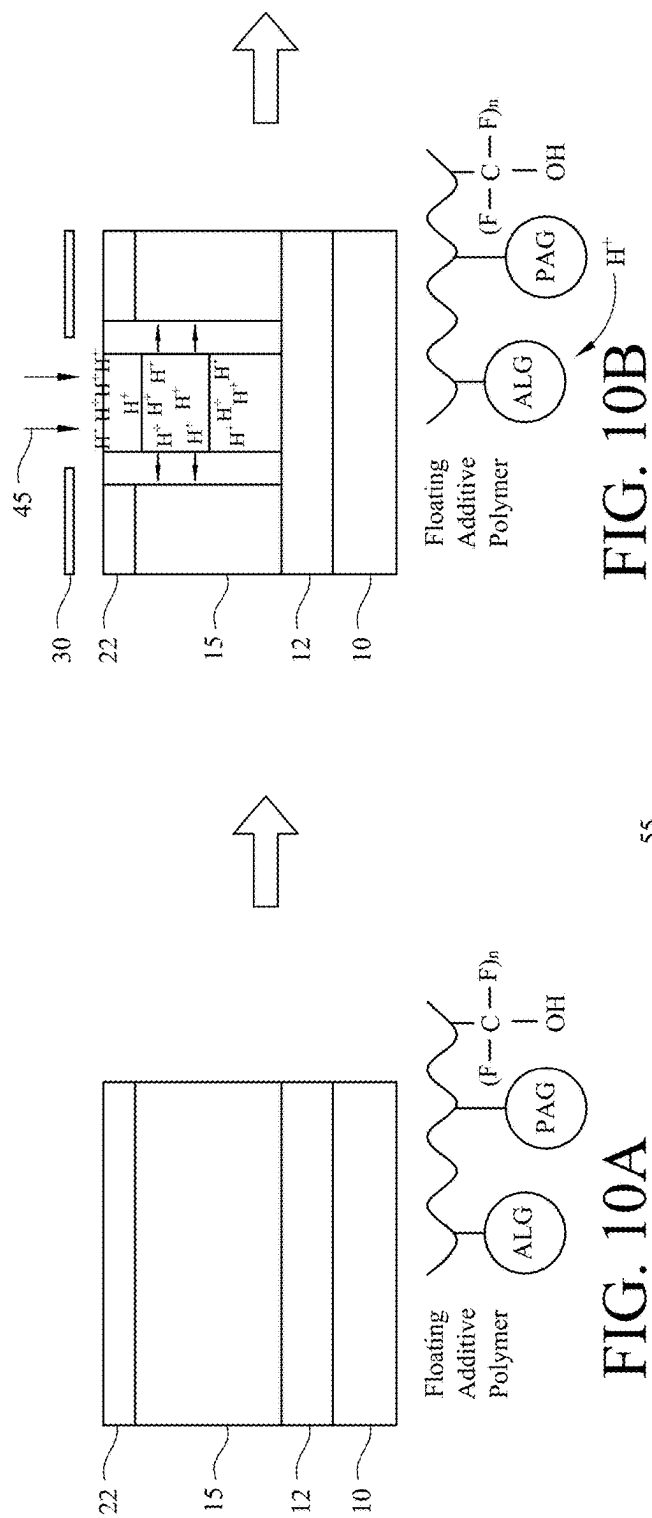


FIG. 8





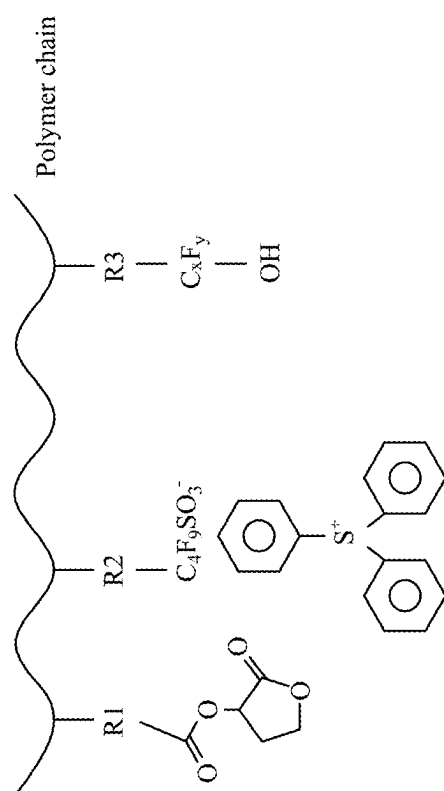
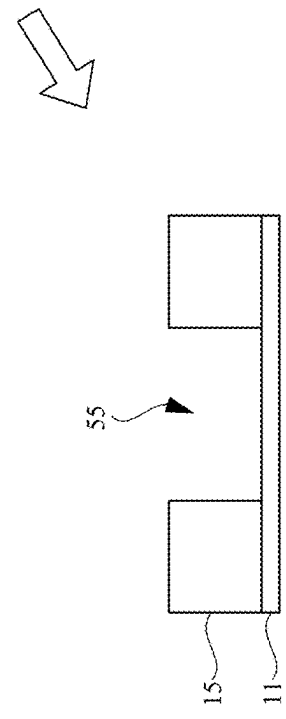
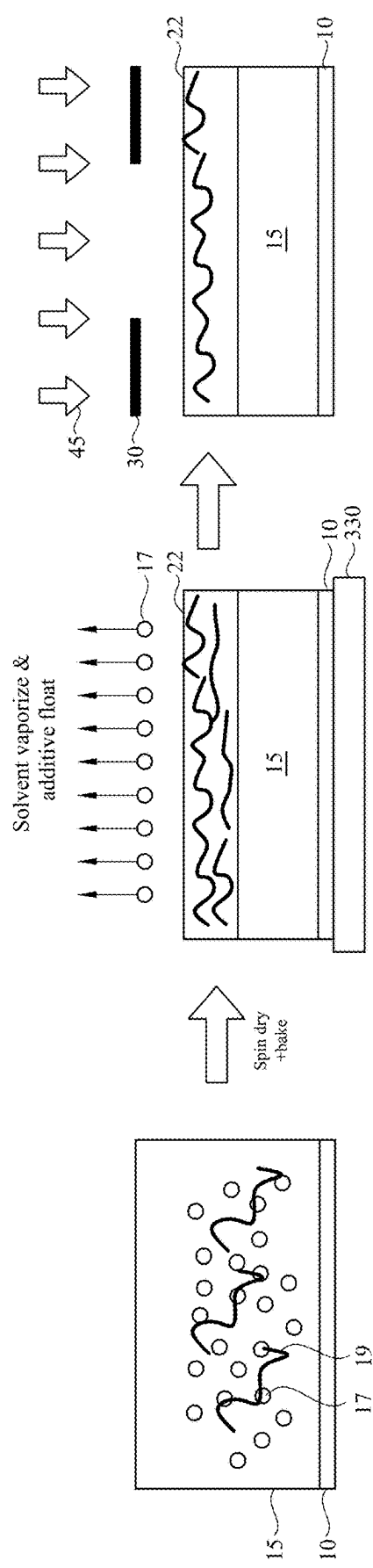
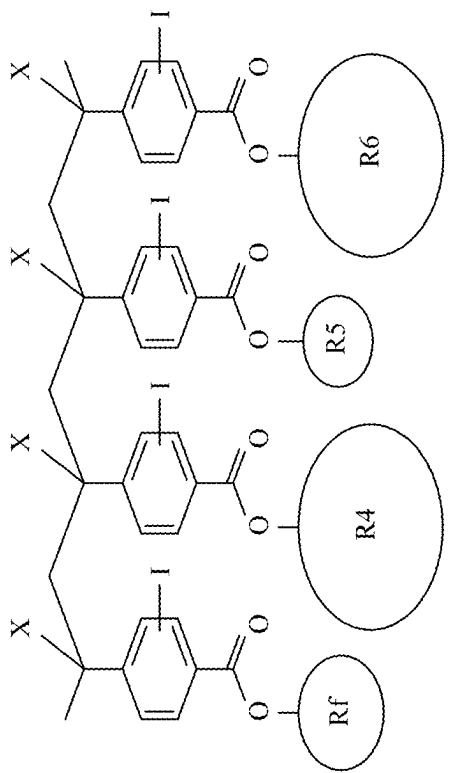


FIG. 10D





- (Rf) Fluorine substituted organic group
- (R4) Acid generating/base group or acid diffusion control group
- (R5) Chromophore group
- (R6) Developer solubility promoter group

FIG. 12B

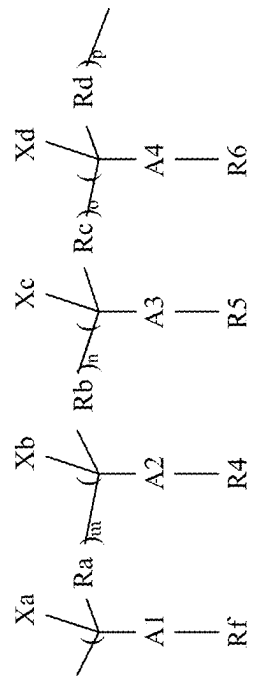


FIG. 12A

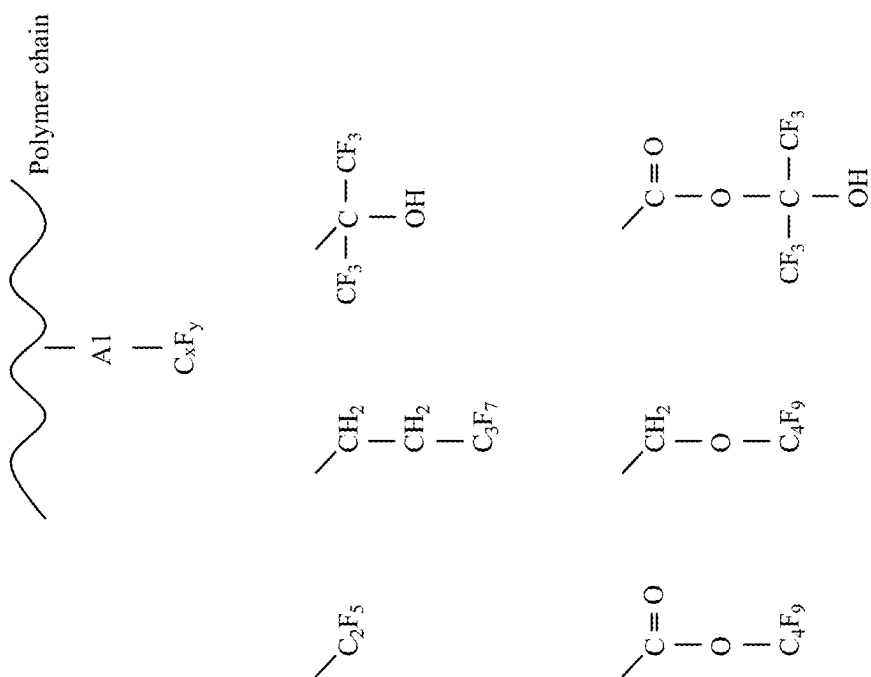


FIG. 13A

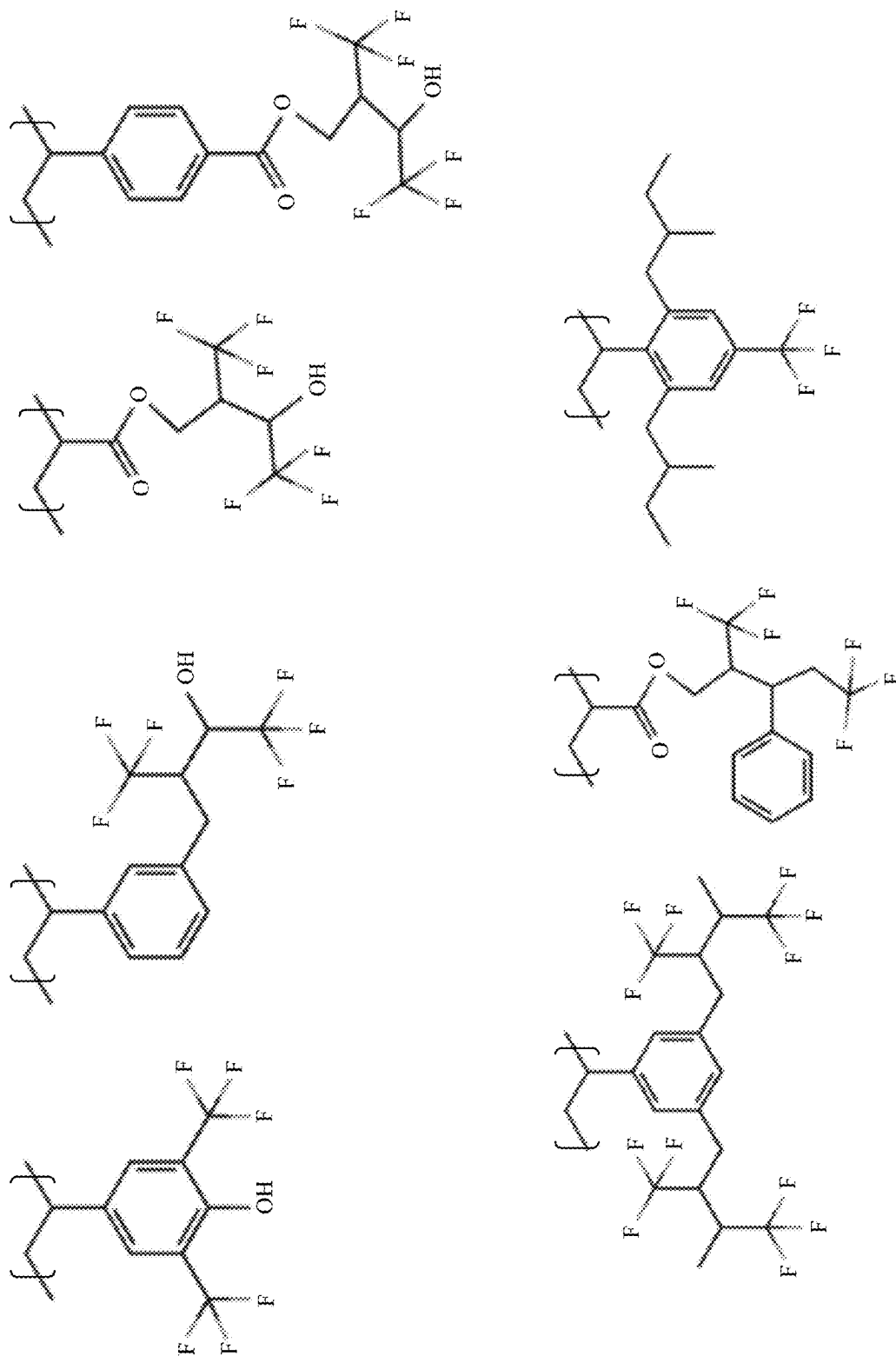


FIG. 13B

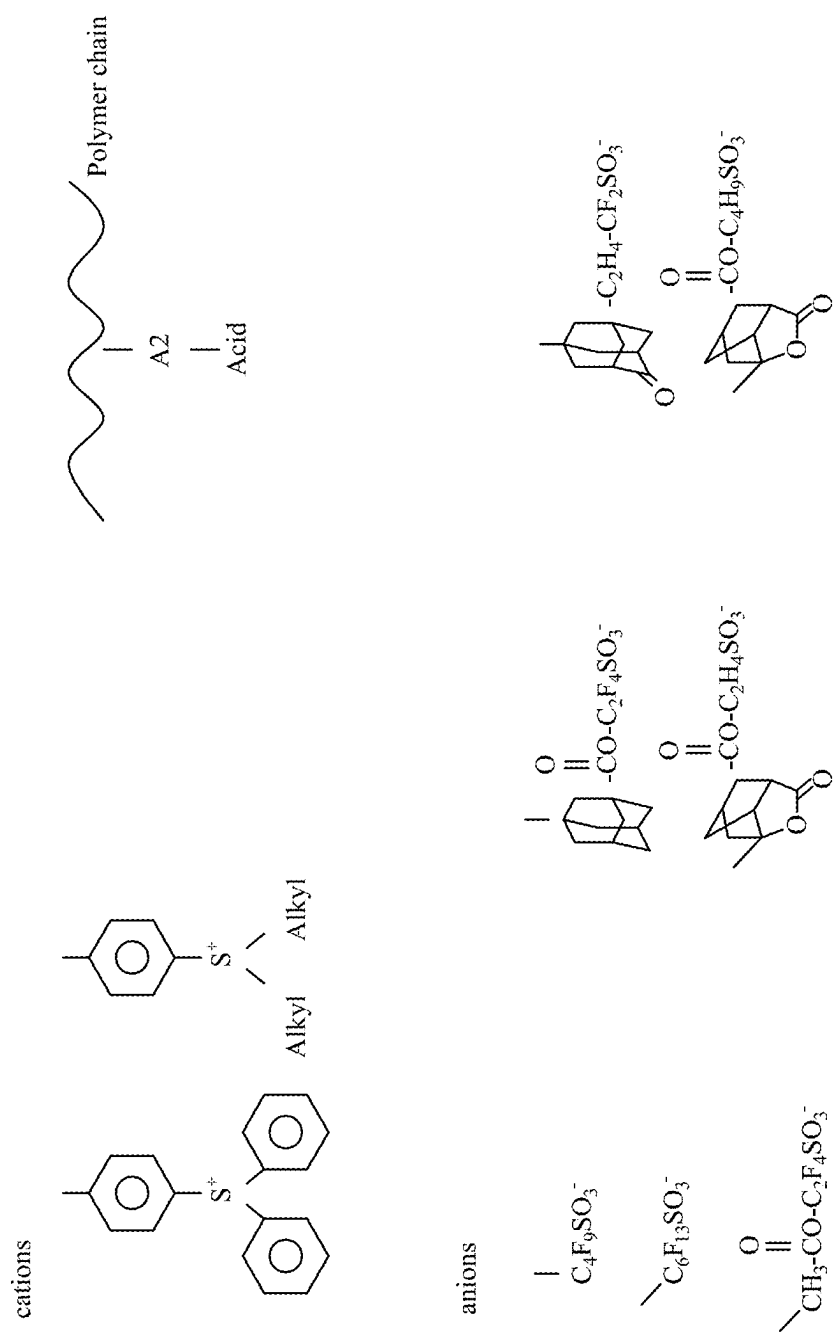


FIG. 14A

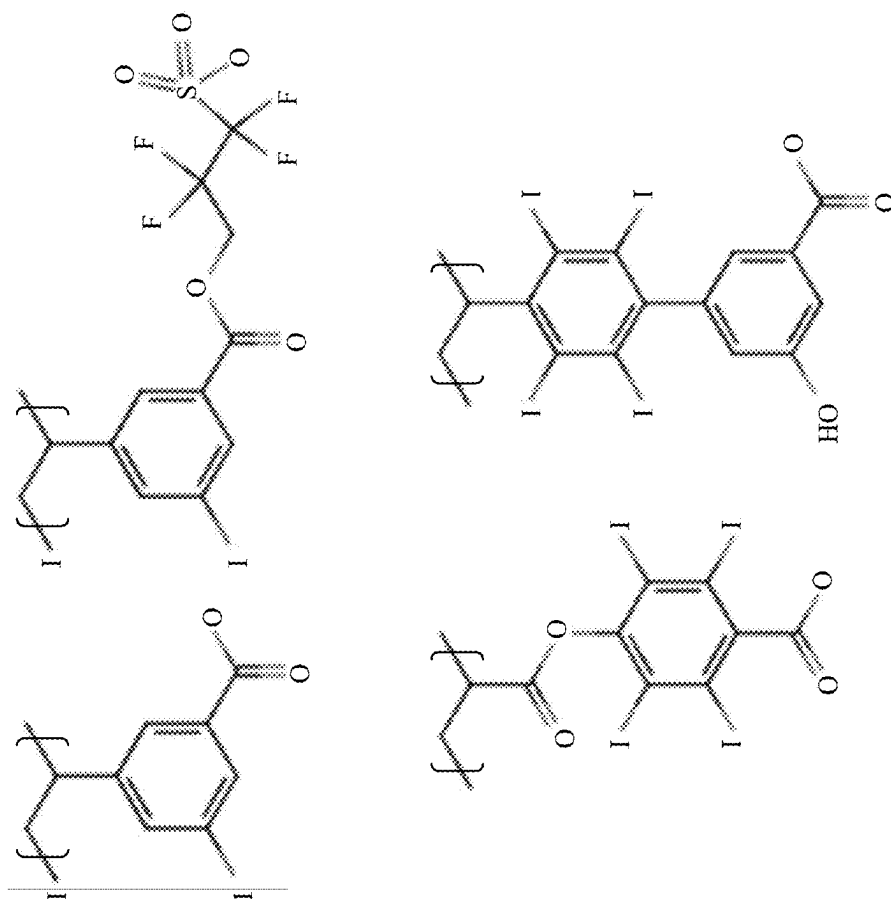


FIG. 14B

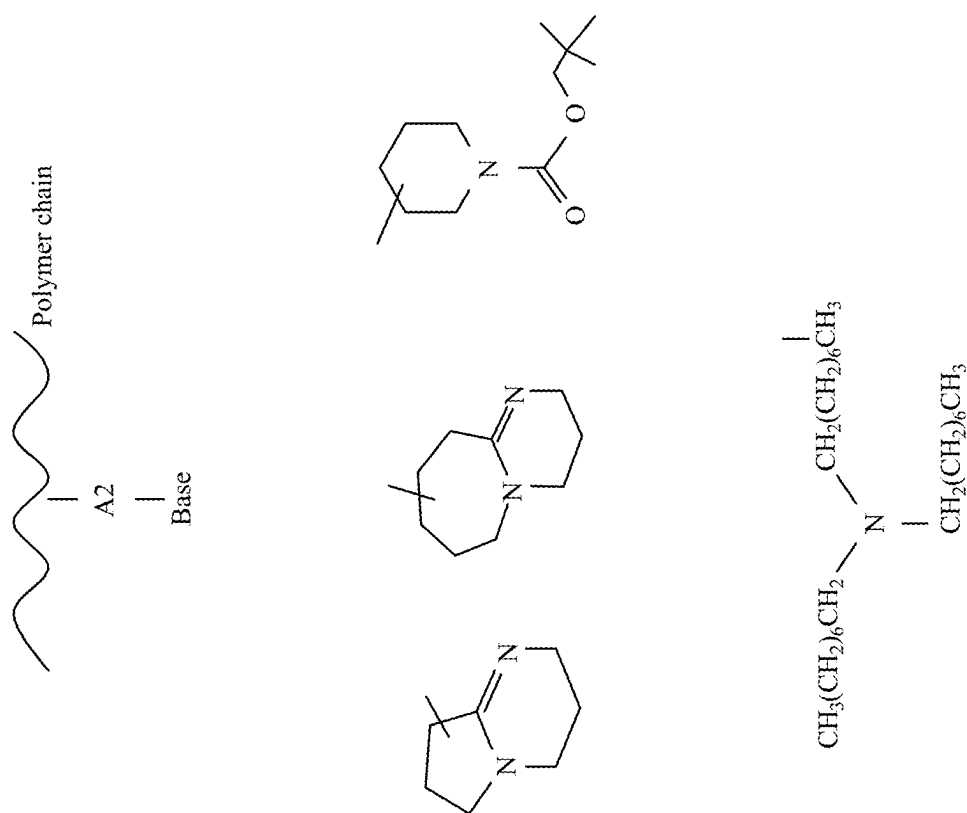


FIG. 14C

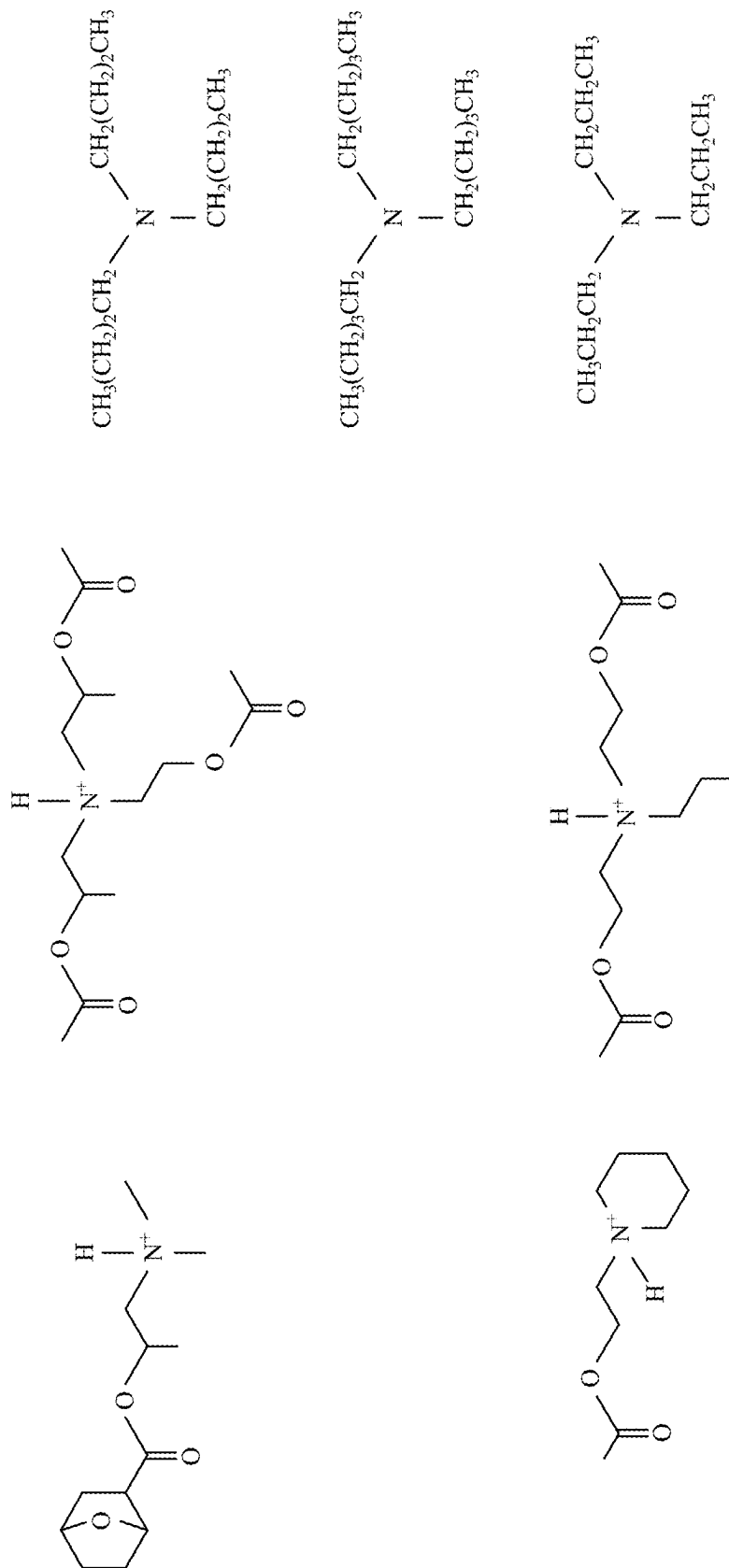


FIG. 14D

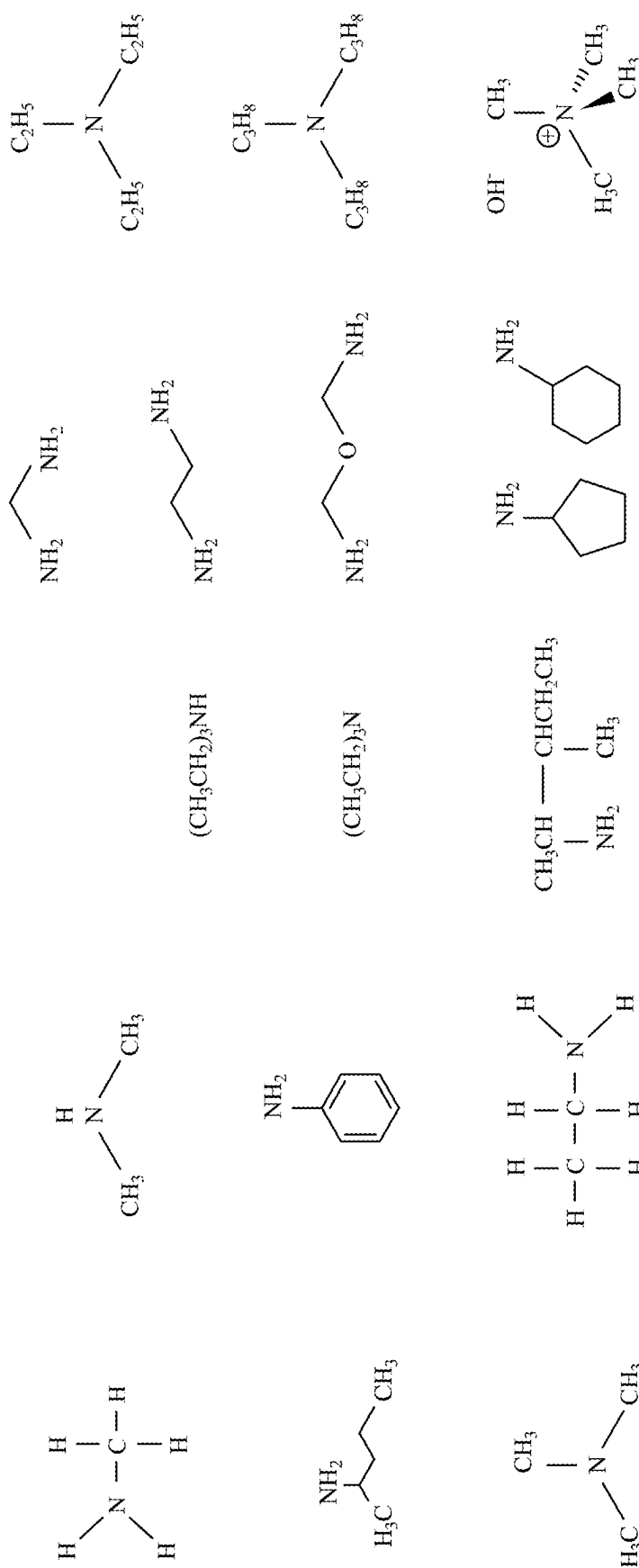


FIG. 14E

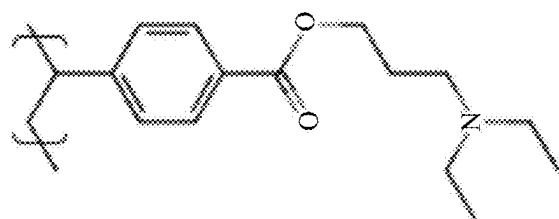
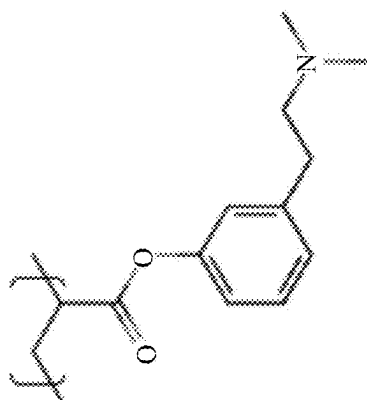
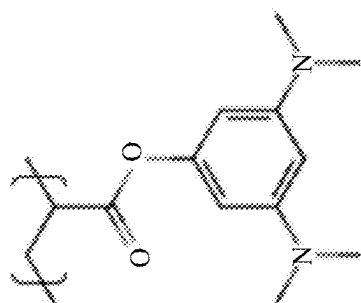
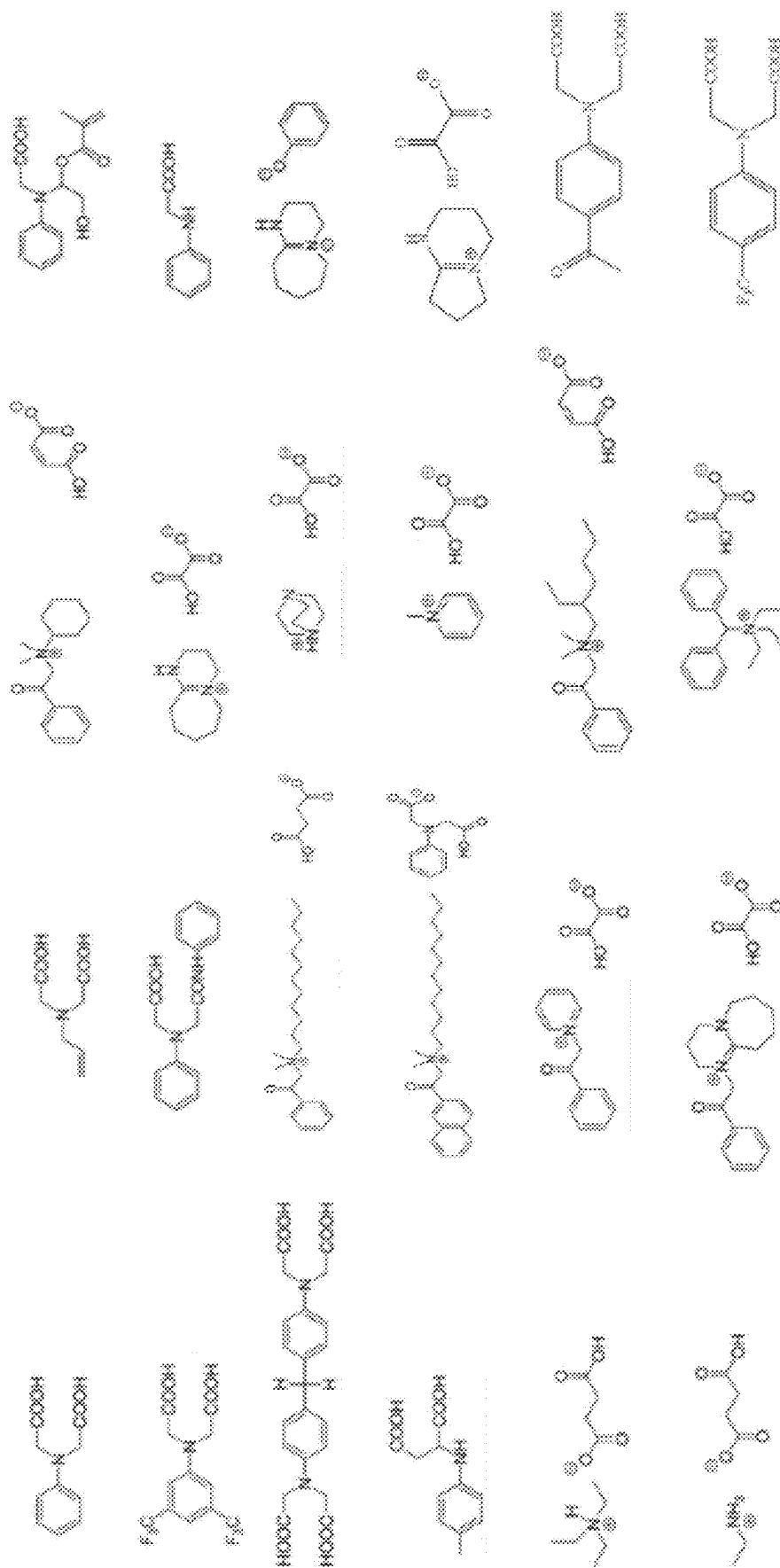


FIG. 14F



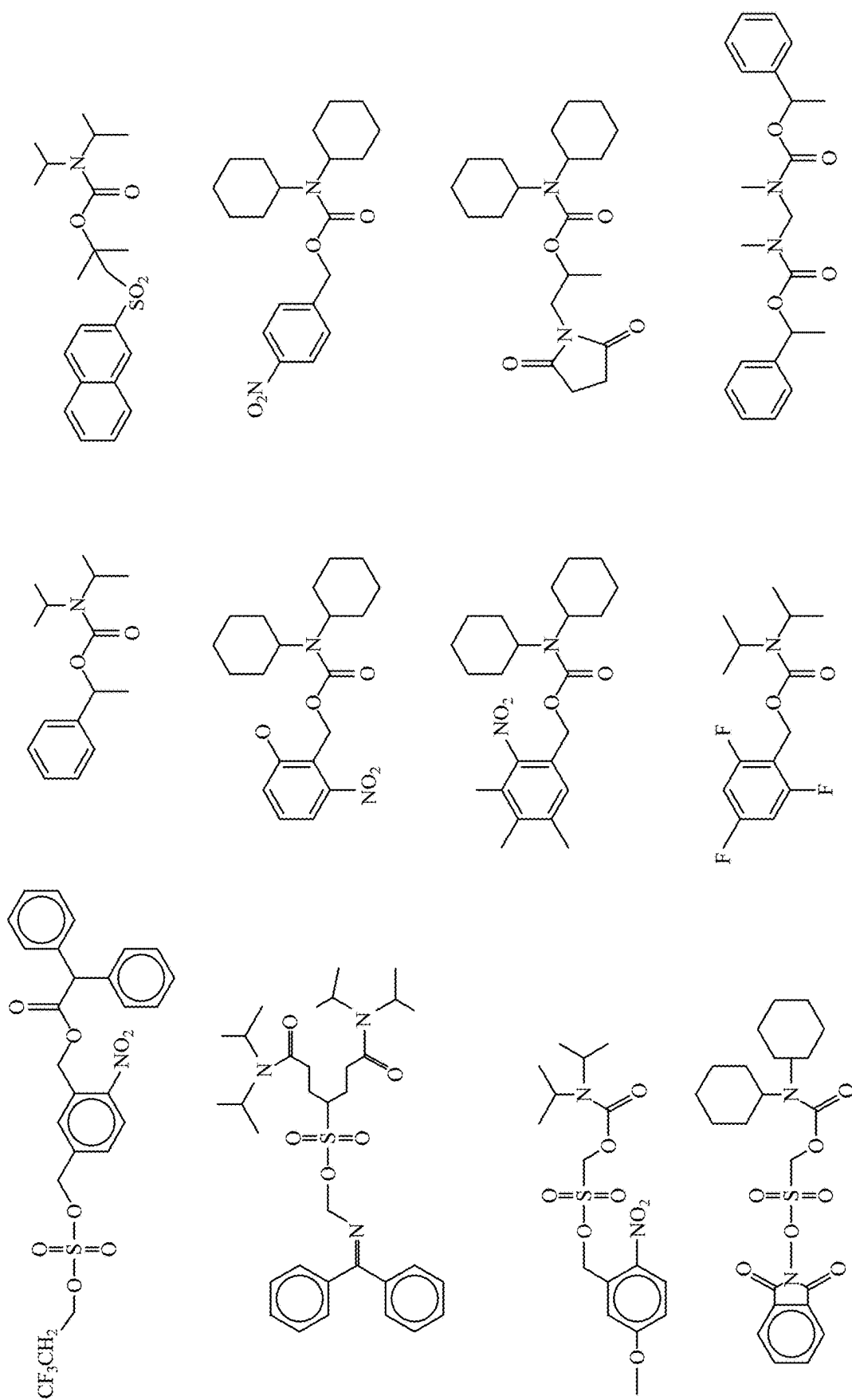


FIG. 14H



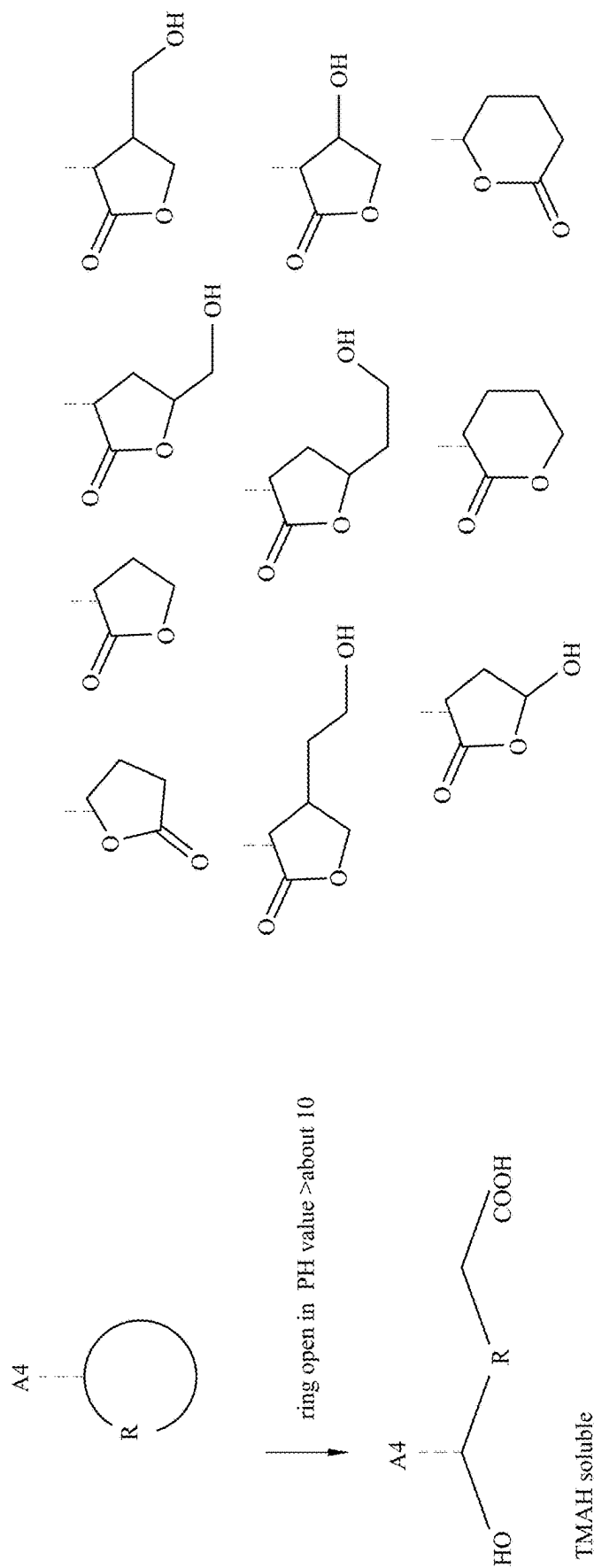


FIG. 16A

FIG. 16B

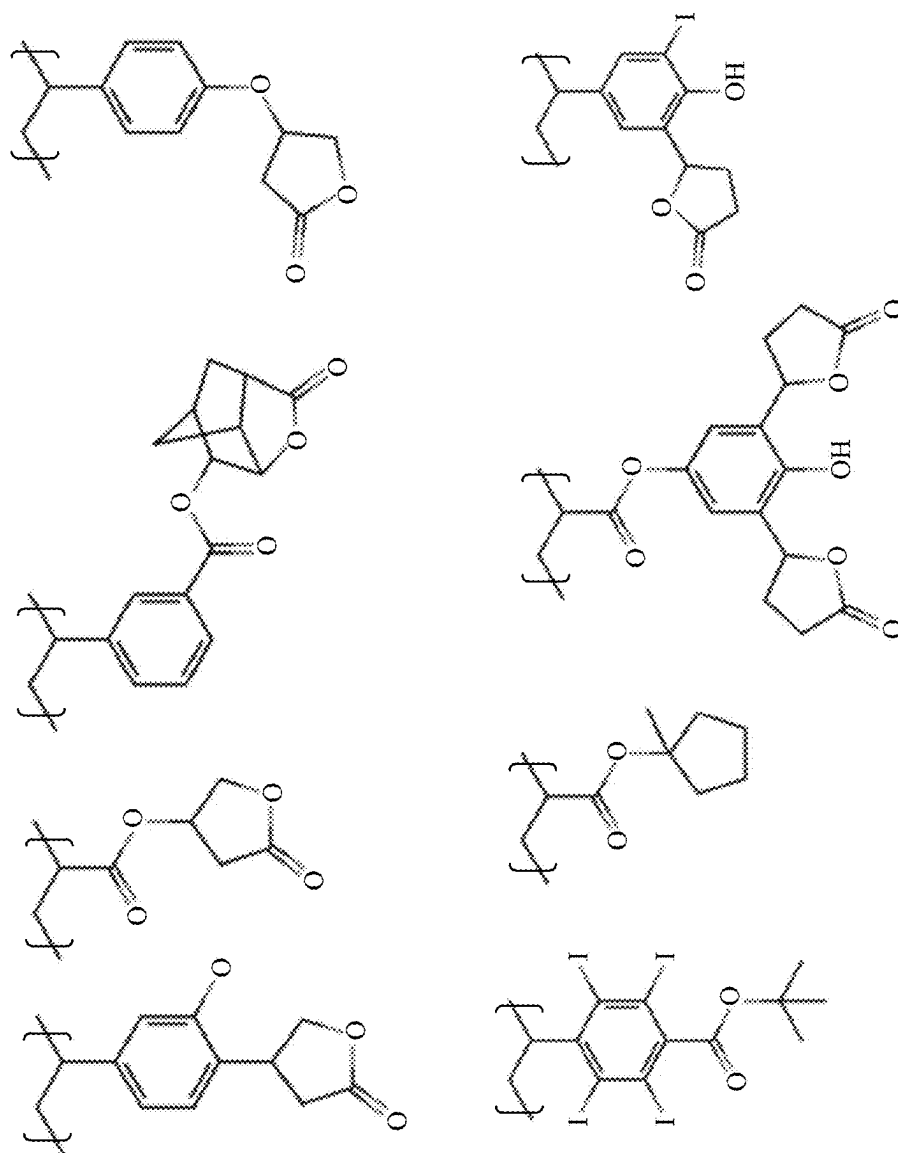


FIG. 16C

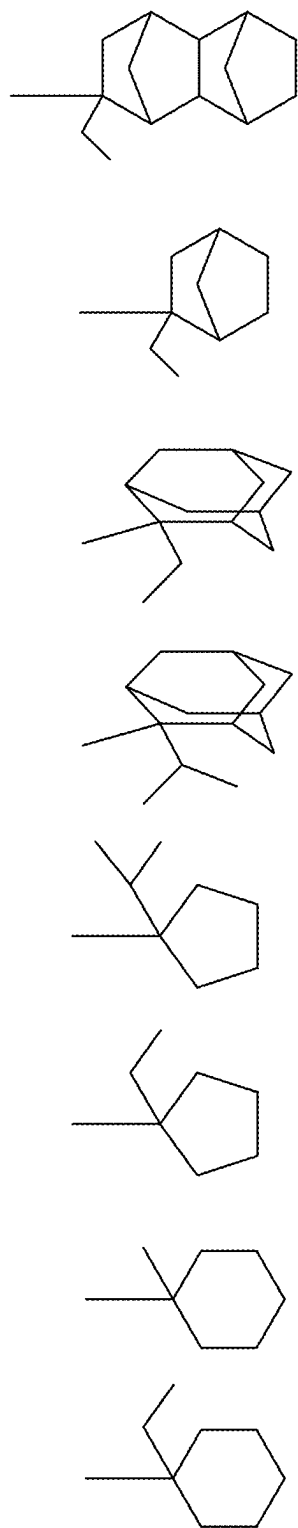


FIG. 16D

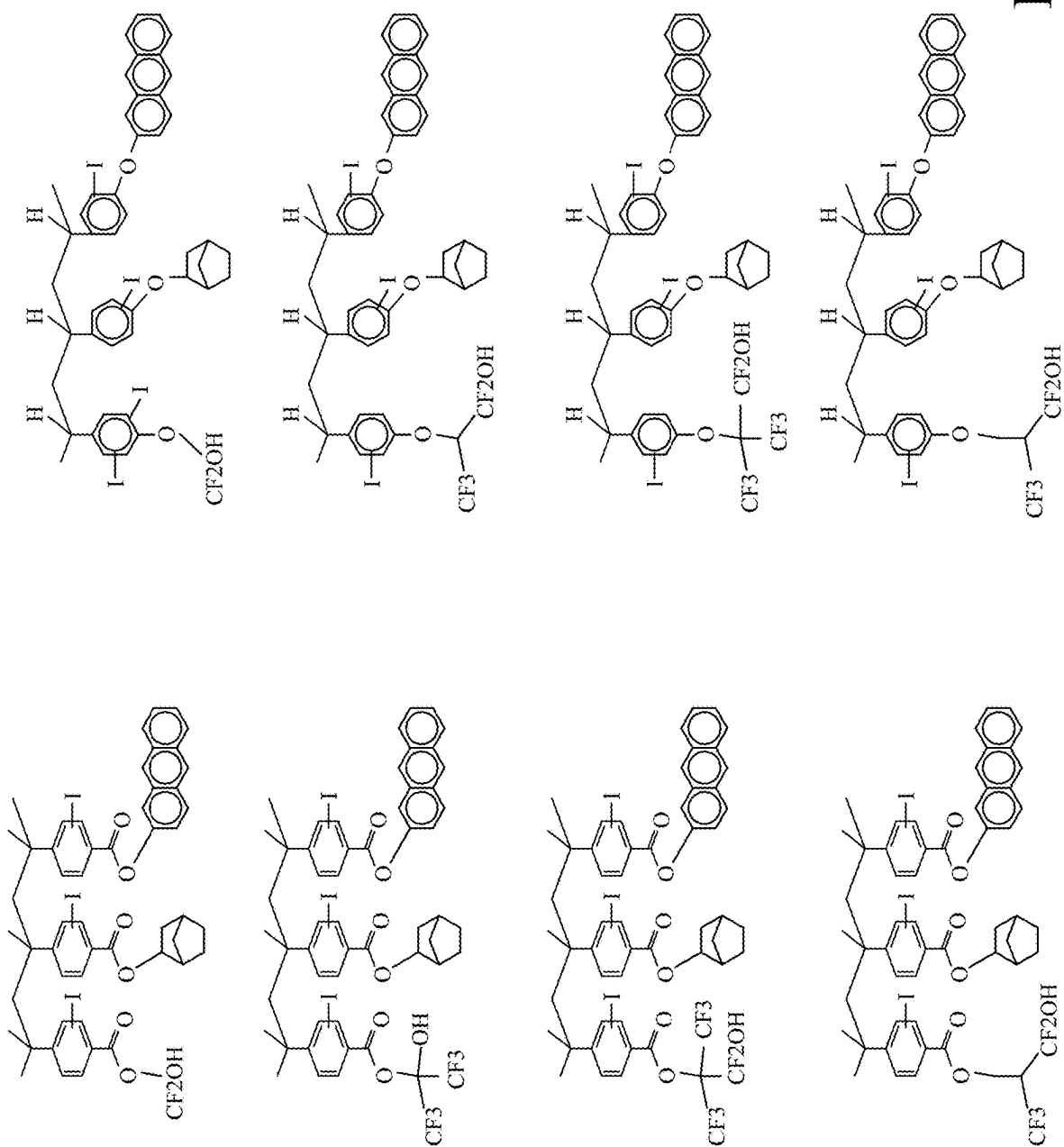
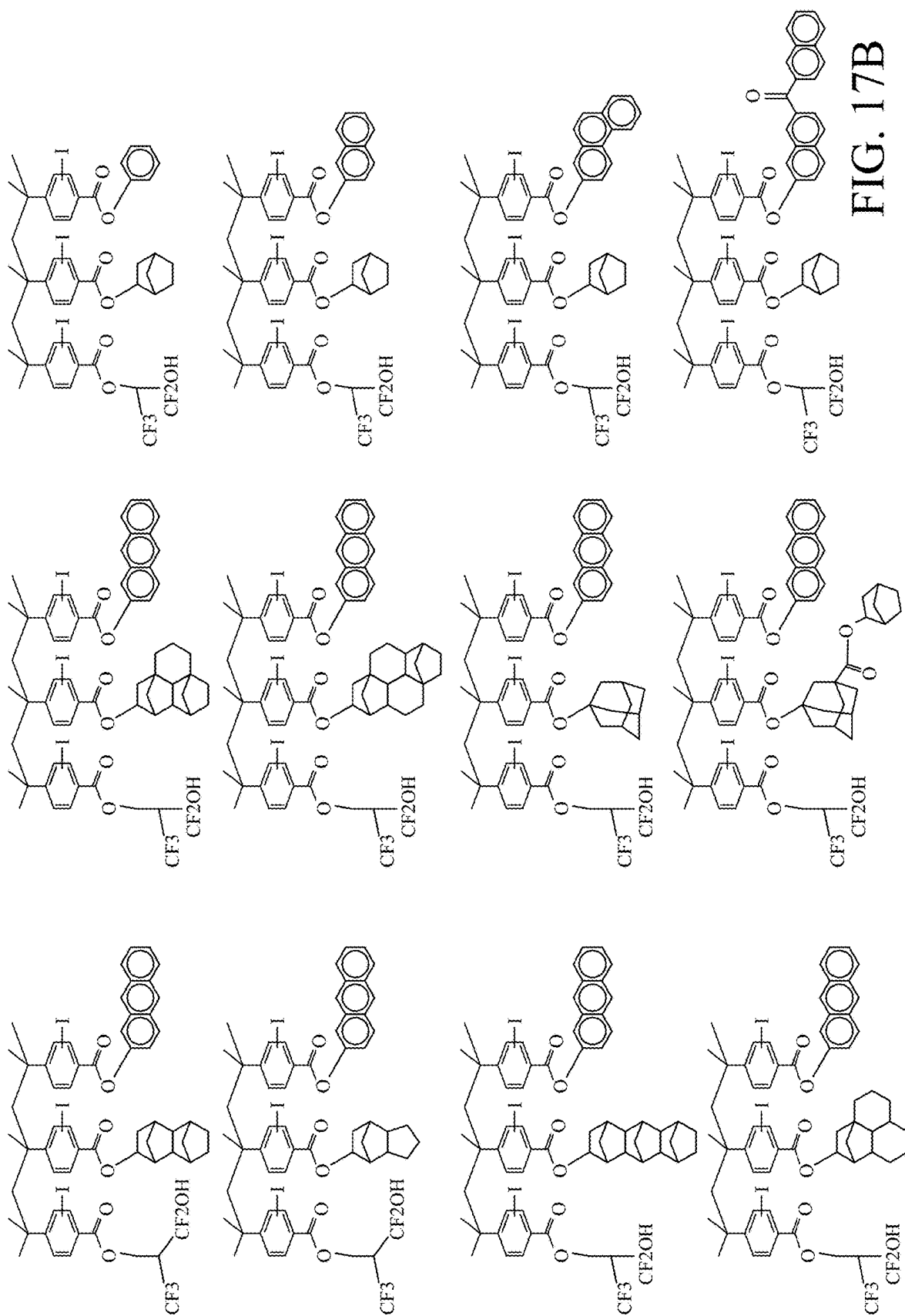
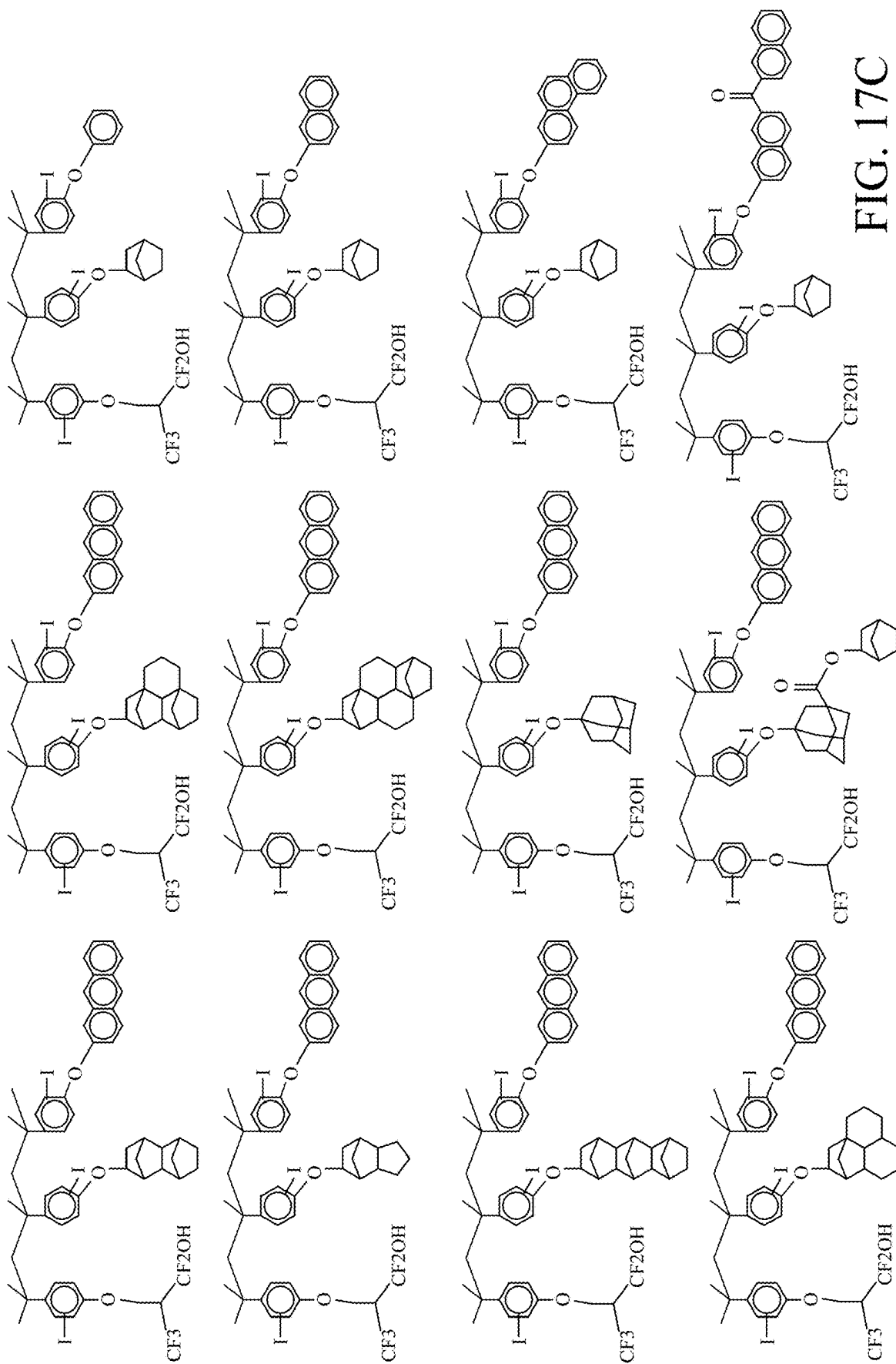


FIG. 17A





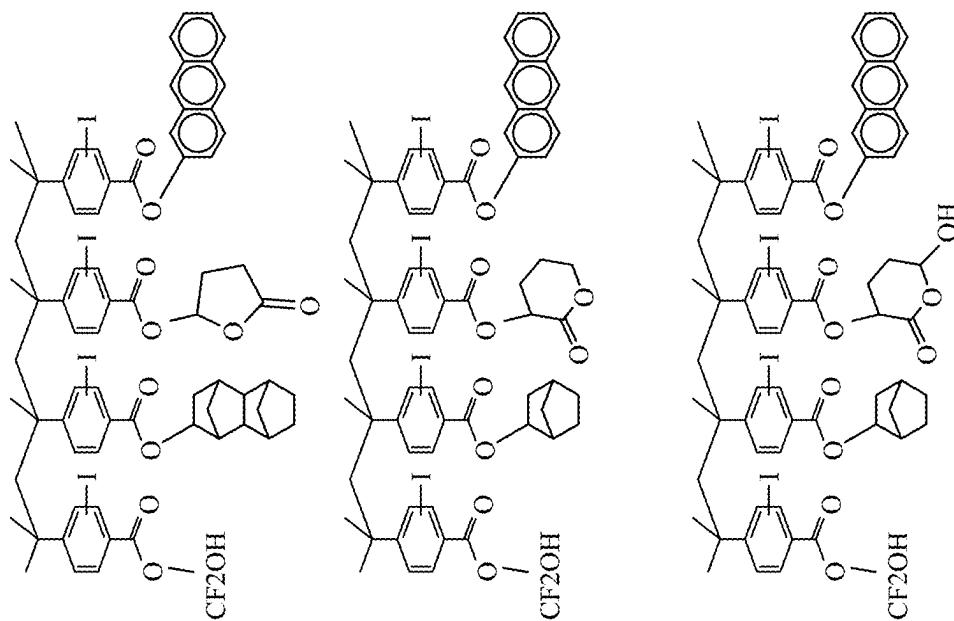
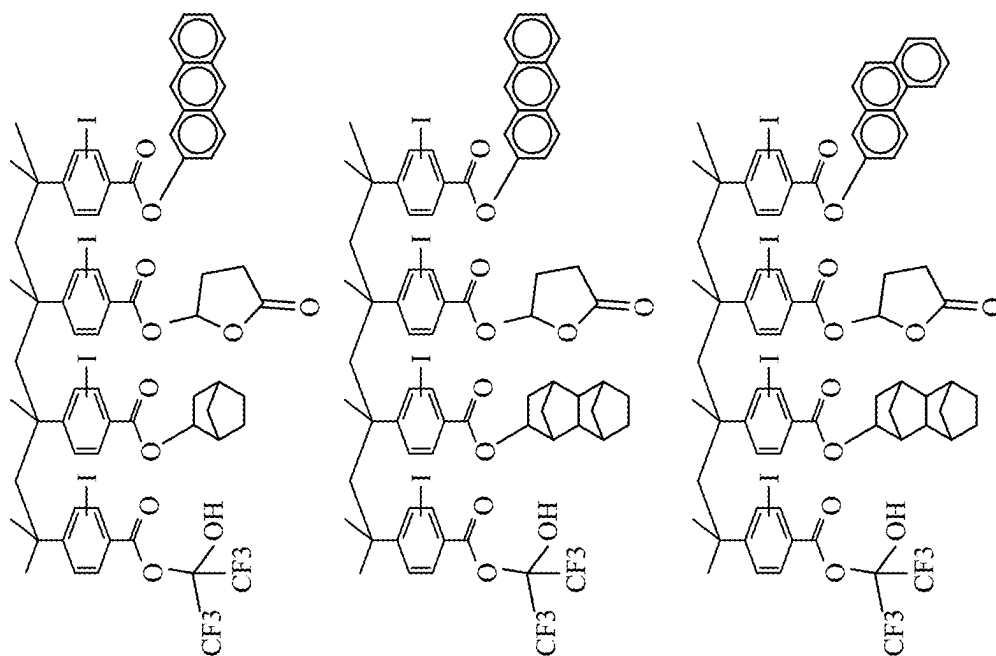


FIG. 17D

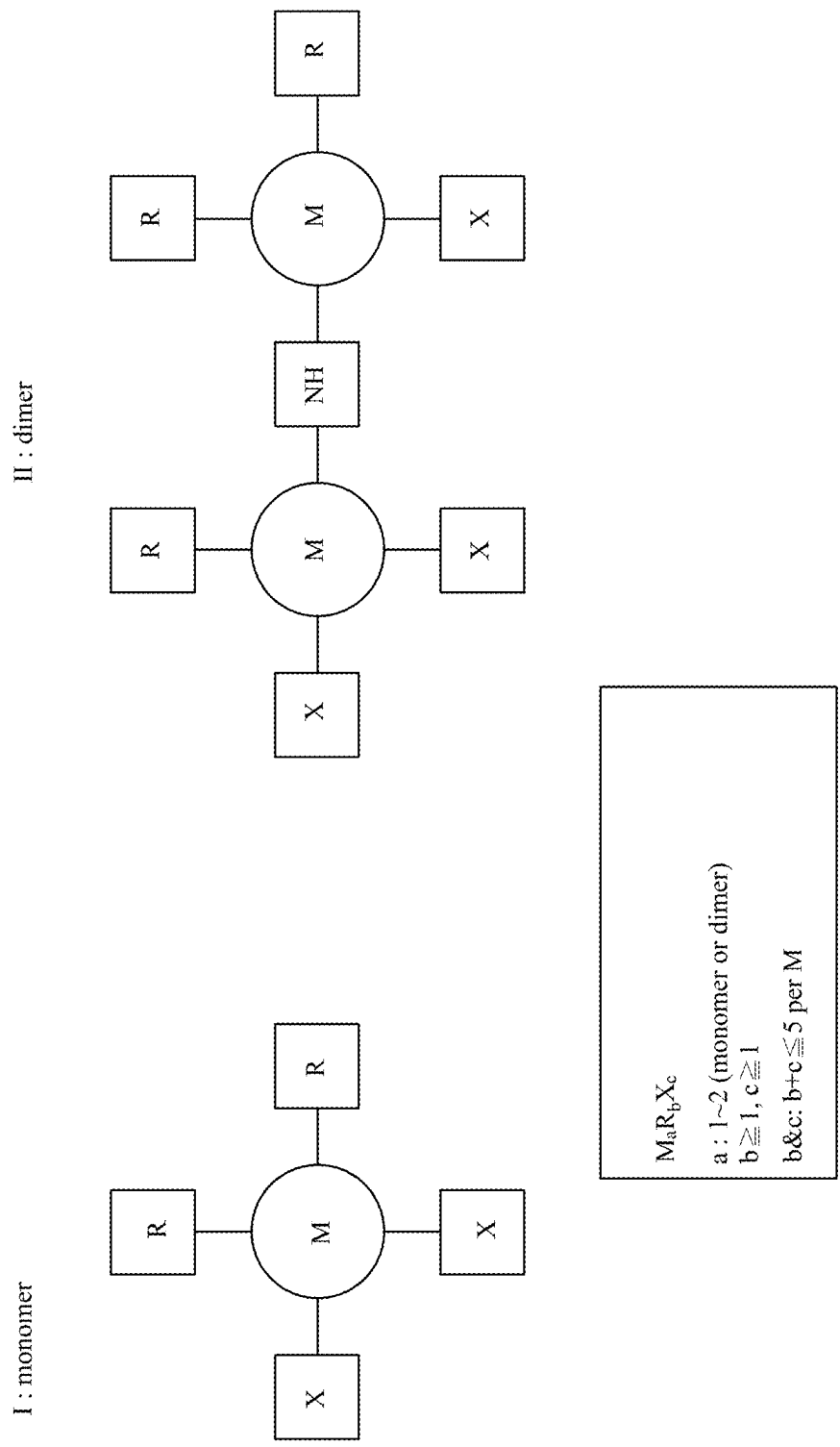


FIG. 18A

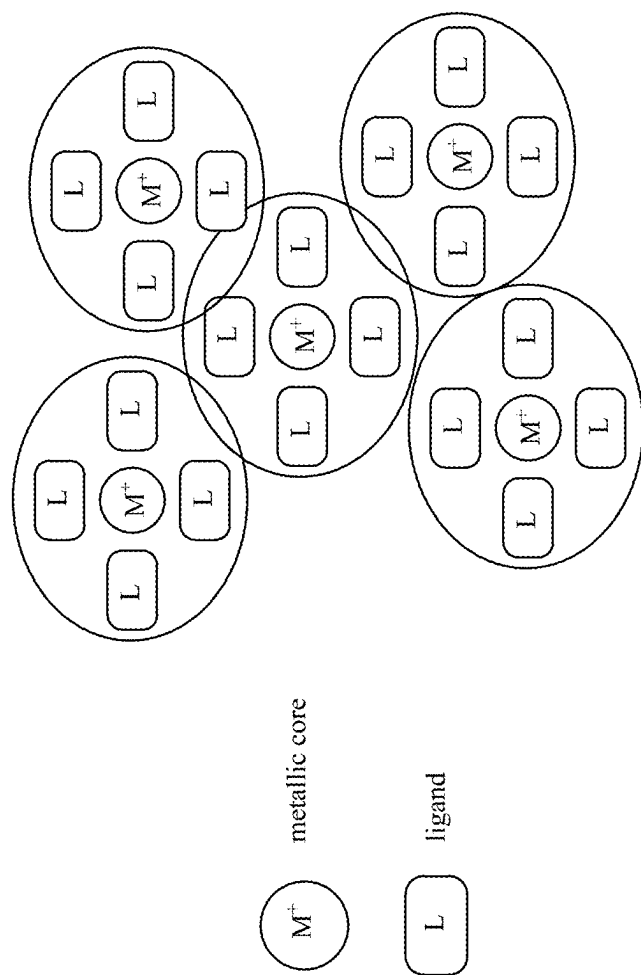


FIG. 18B

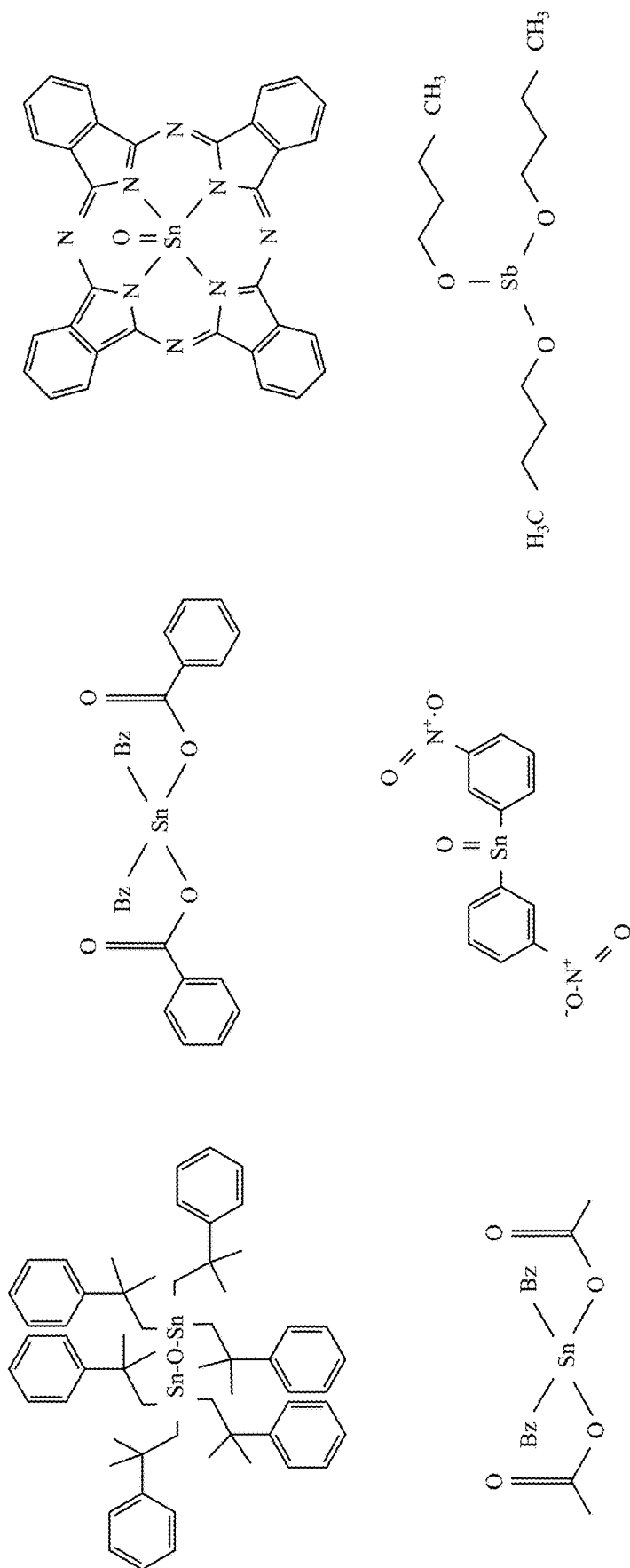


FIG. 18C

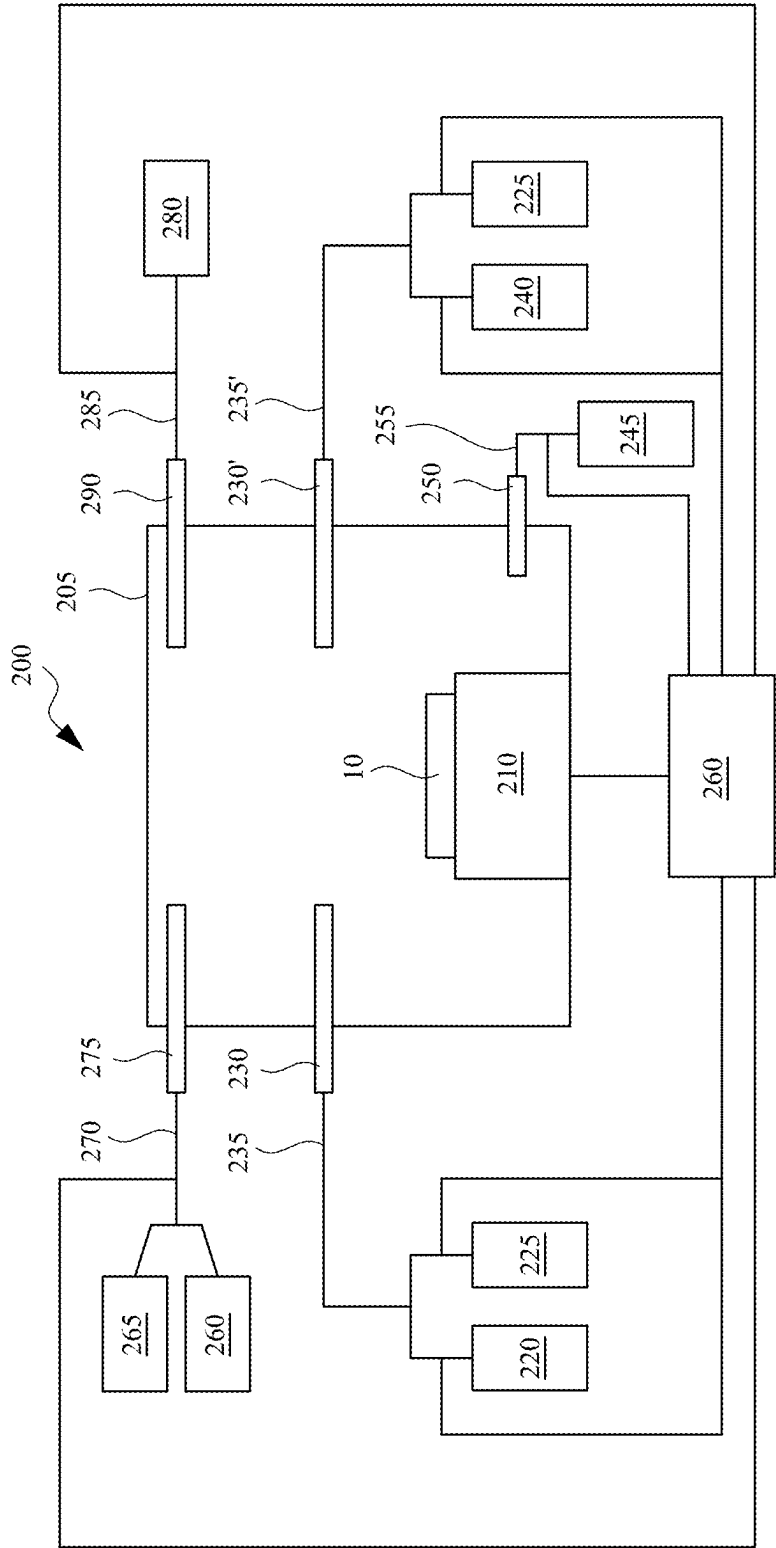


FIG. 19

FIG. 20A

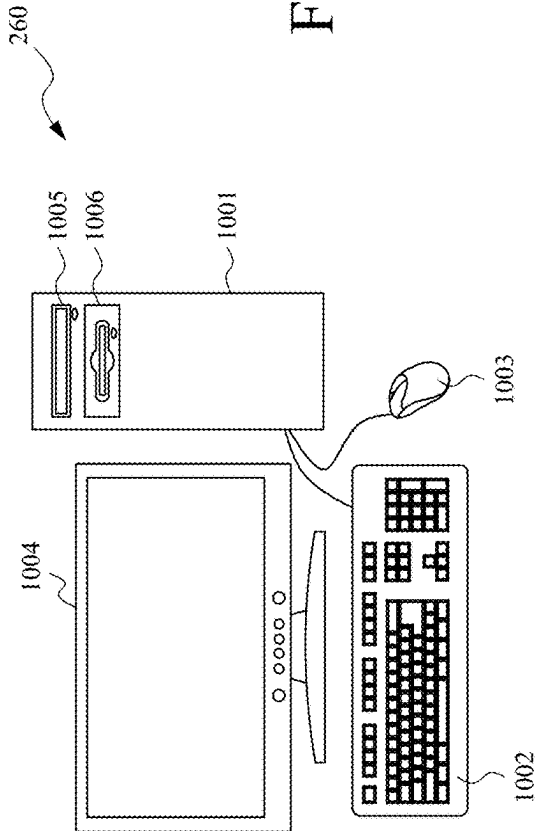
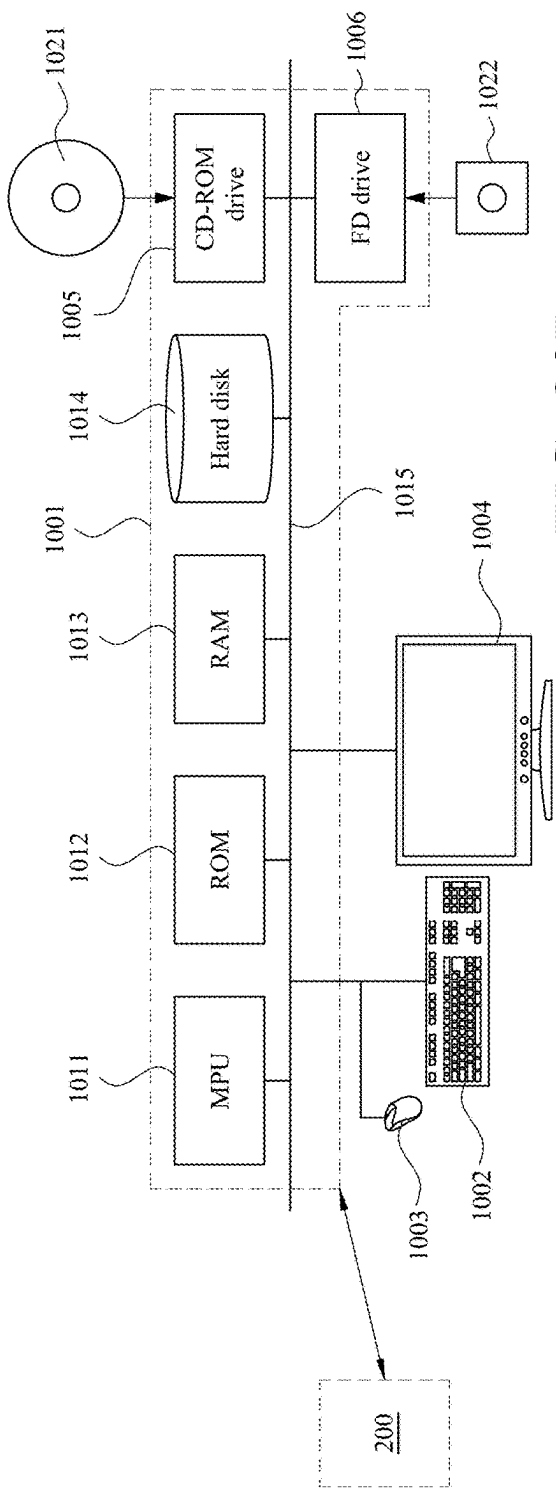


FIG. 20B



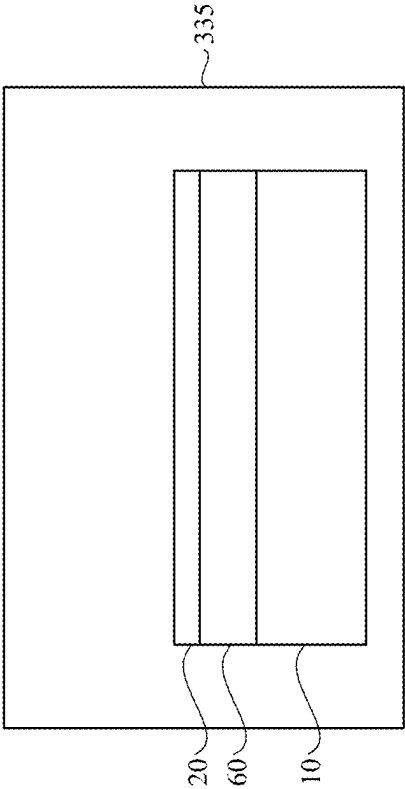


FIG. 21

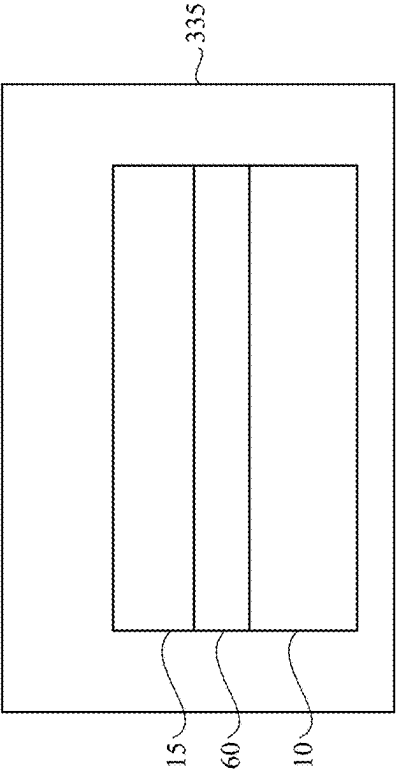


FIG. 22A

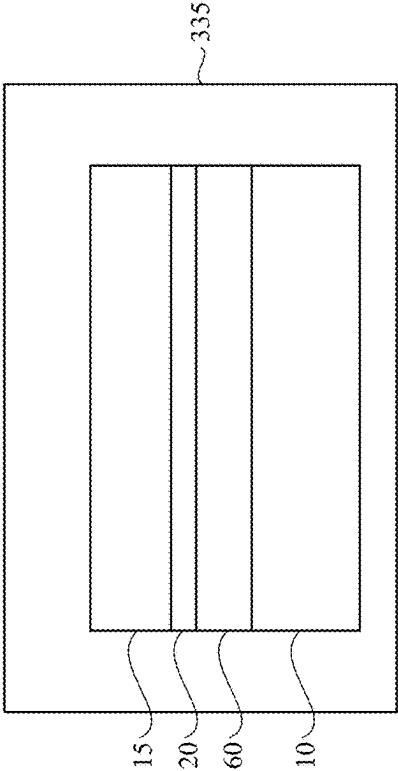


FIG. 22B

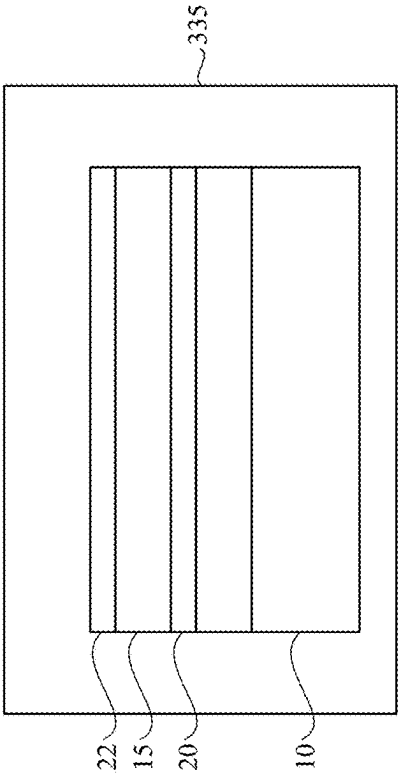


FIG. 23A

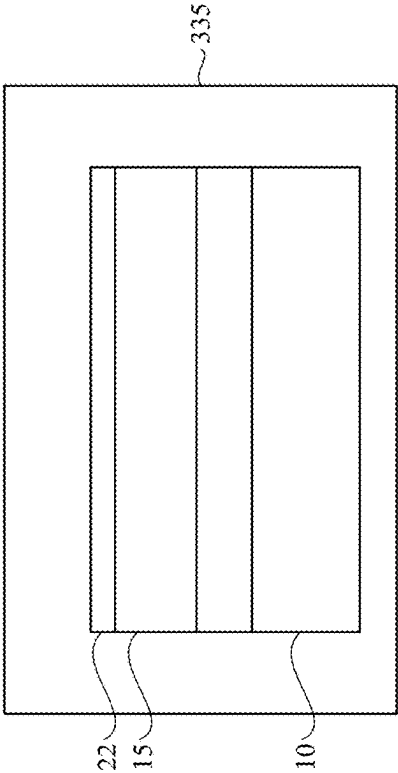


FIG. 23B

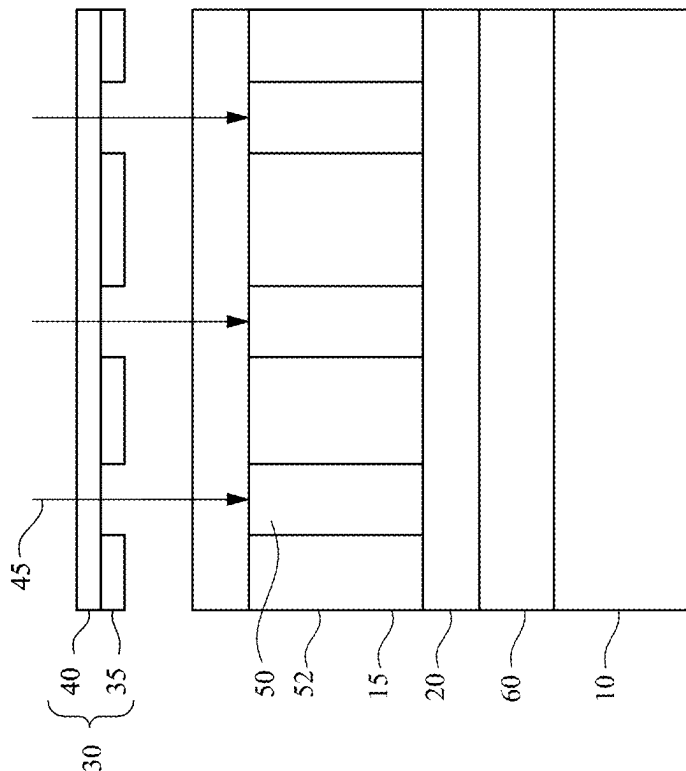


FIG. 24A

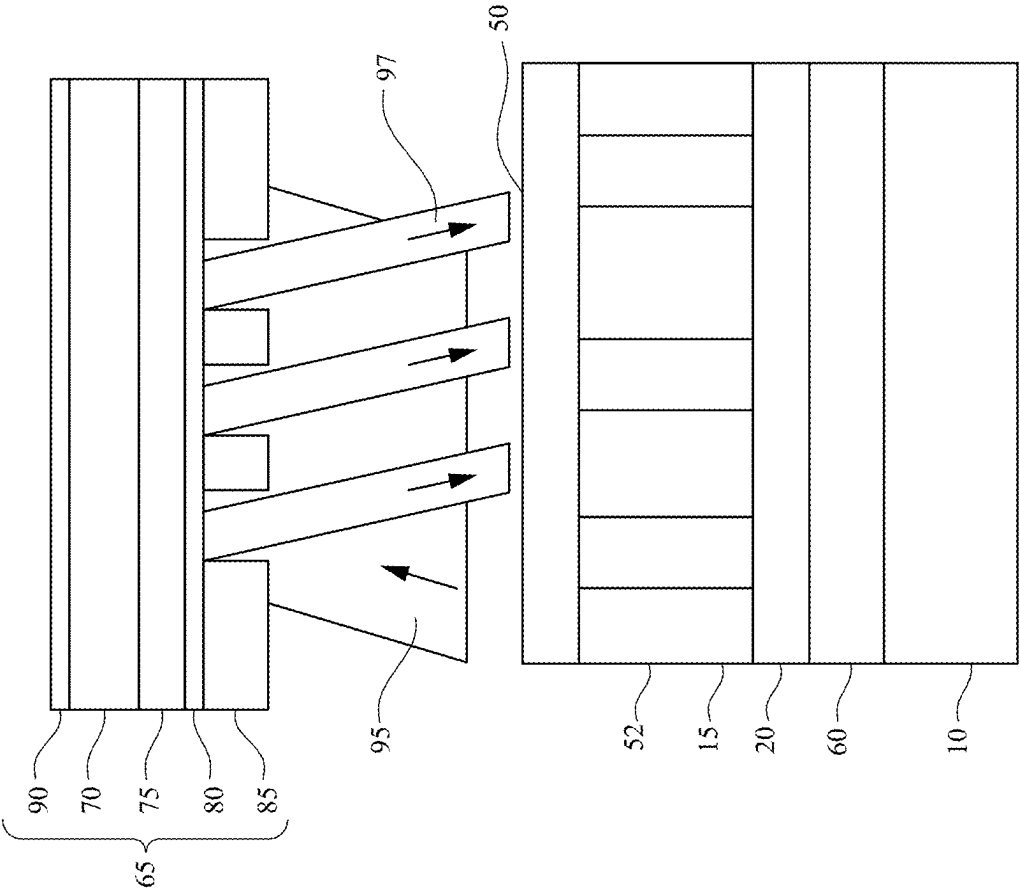


FIG. 24B

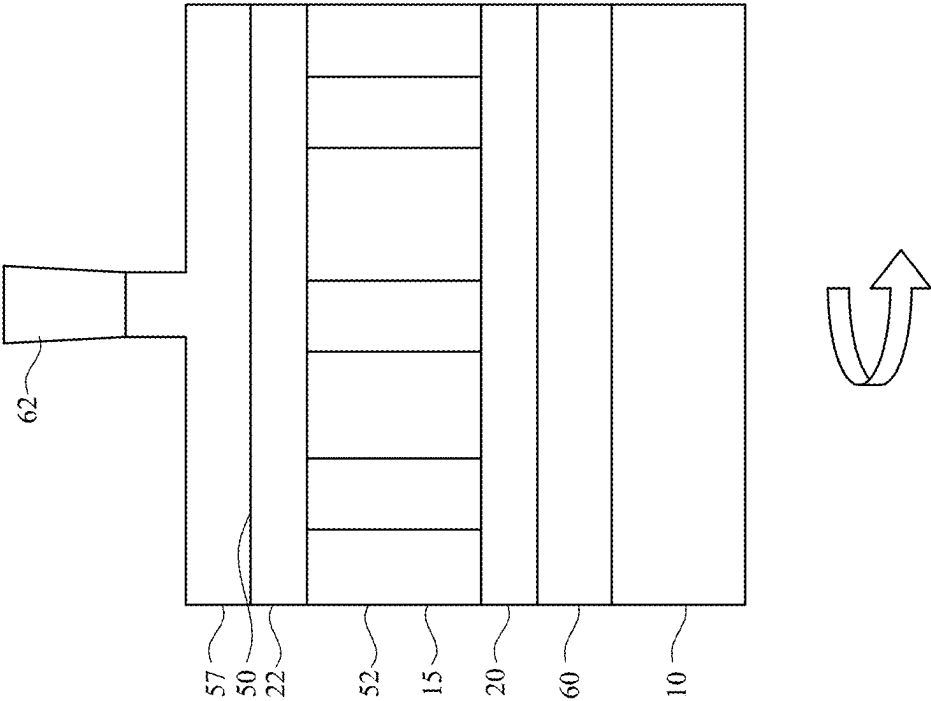


FIG. 25

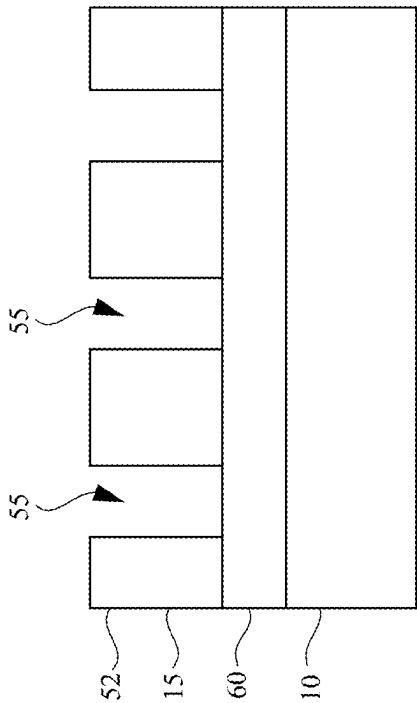


FIG. 26

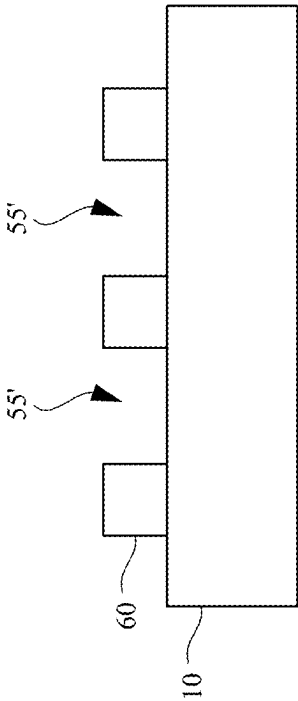


FIG. 27

**METHOD OF MANUFACTURING A
SEMICONDUCTOR DEVICE AND
COMPOSITION INCLUDING FLOATING
ADDITIVE**

**CROSS REFERENCE TO RELATED
APPLICATIONS**

[0001] This application claims priority to U.S. Provisional Application No. 63/553,517 filed Feb. 14, 2024, the entire disclosure of which is incorporated herein by reference.

BACKGROUND

[0002] As consumer devices have gotten smaller and smaller in response to consumer demand, the individual components of these devices have necessarily decreased in size as well. Semiconductor devices, which make up a major component of devices such as mobile phones, computer tablets, and the like, have been pressured to become smaller and smaller, with a corresponding pressure on the individual devices (e.g., transistors, resistors, capacitors, etc.) within the semiconductor devices to also be reduced in size.

[0003] One enabling technology that is used in the manufacturing processes of semiconductor devices is the use of photolithographic materials. Such materials are applied to a surface of a layer to be patterned and then exposed to an energy that has itself been patterned. Such an exposure modifies the chemical and physical properties of the exposed regions of the photosensitive material. This modification, along with the lack of modification in regions of the photosensitive material that were not exposed, can be exploited to remove one region without removing the other, or vice-versa.

[0004] However, as the size of individual devices has decreased, process windows for photolithographic processing have become tighter and tighter. As such, advances in the field of photolithographic processing help to maintain the ability to scale down the devices.

[0005] As the semiconductor industry has progressed into nanometer technology process nodes in pursuit of higher device density, higher performance, and lower costs, there have been challenges in reducing semiconductor feature size.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] The present disclosure is best understood from the following detailed description when read with the accompanying figures. It is emphasized that, in accordance with the standard practice in the industry, various features are not drawn to scale and are used for illustration purposes only. In fact, the dimensions of the various features may be arbitrarily increased or reduced for clarity of discussion.

[0007] FIG. 1 illustrates process flows of manufacturing a semiconductor device according to embodiments of the disclosure.

[0008] FIG. 2 shows a process stage of a sequential operation according to embodiments of the disclosure.

[0009] FIGS. 3A and 3B show process stages of a sequential operation according to embodiments of the disclosure.

[0010] FIGS. 4A and 4B show process stages of a sequential operation according to embodiments of the disclosure.

[0011] FIGS. 5A and 5B show process stages of a sequential operation according to embodiments of the disclosure.

[0012] FIG. 6 shows a process stage of a sequential operation according to embodiments of the disclosure.

[0013] FIG. 7 shows a process stage of a sequential operation according to embodiments of the disclosure.

[0014] FIG. 8 shows a process stage of a sequential operation according to embodiments of the disclosure.

[0015] FIGS. 9A, 9B, and 9C show process stages of a sequential operation according to embodiments of the disclosure.

[0016] FIGS. 10A, 10B, and 10C show process stages of a sequential operation according to embodiments of the disclosure, and FIG. 10D illustrates an example of a polymer according to embodiments of the disclosure.

[0017] FIGS. 11A, 11B, 11C, and 11D show process stages of a sequential operation according to embodiments of the disclosure.

[0018] FIGS. 12A and 12B illustrate examples of polymers according to embodiments of the disclosure.

[0019] FIGS. 13A and 13B illustrate examples of polymers and pendant groups according to embodiments of the disclosure.

[0020] FIGS. 14A, 14B, 14C, 14D, 14E, 14F, 14G, and 14H illustrate examples of polymers and pendant groups according to embodiments of the disclosure.

[0021] FIG. 15 illustrates examples of polymer pendant groups according to embodiments of the disclosure.

[0022] FIG. 16A illustrates a ring opening reaction and FIGS. 16B, 16C, and 16D illustrate examples of polymer pendant groups according to embodiments of the disclosure.

[0023] FIGS. 17A, 17B, 17C, and 17D illustrate examples of polymers according to embodiments of the disclosure.

[0024] FIG. 18A shows organometallic precursors according to embodiments of the disclosure. FIGS. 18B and 18C show examples of organometallic precursors according to embodiments of the disclosure.

[0025] FIG. 19 illustrates a deposition apparatus according to embodiments of the disclosure.

[0026] FIGS. 20A and 20B are diagrams of a controller according to some embodiments of the disclosure.

[0027] FIG. 21 shows a process stage of a sequential operation according to embodiments of the disclosure.

[0028] FIGS. 22A and 22B show process stages of a sequential operation according to embodiments of the disclosure.

[0029] FIGS. 23A and 23B show process stages of a sequential operation according to embodiments of the disclosure.

[0030] FIGS. 24A and 24B show process stages of a sequential operation according to embodiments of the disclosure.

[0031] FIG. 25 shows a process stage of a sequential operation according to an embodiment of the disclosure.

[0032] FIG. 26 shows a process stage of a sequential operation according to an embodiment of the disclosure.

[0033] FIG. 27 shows a process stage of a sequential operation according to an embodiment of the disclosure.

DETAILED DESCRIPTION

[0034] It is to be understood that the following disclosure provides many different embodiments, or examples, for implementing different features of the disclosure. Specific embodiments or examples of components and arrangements are described below to simplify the present disclosure. These are, of course, merely examples and are not intended to be

limiting. For example, dimensions of elements are not limited to the disclosed range or values, but may depend upon process conditions and/or desired properties of the device. Moreover, the formation of a first feature over or on a second feature in the description that follows may include embodiments in which the first and second features are formed in direct contact, and may also include embodiments in which additional features may be formed interposing the first and second features, such that the first and second features may not be in direct contact. Various features may be arbitrarily drawn in different scales for simplicity and clarity.

[0035] Further, spatially relative terms, such as “beneath,” “below,” “lower,” “above,” “upper” and the like, may be used herein for ease of description to describe one element or feature’s relationship to another element(s) or feature(s) as illustrated in the figures. The spatially relative terms are intended to encompass different orientations of the device in use or operation in addition to the orientation depicted in the figures. The device may be otherwise oriented (rotated 90 degrees or at other orientations) and the spatially relative descriptors used herein may likewise be interpreted accordingly. In addition, the term “made of” may mean either “comprising” or “consisting of.” In the present disclosure, a phrase “one of A, B and C” means “A, B and/or C” (A, B, C, A and B, A and C, B and C, or A, B and C), and does not mean one element from A, one element from B and one element from C, unless otherwise described. In the present disclosure, a source and a drain are interchangeably used and may be referred to as a source/drain. Source/drain region(s) may refer to a source or a drain, individually or collectively dependent upon the context.

[0036] Improving the line width roughness (LWR), improving local critical dimension uniformity (LCDU), and reducing the exposure dose (EOP) are desirable in the field of photolithographic processing to continue scaling down the devices and efficiently increase semiconductor device yield. Deep ultraviolet (DUV), electron beam (e-beam) and extreme ultraviolet (EUV) lithography have been developed to decrease the critical dimension and increase device yield. EUV lithography has been developed for use in nanometer technology process nodes, such as below 40 nm process nodes. Organic polymer-based photoresists are used in photolithography in some embodiments. However, C, N, and O atoms in the polymers of organic photoresists are weak in EUV photon absorption. It has been found that certain metals have higher EUV photon absorption. To use the higher EUV photon absorption of metals, metallic resists have been developed. The lithographic performance is further improved by treating the photoresist layer with an additive composition that floats over the photoresist layer during actinic radiation exposure and improves the solubility of the photoresist during the development operation. The additive composition may be applied to the photoresist layer at various times during the photolithographic patterning process.

[0037] FIG. 1 illustrates a process flow 100, and FIGS. 2-10D illustrate various stages of manufacturing a semiconductor device according to embodiments of the disclosure. In some embodiments, a photoresist underlayer 20 is formed over the substrate 10 as shown in FIG. 2, in a photoresist underlayer forming operation S110 as shown in FIG. 1. In some embodiments, a floating additive is mixed with the photoresist underlayer material in operation S115 before

forming the underlayer 20 over the substrate 10. Then, in some embodiments, the underlayer material with the floating additive is applied to the substrate in operation S130a. In some embodiments, the underlayer material is applied by spin-coating techniques. During the spin-coating, phase separation occurs between the underlayer material and the floating additive, and the floating additive rises and covers or floats over the underlayer material layer. In some embodiments, the substrate is rotated at a spin rate of from about 100 rpm to about 3000 rpm during the material dispensing operation. In other embodiments, the substrate is rotated at a spin rate of from about 200 rpm to 1500 rpm. At spin rates below the disclosed range there may be insufficient phase separation. At spin rates above the disclosed range underlayer may be formed too thin. In some embodiments, the rotation of the substrate continues for a time period after the photoresist underlayer is formed or the underlayer material dispensing is completed.

[0038] In some embodiments, the photoresist underlayer 20 is formed, and then, a floating additive layer 22 is formed over the underlayer 20 in operation S130b. In some embodiments, the photoresist underlayer 20 is a bottom anti-reflective coating (BARC) layer. Any suitable BARC material may be used.

[0039] Then, in operation S125 of FIG. 1, a photoresist layer 15 is formed over the photoresist underlayer 20 as shown in FIG. 3A. In some embodiments, a baking operation is performed on the underlayer 20 to drive off solvents in the base composition before forming a photoresist layer over the underlayer 20. In some embodiments, the photoresist layer 15 is formed over the substrate 10 in operation S125, as shown in FIG. 3B. Then a floating additive layer 22 is formed over the photoresist layer 15 in a floating additive layer applying operation S130d, as shown in FIGS. 4A and 4B. FIG. 4A illustrates an embodiment of a stacked structure where a first floating additive layer 20 is formed below the photoresist layer 15 and a second floating additive layer is formed over the photoresist layer 15. FIG. 4B illustrates an embodiment of a stacked structure where the floating additive layer 22 is formed only over the upper surface of the photoresist layer. In some embodiments, the floating additive composition is mixed with the photoresist material composition in operation S120 before forming the photoresist layer. The floating additive/photoresist material composition is then applied to the substrate 10 or photoresist underlayer 20 in operation S130c in a spin coating operation to separate the floating additive from the photoresist material, thereby forming a floating additive layer 22 over the photoresist layer 15. In some embodiments, the spin coating operation is performed at a spin rate of from about 100 rpm to about 3000 rpm during the photoresist/floating additive composition dispensing operation, and at a spin rate of from about 200 rpm to 1500 rpm, similar to the underlayer formation operation.

[0040] In other embodiments, the floating additive layer is formed by chemical vapor deposition (CVD), physical vapor deposition (PVD), or atomic layer deposition (ALD) deposition. In other embodiments, the additive layer is formed by a spray mist technique or through gas, liquid, or solid chemical treatment.

[0041] In some embodiments, the floating additive layers 20, 22 are formed in a chamber 335, such as a vacuum chamber as shown in FIGS. 2, 4A, and 4B. In some embodiments, the vacuum chamber 335 is used in a CVD,

PVD, or ALD operation. In some embodiments, the chamber 335 is the same chamber in which the photoresist layer 15 is formed, as shown in FIGS. 3A and 3B. In other embodiments, the chamber 335 in which the floating additive layer is formed is a different chamber than the one in which the photoresist layer is formed.

[0042] In some embodiments, a gas purge of the chamber 335 is performed before or after the floating additive layers 20, 22 or the photoresist layer 15 are formed. In some embodiments, the chamber is purged with one or more of carbon dioxide, nitrogen, helium, neon, argon, or dry air, where dry air has a dewpoint of about -40° C. or lower. In other embodiments, the humidity of the purge air is varied depending on process requirements, to between about 0 to about 100% relative humidity.

[0043] In some embodiments, a pre-exposure baking operation S140 is performed to drive off solvents in the photoresist layer 15 or to cure the photoresist layer 15. In some embodiments, the baking operation is performed in a chamber 335, such as a vacuum chamber. In some embodiments, the photoresist layer 15 is heated at a temperature ranging from about 40° C. to about 300° C. for about 10 seconds to about 10 minutes. After the pre-exposure baking operation S140, the photoresist layer 15 coated substrate 10 is cooled in a cooling operation. In some embodiments, the heating and cooling is performed using a heater/chiller 330, as shown in FIGS. 3A and 4A. In some embodiments, the heater/chiller 330 is a hot plate that includes internal coolant flow channels. The heating or cooling is controlled by a controller 260 (see FIGS. 20A, 20B) in some embodiments. Likewise, heating and cooling operations may be formed after the forming the lower or first floating additive layer 20 (see FIG. 2) and after forming the upper or second floating additive layer 22 (see FIGS. 4A and 4B).

[0044] In some embodiments, the floating additive layer 22 is formed after the baking and cooling operations S140. The floating additive layer material is applied to the photoresist layer 15 in a floating additive layer application operation S130e after the pre-exposure baking/cooling operations S140 and before a selective exposure of the photoresist layer 15 to actinic radiation S150 in some embodiments.

[0045] After the pre-exposure baking/cooling operations S140 of the photoresist layer 15, the photoresist layer 15 is selectively exposed to actinic radiation 45/97 (see FIGS. 5A and 5B) in operation S150. In some embodiments, the photoresist layer 15 is selectively exposed to ultraviolet radiation. In some embodiments, the radiation is electromagnetic radiation, such as g-line (wavelength of about 436 nm), i-line (wavelength of about 365 nm), ultraviolet radiation, deep ultraviolet radiation, extreme ultraviolet, electron beam, or the like. In some embodiments, the radiation source is selected from the group consisting of a mercury vapor lamp, xenon lamp, carbon arc lamp, a KrF excimer laser light (wavelength of 248 nm), an ArF excimer laser light (wavelength of 193 nm), an F₂ excimer laser light (wavelength of 157 nm), or a CO₂ laser-excited Sn plasma (extreme ultraviolet, wavelength of 13.5 nm).

[0046] As shown in FIG. 5A, the exposure radiation 45 passes through a photomask 30 before irradiating the photoresist layer 15 in some embodiments. In some embodiments, the photomask 30 has a pattern to be replicated in the photoresist layer 15. The pattern is formed by an opaque pattern 35 on the photomask substrate 40, in some embodiments. The opaque pattern 35 may be formed by a material

opaque to ultraviolet radiation, such as chromium, while the photomask substrate 40 is formed of a material that is transparent to ultraviolet radiation, such as fused quartz.

[0047] In some embodiments, the selective exposure of the photoresist layer 15 to form exposed regions 50 and unexposed regions 52 is performed using extreme ultraviolet lithography. In some embodiments of an extreme ultraviolet lithography operation, a reflective photomask 65 is used to form the patterned exposure light in some embodiments, as shown in FIG. 5B. The reflective photomask 65 includes a low thermal expansion glass substrate 70, on which a reflective multilayer 75 of Si and Mo is formed. A capping layer 80 and absorber layer 85 are formed on the reflective multilayer 75. A rear conductive layer 90 is formed on the back side of the low thermal expansion glass substrate 70. In some embodiments of extreme ultraviolet lithography, extreme ultraviolet radiation 95 is directed towards the reflective photomask 65 at an incident angle of about 6° . A portion 97 of the extreme ultraviolet radiation is reflected by the Si/Mo multilayer 75 towards the photoresist coated substrate 10, while the portion of the extreme ultraviolet radiation incident upon the absorber layer 85 is absorbed by the photomask. In some embodiments, additional optics, including mirrors, are between the reflective photomask 65 and the photoresist coated substrate.

[0048] The region of the photoresist layer exposed to radiation 50 undergoes a chemical reaction thereby changing its solubility in a subsequently applied developer relative to the region of the photoresist layer 52 not exposed to radiation. In some embodiments, the portion of the photoresist layer 50 exposed to radiation becomes more soluble in the developer.

[0049] The selectively exposed photoresist layer 15 subsequently undergoes a post exposure baking (PEB) or cooling operation S160. In some embodiments, the photoresist layer 15 is heated or cooled at a temperature ranging from about -30° C. to about 300° C. during the post exposure baking or cooling operation S160. In some embodiments, the temperature is controlled using the heater/chiller 330 and a controller 260 (see FIGS. 21A, 21B). In other embodiments, the photoresist layer 15 is heated at a temperature ranging from about 40° C. to about 160° C. for about 20 s to about 120 s. The post-exposure baking may be used to assist in the generating, dispersing, and reacting of the acid/base/free radical generated from the impingement of the radiation 45/97 upon the photoresist layer 15 during the exposure. Such assistance helps to create or enhance chemical reactions, which generate chemical differences between the exposed region 50 and the unexposed region 52 within the photoresist layer.

[0050] The selectively exposed photoresist layer is subsequently developed by applying a developer to the selectively exposed photoresist layer in operation S170. As shown in FIG. 6, a developer 57 is supplied from a dispenser 62 to the photoresist layer 15. In some embodiments, the exposed region 50 of the photoresist layer, the exposed region of the lower or first floating additive layer 20, and the upper or second floating additive layer 22 are removed by the developer 57 forming a pattern of openings 55 in the photoresist layer 15 to expose the substrate 10, as shown in FIG. 7.

[0051] In some embodiments, the pattern of openings 55 in the patterned photoresist layer 15 is extended into the substrate 10 to create a pattern of openings 55' in the substrate 10, thereby transferring the pattern in the photo-

resist layer **15** into the substrate **10**, as shown in FIG. **8**. The pattern is extended into the substrate by etching, using one or more suitable etchants. In some embodiments, the etching operation removes remaining portions of the lower floating additive layer **20**. The photoresist layer pattern **55** is at least partially removed during the etching operation in some embodiments. In other embodiments, the photoresist layer pattern **55** and any remaining portions of the floating additive layer **20** under the photoresist layer pattern **55** are removed after etching the substrate **10** by using a suitable photoresist stripper solvent or by a photoresist ashing operation.

[0052] The photolithographic patterning operations will be discussed in reference to various embodiments of the disclosure. FIGS. **9A-9C** illustrate a photolithographic patterning operation where a BARC layer **12** is formed over a substrate and floating additive layers **20**, **22** are formed on both major surfaces of the photoresist layer **15**, as shown in FIG. **9A**. In some embodiments, the floating additive layers **20**, **22** each have a thickness of about 1 nm to about 10 nm, about 2 nm to about 7 nm in other embodiments. In some embodiments, the thickness of the floating additive layers **20**, **22** is about 5 nm.

[0053] In this embodiment, the floating additive material includes a polymer having pendant acid labile groups (ALG) and pendant acid generating groups, such as a photoacid generator (PAG) groups, and pendant fluorine substituted organic groups, such as a fluoroalcohol. The pendant fluorine-substituted organic group allows the polymer to phase-separate during the spin-coating operation and float over the photoresist layer.

[0054] In FIG. **9B**, the photoresist layer **15** is exposed to actinic radiation **45** through a photomask **30**. The actinic radiation causes the PAG to release acid (H⁺) in the floating additive layers, which diffuses into the photoresist layer **15** and supplements the acid (H⁺) generated in the exposed area of the photoresist layer. The acid released by the PAG also cleaves the ALG to form a hydrophilic carboxylic acid group, as shown in FIG. **9C**, thereby increasing the solubility of the floating additive layer in the photoresist developing solution. In some embodiments, the floating additive material composition includes a base, such as a quencher, or a base generator.

[0055] The floating additive layer improves after development inspection (ADI), local critical dimension uniformity (LCDU), and line width roughness (LWR) of the resulting pattern **55**, as shown in FIG. **9C**. Because the floating additive has a PAG group it can increase the top and bottom PAG loading in the photoresist layer to improve the photoresist's PAG uniformity. The floating additive according to the present disclosure has a low surface energy of less than about 35 mJ/m², absorbs EUV radiation, and generates secondary electrons.

[0056] FIGS. **10A-10C** illustrates an embodiment similar to the embodiment of FIGS. **9A-9C**. In FIGS. **10A-10C**, the floating additive layer **22** is formed only on the upper surface of the photoresist layer **15**. The floating additive material was blended into a photoresist solution. After the photoresist spin-coating operation **S125**, the floating additive phase separation occurs in the upper portion of the photoresist layer because of the pendant fluorine-substituted organic group.

[0057] FIG. **10D** illustrates an example of a floating additive polymer according to an embodiment of the disclosure.

The polymer includes a pendant acid labile group attached to the polymer backbone via a linkage R1, a pendant photoacid generator attached to polymer backbone via a linkage R2, and a pendant fluorine substituted organic group attached to the polymer backbone via a linkage R3, where x and y represent the number of carbon atoms and fluorine atoms, respectively. In some embodiments, $1 \leq x \leq 9$ and $1 \leq y \leq 19$. In some embodiments, the polymer backbone is a polystyrene or poly(meth)acrylate.

[0058] In some embodiments, the floating additive polymer includes a pendant photoacid generator in an amount of about 0 wt. % to about 50 wt. % based on the total weight of floating additive polymer, a pendant fluorine-substituted organic group in an amount of about 1 wt. % to about 90 wt. %, and a pendant ALG in an amount of about 0 wt. % to about 90 wt. %. In some embodiments the amount of the PAG, ALG, and fluorine-substituted organic groups are all greater than 0 wt. %.

[0059] Embodiments of the R1, R2, and R3 linkage units independently include a 1-9 carbon (C1-C9) unbranched, C3-C9 branched, C3-C9 cyclic or noncyclic, saturated or unsaturated, aromatic or non-aromatic, unsubstituted or halogen-substituted group; or —S—; —P—; —P(O₂)—; —C(=O)S—; —C(=O)O—; —O—; —N—; —C(=O)N—; —SO₂O—; —SO₂S—; —SO—; —SO₂—; a carboxylic acid group, an ether group, a ketone group, or an ester group. In some embodiments, the R1, R2, and R3 linkage units include iodine substituents.

[0060] The floating additive polymer concentration in the photoresist material or photoresist underlayer composition may range from about 0.1 wt. % to about 50 wt. % based on the total weight of the floating additive polymer and the photoresist composition or photoresist underlayer composition. The weight average molecular weight range of the floating additive polymer ranges from about 100 to about 50,000 in some embodiments, from about 400 to about 20,000 in other embodiments, from about 1,000 to about 15,000, and from about 5,000 to about 10,000 in other embodiments.

[0061] The floating additive polymer and the floating additive polymer and the photoresist material composition or underlayer material composition are dissolved in a casting solvent in some embodiments. The casting solvent can be one or more of propylene glycol methyl ether acetate (PGMEA), propylene glycol monomethyl ether (PGME), 1-ethoxy-2-propanol (PGEE), gamma-butyrolactone (GBL), cyclohexanone (CHN), ethyl lactate (EL), methanol, ethanol, propanol, n-butanol, acetone, dimethylformamide (DMF), isopropyl alcohol (IPA), tetrahydrofuran (THF), methyl isobutyl carbinol (MIBC), n-butyl acetate (nBA), 2-heptanone (MAK), or any other suitable solvent.

[0062] FIGS. **11A-11D** illustrate a photolithographic patterning operation according to embodiments of the disclosure. In FIG. **11A**, the floating additive polymer **19** is mixed in the photoresist material along with a casting solvent **17**, and the resulting composition is disposed on a substrate **10** according to any of the techniques disclosed herein. The coated substrate is rotated by a spin-coating operation or rotated after depositing the floating additive polymer/photoresist mixture on the substrate as disclosed herein to phase separate the mixture forming the floating additive layer **22**. During or after spinning the substrate, the photoresist layer **15** and floating additive layer **22** are baked using a heater **330**, such as hotplate as disclosed herein, to drive off

(vaporize) the casting solvent **17** (see FIG. **11B**). The floating additive layer **22** and the photoresist layer **15** are subsequently exposed to actinic radiation **45** in FIG. **11C** and developed in FIG. **11D** to form a patterned **55** photoresist layer. As shown in FIG. **11D**, the floating additive layer **22** is a sacrificial layer that is removed during the development operation.

[0063] Another floating additive polymers according to embodiments of the disclosure, are illustrated in FIGS. **12A** and **12B**. The backbone of the additive is a styrene polymer including one or more iodine atom substituents in some embodiments. The iodine atom can enhance the photoresist's sensitivity by producing more secondary electrons. Styrene polymers improve the glass transition (T_g) value and lower the etch rate.

[0064] The fluorine-substituted organic group, R_f , helps the floating additive float on top of the photoresist during spin coating/drying or post coating baking due to presence of the fluorine atoms. R_f may also have a developer solubility improving function, which helps remove the additive during the development process.

[0065] R_5 is a pendant chromophore group. The pendant chromophore group absorbs out of band (OOB) radiation to improve the LWR and LCDU.

[0066] R_4 is a bulky group having a high T_g group that can help to control the photoacid generator diffusion at the top of photoresist, which improves the resist profile in some embodiments. In other embodiments, R_4 is an acid generating group, a base or quencher group, or a base generating group.

[0067] R_6 is a developer solubility promoter in some embodiments. The R_6 developer solubility promoter undergoes a ring opening in a liquid having a PH value > about 10, and is converted to a carboxylic acid that will dissolve in aqueous-based developers, such as tetramethyl ammonium hydroxide (TMAH) developers. In other embodiments, R_6 is an acid labile group (ALG). The R_6 group improves the solubility of the floating additive layer so that it is removed during development, which may reduce the aspect ratio for peeling window improvement.

[0068] Floating additive polymers according to the present disclosure have two to six different monomer units selected from: 1) a fluorine-substituted organic group, 2) an acid generating group or base group, 3) a high T_g acid diffusion control group, 4) a developer solubility promoter group, 5) a chromophore group (an OOB controller group), and 6) an acid labile group.

[0069] In the polymer illustrated in the embodiment of FIG. **12A**, X_a , X_b , X_c , X_d are independently H; an F atom; a C0 to C20 alkyl group; a C3-C20 cycloalkyl group; a C1-C20 hydroxyalkyl group; a C1-C20 alkoxy group; C2-C20 alkoxy alkyl group; a C2-C20 acetyl group; a C3-C20 acetyl alkyl group; a C1-C20 carboxyl group; a C2-C20 alkyl carboxyl group; a C4-C20 cycloalkyl carboxyl group; a C3-C20 saturated or unsaturated hydrocarbon ring; or a C2 to C20 heterocyclic group, which can be a 2-D ring, or 3-D structure; or a C6-C20 aromatic group. A_1 , A_2 , A_3 , and A_4 are independently $PhCOO-$, $PhO-$, a C1-C20 alkyl group, a C3-C20 cycloalkyl group, a C1-C20 hydroxyalkyl group, a C1-C20 alkoxy group, a C1-C20 alkoxy alkyl group, a C1-C20 acetyl group, a C3-C20 acetyl alkyl group, or a C1-C20 aromatic group. Any of A_1 , A_2 , A_3 , and A_4 may be unsubstituted or substituted with a halogen. In some embodiments, A_1 , A_2 , A_3 , and A_4 absorb radiation

within a wavelength ranging from about 10 nm to about 500 nm. In some embodiments the $PhCOO-$ and $PhO-$ groups are substituted with at least one I atom. In some embodiments, A_1 , A_2 , A_3 , and A_4 are independently a direct bond respectively between R_f , R_4 , R_5 , and R_6 and the polymer chain, where no more than two of A_1 , A_2 , A_3 , and A_4 are direct bonds. R_a , R_b , R_c , and R_d are independently a direct bond, an oxygen atom, a C1-C7 alkyl group, a C1-C7 carboxyl group, a C3-C7 cycloalkyl group, a C1-C7 hydroxyalkyl group, a C1-C7 alkoxy group, a C2-C7 alkoxy alkyl group, a C2-C7 acetyl group, a C3-C7 acetyl alkyl group. A_1 , A_2 , A_3 , A_4 , R_f , R_4 , R_5 , and R_6 combined contain about one to about ten aromatic rings for OOB absorption and about one to about ten iodine atoms for EUV sensitivity in some embodiments. In the polymer of FIG. **12A**, $m+n+o+p=1$; about $0.2 < m < \text{about } 0.8$; about $0.2 < n < \text{about } 0.8$; about $0 \leq o < \text{about } 0.5$, and about $0.2 < p < \text{about } 0.5$ in some embodiments. In other embodiments, $m+n+o+p=1$; about $0.2 \leq m < \text{about } 1$; about $0 \leq n \leq \text{about } 0.9$; about $0 \leq o < \text{about } 1$; and about $0 \leq p < \text{about } 1$.

[0070] The floating additive polymer can float on top of the photoresist layer due to the floating fluorine atoms. The fluorine atoms reduce the surface energy, thereby allowing the polymer to float more easily in some embodiments. In some embodiments, R_f is a fluoroalcohol group, which helps to make the floating additive more soluble in aqueous developers, such as TMAH. In some embodiments, R_f is C1-C9 fluorine-containing organic group, a C1-C9 fluoroalcohol group, a C1-C9 fluorocarbon group, a C1-C9 fluoroalkoxy group, a C1-C9 fluoroester group, a C1-C9 hydroxyfluoroester group, or a C1-C9 fluoroether group. In some embodiments, there are two or more R_f groups bonded to A_1 . In some embodiments, A_1 is a direct bond. Some examples of the monomer units comprising the fluorine-substituted organic groups include, but are not limited to, the embodiments illustrated in FIGS. **13A** and **13B**. In FIG. **13A**, x and y represent the number of carbon atoms and fluorine atoms, respectively. In some embodiments, $1 \leq x \leq 9$ and $1 \leq y \leq 19$.

[0071] The pendant acid generating and base groups can be any suitable acid generating group, such as a photoacid generator (PAG) or thermal acid generator (TAG); base or quencher groups; or base generating groups, such as thermal base generator (TBG) groups or photobase generator (PBG) groups.

[0072] In some embodiments, the pendant base group is of a monoethanolamine, a monoisopropanolamine, a 2-amino-2-methyl-1-propanol, a H-benzotriazole, a 1,2,4-triazole, a 1,8-diazabicycloundec-7-ene, $-NR_2$, $-NHR$, $-NR_2$, $-C_3H_4O_2NH_2$, $-CH_2O_2NH_2$, $-NHCH_2NH_2$, $-NHC_2H_4NH_2$, $-(NH)_xR_x$, $-(NH)_xO_2R_x$, and $-(NH)_xOR_x$, where $x=1-8$ and R is a hydrocarbon having 1 to 15 carbons.

[0073] Some examples of pendant acid generating groups include, but are not limited to, the embodiments illustrated in FIGS. **14A** and **14B**. Some examples of pendant base or pendant quencher groups include but are not limited to the embodiments illustrated in FIGS. **14D** and **14E**. Some examples of monomer units including the pendant base groups include, but are not limited to, the embodiments illustrated in FIG. **14F**. Some examples of the pendant TBG groups include, but are not limited to, the embodiments illustrated in FIG. **14G**. Some examples of the pendant PBG

groups include, but are not limited to, the embodiments illustrated in FIG. 14H. In some embodiments, A2 or A3 in FIG. 12A is a direct bond.

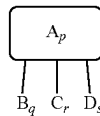
[0074] In some embodiments, R4 in FIG. 12A pendant group is a bulky or high Tg, which helps to control the resist profile. In some embodiments, the R4 pendant group includes 2D and 3D C6-C20 ring and fused ring structures. In some embodiments, the R4 pendant group includes adamantyl or norbornyl groups.

[0075] In some embodiments, R5 in FIG. 12A pendant group is a chromophore that absorbs radiation in the wavelength range of about 100 nm to about 400 nm. In some embodiments, the R5 pendant group absorbs out of band (OOB) radiation that can degrade the lithographic performance. In some embodiments, the R5 pendant group improves the LWR and LCDU of the photoresist pattern in some embodiments. In some embodiments, R5 includes phenyl, naphthalenyl, anthracenyl, phenanthrenyl, and pentacenquinonyl groups. Some examples of monomer units including the pendant chromophore groups include, but are not limited to, the embodiments illustrated in FIG. 15.

[0076] In some embodiments, the R6 pendant group in FIG. 12A is a developer solubility promoter or an acid labile group. In some embodiments, the developer solubility promoter contains a heterocyclic ring structure that opens when exposed to a liquid having a pH of greater than about 10 to form a carboxylic acid having increased solubility in an aqueous alkaline developer, as such as a TMAH developer, as shown in FIG. 16A. In some embodiments, the R6 pendant groups in FIG. 12A include, but are not limited to, the lactones shown in FIG. 16B. In some embodiments, the R6 pendant group is alkyl or hydroxyalkyl substituted lactone. In some embodiments, the lactone includes a five or six member heterocyclic ring. Some examples of monomer units including the pendant developer solubility promoter include, but are not limited to, the embodiments illustrated in FIG. 16C.

[0077] In some embodiments, the R6 pendant group in FIG. 12A is an acid labile group. Some examples of the acid labile groups include, but are not limited to, the embodiments illustrated in FIG. 16D.

[0078] In some embodiments, the floating additive polymer has the following structure:



where: A is the polymer backbone, B is the pendant fluorine-containing organic group, C is the pendant acid generating group, and D is the pendant base, quencher, or base generating group.

[0079] In some embodiments, the polymer backbone is a polystyrene, a polyacrylate, a polymethacrylate, a polyethylene, a polypropylene, a polyvinyl chloride, a polytetrafluoroethylene, a polyamide, a polyurethane, a polyamic acid, a polyimide, a polyacrylonitrile, a polyester, a polysiloxane, a polyphosphazene, and a poly metallic polymer. The poly metallic polymer may include one or more of Ag, Cd, In, Sn, Sb, Te, Cs, Au, Hg, Tl, Pb, Bi, Po, and At. The

degree of polymerization is p, and p may be about $3 \leq p \leq \text{about } 1000$ in some embodiments.

[0080] B is the pendant fluorine containing organic group, and it may be any of the pendant fluorine-containing groups disclosed herein. The number of fluorine-containing organic groups in the floating additive polymer is q, and q may be about $2 \leq q \leq \text{about } 5000$.

[0081] C is the pendant acid generating group, and it may be any of the pendant acid generating groups disclosed herein. The number of acid generating groups in the additive is r, and r is about $2 \leq r \leq \text{about } 5000$.

[0082] D is the pendant base, quencher, or base generating group, and it may be any of the base, quencher, or base generating groups disclosed herein. The number of base, quencher, or base generating groups is s, and s may be about $2 \leq s \leq \text{about } 5000$.

[0083] Some examples of floating additive polymers according to the present disclosure include, but are not limited to, the embodiments disclosed in FIGS. 17A, 17B, 17C, and 17D.

[0084] In some embodiments, the solvent is selected based on the dissolution rate of the base. Suitable solvents for the base composition include one or more selected from the group consisting of acetonitrile, acetic acid, propylene glycol methyl ether acetate (PGMEA), propylene glycol monomethyl ether (PGME), 1-ethoxy-2-propanol (PGEE), gamma-butyrolactone (GBL), cyclohexanone (CHN), ethyl lactate (EL), methanol, ethanol, propanol, n-butanol, acetone, dimethylformamide (DMF), isopropyl alcohol (IPA), tetrahydrofuran (THF), methyl isobutyl carbinol (MIBC), n-butyl acetate (nBA), 2-heptanone (MAK), 5-15 carbon alkyl chain solvents, including n-pentane, cyclohexane, 2,2-dimethylpentane, 2,4-dimethylpentane, and the like.

[0085] In FIGS. 2-11D, in some embodiments, the substrate 10 includes a single crystalline semiconductor layer on at least its surface portion. The substrate 10 may include a single crystalline semiconductor material such as, but not limited to Si, Ge, SiGe, GaAs, InSb, GaP, GaSb, InAlAs, InGaAs, GaSbP, GaAsSb and InP. In some embodiments, the substrate 10 is a silicon layer of an SOI (silicon-on insulator) substrate. In certain embodiments, the substrate 10 is made of crystalline Si.

[0086] The substrate 10 may include in its surface region, one or more buffer layers (not shown). The buffer layers can serve to gradually change the lattice constant from that of the substrate to that of subsequently formed source/drain regions. The buffer layers may be formed from epitaxially grown single crystalline semiconductor materials such as, but not limited to Si, Ge, GeSn, SiGe, GaAs, InSb, GaP, GaSb, InAlAs, InGaAs, GaSbP, GaAsSb, GaN, GaP, and InP. In an embodiment, the silicon germanium (SiGe) buffer layer is epitaxially grown on the silicon substrate 10. The germanium concentration of the SiGe buffer layers may increase from 30 atomic % for the bottom-most buffer layer to 70 atomic % for the top-most buffer layer.

[0087] In some embodiments, the substrate 10 includes one or more layers of at least one metal, metal alloy, and metal nitride sulfide/oxide/silicide having the formula MX_n , where M is a metal and X is N, S, Se, O, Si, and a is from about 0.4 to about 2.5. In some embodiments, the substrate 10 includes titanium, aluminum, cobalt, ruthenium, titanium nitride, tungsten nitride, tantalum nitride, and combinations thereof.

[0088] In some embodiments, the substrate **10** includes a dielectric having at least a silicon or metal oxide or nitride of the formula MX_b , where M is a metal or Si, X is N or O, and b ranges from about 0.4 to about 2.5. In some embodiments, the substrate **10** includes silicon dioxide, silicon nitride, aluminum oxide, hafnium oxide, lanthanum oxide, and combinations thereof.

[0089] The photoresist layer **15** is a photosensitive layer that is patterned by exposure to actinic radiation. Typically, the chemical properties of the photoresist regions struck by incident radiation change in a manner that depends on the type of photoresist used. Photoresist layers **15** may be positive tone resists or negative tone resists. A positive tone resist refers to a photoresist material that when exposed to actinic radiation (e.g., UV light or e-beam) becomes soluble in a developer, while the region of the photoresist that is non-exposed (or exposed less) is insoluble in the developer. A negative tone resist, on the other hand, refers to a photoresist material that when exposed to actinic radiation becomes insoluble in the developer, while the region of the photoresist that is non-exposed (or exposed less) is soluble in the developer. The region of a negative tone resist that becomes insoluble upon exposure to radiation may become insoluble due to a cross-linking reaction caused by the exposure to radiation. In some embodiments, the resist is a negative tone developed (NTD) resist. In an NTD resist, the portions of the photoresist layer exposed to actinic radiation do not crosslink, however, a developer is selected to selectively dissolve the unexposed portions of the photoresist layer, so that the exposed portions remain on the substrate. In some embodiments, the NTD develop is an organic developer such as n-butyl acetate.

[0090] Photoresist compositions used in some embodiments according to the present disclosure include a polymer along with one or more photoactive compounds (PACs) in a solvent. In some embodiments, the polymer includes a hydrocarbon structure (such as an alicyclic hydrocarbon structure) that contains one or more groups that will decompose (e.g., acid labile groups) or otherwise react when mixed with acids, bases, or free radicals generated by the PACs (as further described below). In some embodiments, the hydrocarbon structure includes a repeating unit that forms a skeletal backbone of the polymer. This repeating unit may include acrylic esters, methacrylic esters, crotonic esters, vinyl esters, maleic diesters, fumaric diesters, itaconic diesters, (meth)acrylonitrile, (meth)acrylamides, styrenes, vinyl ethers, combinations of these, or the like.

[0091] In some embodiments, the photoresist includes a polymer having acid labile groups. The acid labile groups may be one or more of the groups illustrated in FIG. 16D.

[0092] Specific structures that are utilized for the repeating unit of the hydrocarbon structure in some embodiments, include one or more of methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, tert-butyl acrylate, n-hexyl acrylate, 2-ethylhexyl acrylate, acetoxyethyl acrylate, phenyl acrylate, 2-hydroxyethyl acrylate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, 2-(2-methoxyethoxy)ethyl acrylate, cyclohexyl acrylate, benzyl acrylate, 2-alkyl-2-adamantyl (meth)acrylate or dialkyl(1-adamantyl)methyl (meth)acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, n-hexyl methacrylate, 2-ethylhexyl methacrylate, acetoxyethyl

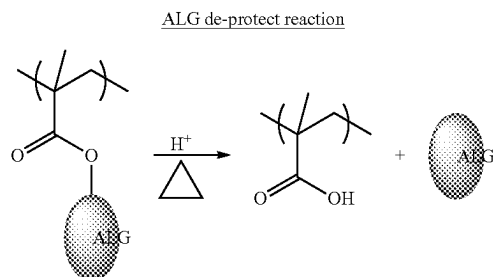
methacrylate, phenyl methacrylate, 2-hydroxyethyl methacrylate, 2-methoxyethyl methacrylate, 2-ethoxyethyl methacrylate, 2-(2-methoxyethoxy)ethyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, 3-chloro-2-hydroxypropyl methacrylate, 3-acetoxy-2-hydroxypropyl methacrylate, 3-chloroacetoxy-2-hydroxypropyl methacrylate, butyl crotonate, hexyl crotonate, or the like. Examples of the vinyl esters include vinyl acetate, vinyl propionate, vinyl butylate, vinyl methoxyacetate, vinyl benzoate, dimethyl maleate, diethyl maleate, dibutyl maleate, dimethyl fumarate, diethyl fumarate, dibutyl fumarate, dimethyl itaconate, diethyl itaconate, dibutyl itaconate, acrylamide, methyl acrylamide, ethyl acrylamide, propyl acrylamide, n-butyl acrylamide, tert-butyl acrylamide, cyclohexyl acrylamide, 2-methoxyethyl acrylamide, dimethyl acrylamide, diethyl acrylamide, phenyl acrylamide, benzyl acrylamide, methacrylamide, methyl methacrylamide, ethyl methacrylamide, propyl methacrylamide, n-butyl methacrylamide, tert-butyl methacrylamide, cyclohexyl methacrylamide, 2-methoxyethyl methacrylamide, dimethyl methacrylamide, diethyl methacrylamide, phenyl methacrylamide, benzyl methacrylamide, methyl vinyl ether, butyl vinyl ether, hexyl vinyl ether, methoxyethyl vinyl ether, dimethylaminoethyl vinyl ether, or the like. Examples of styrenes include styrene, methyl styrene, dimethyl styrene, trimethyl styrene, ethyl styrene, isopropyl styrene, butyl styrene, methoxy styrene, butoxy styrene, acetoxy styrene, chloro styrene, dichloro styrene, bromo styrene, vinyl methyl benzoate, α -methyl styrene, maleimide, vinylpyridine, vinylpyrrolidone, vinylcarbazole, combinations of these, or the like.

[0093] In some embodiments, the repeating unit of the hydrocarbon structure also has either a monocyclic or a polycyclic hydrocarbon structure substituted into it, or the monocyclic or polycyclic hydrocarbon structure is the repeating unit, in order to form an alicyclic hydrocarbon structure. Specific examples of monocyclic structures in some embodiments include bicycloalkane, tricycloalkane, tetracycloalkane, cyclopentane, cyclohexane, or the like. Specific examples of polycyclic structures in some embodiments include adamantane, norbornane, isobornane, tricyclodecane, tetracyclodecane, or the like.

[0094] The group which will decompose is attached to the hydrocarbon structure so that it will react with the acids/bases/free radicals generated by the PACs during exposure. Groups that react with acids are known as acid labile groups. In some embodiments, the group which will decompose is a carboxylic acid group, a fluorinated alcohol group, a phenolic alcohol group, a sulfonic group, a sulfonamide group, a sulfonylimido group, an (alkylsulfonyl) (alkylcarbonyl) methylene group, an (alkylsulfonyl)(alkyl-carbonyl)imido group, a bis(alkylcarbonyl)methylene group, a bis(alkylcarbonyl)imido group, a bis(alkylsulfonyl)methylene group, a bis(alkylsulfonyl)imido group, a tris(alkylcarbonyl)methylene group, a tris(alkylsulfonyl)methylene group, combinations of these, or the like. Specific groups that are used for the fluorinated alcohol group include fluorinated hydroxy-alkyl groups, such as a hexafluoroisopropanol group in some embodiments. Specific groups that are used for the carboxylic acid group include acrylic acid groups, methacrylic acid groups, or the like.

[0095] In some embodiments, the acid labile group (ALG) decomposes by the action of the acid generated by the

photoacid generator leaving a carboxylic acid group pendant to the polymer resin chain, as shown in the ALG de-protect reaction:



[0096] In some embodiments, the polymer also includes other groups attached to the hydrocarbon structure that help to improve a variety of properties of the polymerizable resin. For example, inclusion of a lactone group to the hydrocarbon structure assists to reduce the amount of line edge roughness after the photoresist has been developed, thereby helping to reduce the number of defects that occur during development. In some embodiments, the lactone groups include rings having five to seven members, although any suitable lactone structure may alternatively be used for the lactone group.

[0097] The individual components of the photoresist are placed into a solvent in order to aid in the mixing and dispensing of the photoresist. To aid in the mixing and dispensing of the photoresist, the solvent is chosen at least in part based upon the materials chosen for the polymer resin as well as the PACs. In some embodiments, the solvent is chosen such that the polymer resin and the PACs can be evenly dissolved into the solvent and dispensed upon the layer to be patterned.

[0098] In some embodiments, the polymer includes groups that can assist in increasing the adhesiveness of the photoresist layer **15** to underlying structures (e.g., substrate **10**). Polar groups may be used to help increase the adhesiveness. Suitable polar groups include hydroxyl groups, cyano groups, or the like, although any suitable polar group may, alternatively, be used.

[0099] Optionally, the polymer includes one or more alicyclic hydrocarbon structures that do not also contain a group which will decompose in some embodiments. In some embodiments, the hydrocarbon structure that does not contain a group which will decompose includes structures such as 1-adamantyl(meth)acrylate, tricyclodecanyl (meth)acrylate, cyclohexyl (methacrylate), combinations of these, or the like. In some embodiments, the photoresist composition includes one or more photoactive compounds (PAC).

[0100] In some embodiments, the PACs include photoacid generators, photobase generators, photo decomposable bases, free-radical generators, or the like. In some embodiments in which the PACs are photoacid generators, the PACs include halogenated triazines, onium salts, diazonium salts, aromatic diazonium salts, phosphonium salts, sulfonium salts, iodonium salts, imide sulfonate, oxime sulfonate, diazodisulfone, disulfone, o-nitrobenzylsulfonate, sulfonated esters, halogenated sulfonyloxy dicarboximides, diazodisulfones, α -cyanooxyamine-sulfonates, imides-sulfonates, ketodiazosulfones, sulfonyldiazoesters, 1,2-di(ar-

ylsulfonyl) hydrazines, nitrobenzyl esters, and the s-triazine derivatives, combinations of these, or the like.

[0101] Specific examples of photoacid generators include α -(trifluoromethylsulfonyloxy)-bicyclo[2.2.1]hept-5-ene-2, 3-dicarb-o-ximide (MDT), N-hydroxy-naphthalimide (DDSN), benzoin tosylate, t-butylphenyl- α -(p-toluenesulfonyloxy)-acetate and t-butyl- α -(p-toluenesulfonyloxy)-acetate, triarylsulfonium and diaryliodonium hexafluoroantimonates, hexafluoroarsenates, trifluoromethanesulfonates, iodonium perfluorooctanesulfonate, N-camphorsulfonyloxynaphthalimide, N-pentafluorophenylsulfonyloxynaphthalimide, ionic iodonium sulfonates such as diaryl iodonium (alkyl or aryl) sulfonate and bis-(di-t-butylphenyl) iodonium camphanylsulfonate, perfluoroalkanesulfonates such as perfluoropentanesulfonate, perfluorooctanesulfonate, perfluoromethanesulfonate, aryl (e.g., phenyl or benzyl) triflates such as triphenylsulfonium triflate or bis-(t-butylphenyl) iodonium triflate; pyrogallol derivatives (e.g., trimesylate of pyrogallol), trifluoromethanesulfonate esters of hydroxyimides, α,α' -bis-sulfonyl-diazomethanes, sulfonate esters of nitro-substituted benzyl alcohols, naphthoquinone-4-diazides, alkyl disulfones, or the like.

[0102] In some embodiments in which the PACs are free-radical generators, the PACs include n-phenylglycine; aromatic ketones, including benzophenone, N,N'-tetramethyl-4,4'-diaminobenzophenone, N,N'-tetraethyl-4,4'-diaminobenzophenone, 4-methoxy-4'-dimethylaminobenzophenone, 3,3'-dimethyl-4-methoxybenzophenone, p,p'-bis(dimethylamino)benzo-phenone, p,p'-bis(diethylamino)benzophenone; anthraquinone, 2-ethylanthraquinone; naphthaquinone; and phenanthraquinone; benzoin including benzoin, benzoinmethylether, benzoinisopropylether, benzoin-n-butylether, benzoin-phenylether, methylbenzoin and ethylbenzoin; benzyl derivatives, including dibenzyl, benzyldiphenyldisulfide, and benzyldimethylketal; acridine derivatives, including 9-phenylacridine, and 1,7-bis(9-acridinyl)heptane; thioxanthenes, including 2-chlorothioxanthone, 2-methylthioxanthone, 2,4-diethylthioxanthone, 2,4-dimethylthioxanthone, and 2-isopropylthioxanthone; acetophenones, including 1,1-dichloroacetophenone, p-t-butylidichloro-acetophenone, 2,2-diethoxyacetophenone, 2,2-dimethoxy-2-phenylacetophenone, and 2,2-dichloro-4-phenoxyacetophenone; 2,4,5-triarylimidazole dimers, including 2-(o-chlorophenyl)-4,5-diphenylimidazole dimer, 2-(o-chlorophenyl)-4,5-di-(m-methoxyphenyl) imidazole dimer, 2-(o-fluorophenyl)-4,5-diphenylimidazole dimer, 2-(o-methoxyphenyl)-4,5-diphenylimidazole dimer, 2-(p-methoxyphenyl)-4,5-diphenylimidazole dimer, 2,4-di(p-methoxyphenyl)-5-phenylimidazole dimer, 2-(2,4-dimethoxyphenyl)-4,5-diphenylimidazole dimer and 2-(p-methylmercaptophenyl)-4,5-diphenylimidazole dimer; combinations of these, or the like.

[0103] In some embodiments, the solvent is an organic solvent, and includes one or more of any suitable solvent such as ketones, alcohols, polyalcohols, ethers, glycol ethers, cyclic ethers, aromatic hydrocarbons, esters, propionates, lactates, lactic esters, alkylene glycol monoalkyl ethers, alkyl lactates, alkyl alkoxypropionates, cyclic lactones, monoketone compounds that contain a ring, alkylene carbonates, alkyl alkoxyacetate, alkyl pyruvates, lactate esters, ethylene glycol alkyl ether acetates, diethylene glycols, propylene glycol alkyl ether acetates, alkylene glycol alkyl ether esters, alkylene glycol monoalkyl esters, or the like.

[0104] The photoresist compositions may also include a number of other additives that assist the photoresist to obtain high resolution. For example, some embodiments of the photoresist also include surfactants to help improve the ability of the photoresist to coat the surface on which it is applied. Other additives added to some embodiments of the photoresist is a stabilizer, which assists in preventing undesired diffusion of the acids generated during exposure of the photoresist; a dissolution inhibitor to help control dissolution of the photoresist during development; a plasticizer, to reduce delamination and cracking between the photoresist and underlying layers (e.g., the layer to be patterned); and an adhesion promoter.

[0105] In some embodiments, the photoresist layer 15 is made of a metallic photoresist composition, including a first compound or a first precursor and a second compound or a second precursor combined in a vapor state. The first precursor or first compound is an organometallic having a formula: $M_aR_bX_c$, as shown in FIG. 18A, where M is at least one of Sn, Bi, Sb, In, Te, Ti, Zr, Hf, V, Co, Mo, W, Al, Ga, Si, Ge, P, As, Y, La, Ce, or Lu; and R is a substituted or unsubstituted alkyl, alkenyl, or carboxylate group. In some embodiments, M is selected from the group consisting of Sn, Bi, Sb, In, Te, and combinations thereof. In some embodiments, R is a C3-C6 alkyl, alkenyl, or carboxylate. In some embodiments, R is selected from the group consisting of propyl, isopropyl, butyl, iso-butyl, sec-butyl, tert-butyl, pentyl, isopentyl, sec-pentyl, tert-pentyl, hexyl, iso-hexyl, sec-hexyl, tert-hexyl, and combinations thereof. X is a ligand, ion, or other moiety, which is reactive with the second compound or second precursor; and $1 \leq a \leq 2$, $b \geq 1$, $c \geq 1$, and $b+c \leq 5$ in some embodiments. In some embodiments, the alkyl, alkenyl, or carboxylate group is substituted with one or more fluoro groups. In some embodiments, the organometallic precursor is a dimer, as shown in FIG. 18A, where each monomer unit is linked by an amine group and has a formula: $M_aR_bX_c$, as defined above.

[0106] In some embodiments, R is alkyl, such as C_nH_{2n+1} where $n \geq 3$. In some embodiments, R is fluorinated, e.g., having the formula $C_nF_xH_{(2n+1)-x}$. In some embodiments, R has at least one beta-hydrogen or beta-fluorine. In some embodiments, R is selected from the group consisting of i-propyl, n-propyl, t-butyl, i-butyl, n-butyl, sec-butyl, n-pentyl, i-pentyl, t-pentyl, and sec-pentyl, and combinations thereof.

[0107] In some embodiments, X is any moiety readily displaced by the second compound or second precursor to generate an M-OH moiety, such as a moiety selected from the group consisting of amines, including dialkylamino and monalkylamino; alkoxy; carboxylates, halogens, and sulfonates. In some embodiments, the sulfonate group is substituted with one or more amine groups. In some embodiments, the halide is one or more selected from the group consisting of F, Cl, Br, and I. In some embodiments, the sulfonate group includes a substituted or unsubstituted C1-C3 group.

[0108] In some embodiments, the first organometallic compound or first organometallic precursor includes a metallic core M^+ with ligands L attached to the metallic core M^+ , as shown in FIG. 18B. In some embodiments, the metallic core M^+ is a metal oxide. The ligands L include C3-C12 aliphatic or aromatic groups in some embodiments. The aliphatic or aromatic groups may be unbranched or branched with cyclic, or noncyclic saturated pendant groups

containing 1-9 carbons, including alkyl groups, alkenyl groups, and phenyl groups. The branched groups may be further substituted with oxygen or halogen. In some embodiments, the C3-C12 aliphatic or aromatic groups include heterocyclic groups. In some embodiments, the C3-C12 aliphatic or aromatic groups are attached to the metal by an ether or ester linkage. In some embodiments, the C3-C12 aliphatic or aromatic groups include nitrite and sulfonate substituents.

[0109] In some embodiments, the organometallic precursor or organometallic compound include a sec-hexyl tris(dimethylamino) tin, t-hexyl tris(dimethylamino) tin, i-hexyl tris(dimethylamino) tin, n-hexyl tris(dimethylamino) tin, sec-pentyl tris(dimethylamino) tin, t-pentyl tris(dimethylamino) tin, i-pentyl tris(dimethylamino) tin, n-pentyl tris(dimethylamino) tin, sec-butyl tris(dimethylamino) tin, t-butyl tris(dimethylamino) tin, i-butyl tris(dimethylamino) tin, n-butyl tris(dimethylamino) tin, sec-butyl tris(dimethylamino) tin, i-propyl tris(dimethylamino) tin, n-propyl tris(dimethylamino) tin, and analogous alkyl(tris)(t-butoxy) tin compounds, including sec-hexyl tris(t-butoxy) tin, t-hexyl tris(t-butoxy) tin, i-hexyl tris(t-butoxy) tin, n-hexyl tris(t-butoxy) tin, sec-pentyl tris(t-butoxy) tin, t-pentyl tris(t-butoxy) tin, i-pentyl tris(t-butoxy) tin, n-pentyl tris(t-butoxy) tin, t-butyl tris(t-butoxy) tin, i-butyl tris(t-butoxy) tin, n-butyl tris(t-butoxy) tin, sec-butyl tris(t-butoxy) tin, i-propyl tris(t-butoxy) tin, or n-propyl tris(t-butoxy) tin. In some embodiments, the organometallic precursors or organometallic compounds are fluorinated. In some embodiments, the organometallic precursors or compounds have a boiling point less than about 200° C.

[0110] In some embodiments, the first compound or first precursor includes one or more unsaturated bonds that can be coordinated with a functional group, such as a hydroxyl group, on the surface of the substrate or an intervening underlayer to improve adhesion of the photoresist layer to the substrate or underlayer.

[0111] In some embodiments, the second precursor or second compound is at least one of an amine, a borane, a phosphine, or water. In some embodiments, the amine has a formula $N_pH_nX_m$, where $0 \leq n \leq 3$, $0 \leq m \leq 3$, $n+m=3$ when p is 1, and $n+m=4$ when p is 2, and each X is independently a halogen selected from the group consisting of F, Cl, Br, and I. In some embodiments, the borane has a formula $B_pH_nX_m$, where $0 \leq n \leq 3$, $0 \leq m \leq 3$, $n+m=3$ when p is 1, and $n+m=4$ when p is 2, and each X is independently a halogen selected from the group consisting of F, Cl, Br, and I. In some embodiments, the phosphine has a formula $P_pH_nX_m$, where $0 \leq n \leq 3$, $0 \leq m \leq 3$, $n+m=3$, when p is 1, or $n+m=4$ when p is 2, and each X is independently a halogen selected from the group consisting of F, Cl, Br, and I.

[0112] FIG. 18C shows examples of organometallic precursors according to embodiments of the disclosure. In FIG. 18C, Bz is a benzene group.

[0113] In some embodiments, the operation S125 of forming a photoresist layer is performed by a vapor phase deposition operation. In some embodiments, the vapor phase deposition operation includes atomic layer deposition (ALD) and chemical vapor deposition (CVD). In some embodiments, the ALD includes plasma-enhanced atomic layer deposition (PE-ALD); the CVD includes plasma-enhanced chemical vapor deposition (PE-CVD), metal-organic chemical vapor deposition (MO-CVD), atmospheric

pressure chemical vapor deposition (AP-CVD), and low pressure chemical vapor deposition (LP-CVD).

[0114] A resist layer deposition apparatus **200** according to some embodiments of the disclosure is shown in FIG. **19**. In some embodiments, the deposition apparatus **200** is an ALD or CVD apparatus. The deposition apparatus **200** includes a vacuum chamber **205**. A substrate support stage **210** in the vacuum chamber **205** supports a substrate **10**, such as silicon wafer. In some embodiments, the substrate support stage **210** includes a heater or a chiller. A first precursor or compound gas supply **220** and carrier/purge gas supply **225** are connected to an inlet **230** in the chamber via a gas line **235**, and a second precursor or compound gas supply **240** and carrier/purge gas supply **225** are connected to another inlet **230'** in the chamber via another gas line **235'** in some embodiments. The chamber is evacuated, and excess reactants and reaction byproducts are removed by a vacuum pump **245** via an outlet **250** and exhaust line **255**. In some embodiments, the flow rate or pulses of precursor gases and carrier/purge gases, evacuation of excess reactants and reaction byproducts, pressure inside the vacuum chamber **205**, and temperature of the vacuum chamber **205** or wafer support stage **210** are controlled by a controller **260** configured to control each of these parameters.

[0115] Depositing a photoresist layer includes combining the first compound or first precursor and the second compound or second precursor in a vapor state to form the photoresist composition in some embodiments. In some embodiments, the first compound or first precursor and the second compound or second precursor of the photoresist composition are introduced into the deposition chamber **205** (CVD chamber) at about the same time via the inlets **230**, **230'**. In some embodiments, the first compound or first precursor and second compound or second precursor are introduced into the deposition chamber **205** (ALD chamber) in an alternating manner via the inlets **230**, **230'**, i.e. first one compound or precursor then a second compound or precursor, and then subsequently alternately repeating the introduction of the one compound or precursor followed by the second compound or precursor.

[0116] In some embodiments, the deposition chamber **205** temperature ranges from about 30° C. to about 400° C. during the deposition operation, and between about 50° C. to about 250° C. in other embodiments. In some embodiments, the pressure in the deposition chamber **205** ranges from about 5 mTorr to about 100 Torr during the deposition operation, and between about 100 mTorr to about 10 Torr in other embodiments. In some embodiments, the plasma power is less than about 1000 W. In some embodiments, the plasma power ranges from about 100 W to about 900 W. In some embodiments, the flow rate of the first compound or precursor and the second compound or precursor ranges from about 100 sccm to about 1000 sccm. In some embodiments, the ratio of the flow of the organometallic compound precursor to the second compound or precursor ranges from about 1:1 to about 1:5. At operating parameters outside the above-recited ranges, unsatisfactory photoresist layers result in some embodiments. In some embodiments, the photoresist layer formation occurs in a single chamber (a one-pot layer formation).

[0117] In a CVD process according to some embodiments of the disclosure, two or more gas streams, in separate inlet paths **230**, **235** and **230'**, **235'**, of an organometallic precursor and a second precursor are introduced to the deposition

chamber **205** of a CVD apparatus, where they mix and react in the gas phase, to form a reaction product. The streams are introduced using separate injection inlets **230**, **230'** or a dual-plenum showerhead in some embodiments. The deposition apparatus is configured so that the streams of organometallic precursor and second precursor are mixed in the chamber, allowing the organometallic precursor and second precursor to react to form a reaction product. Without limiting the mechanism, function, or utility of the disclosure, it is believed that the product from the vapor-phase reaction becomes heavier in molecular weight, and is then condensed or otherwise deposited onto the substrate **10**.

[0118] In some embodiments, an ALD process is used to deposit the photoresist layer. During ALD, a layer is grown on a substrate **10** by exposing the surface of the substrate to alternate gaseous compounds (or precursors). In contrast to CVD, the precursors are introduced as a series of sequential, non-overlapping pulses. In each of these pulses, the precursor molecules react with the surface in a self-limiting way, so that the reaction terminates once all the reactive sites on the surface are consumed. Consequently, the maximum amount of material deposited on the surface after a single exposure to all of the precursors (a so-called ALD cycle) is determined by the nature of the precursor-surface interaction.

[0119] In an embodiment of an ALD process, an organometallic precursor is pulsed to deliver the metal-containing precursor to the substrate **10** surface in a first half reaction. In some embodiments, the organometallic precursor reacts with a suitable underlying species (for example OH or NH functionality on the surface of the substrate) to form a new self-saturating surface. Excess unused reactants and the reaction by-products are removed, by an evacuation-pump down using a vacuum pump **245** and/or by a flowing an inert purge gas in some embodiments. Then, a second precursor, such as ammonia (NH₃), is pulsed to the deposition chamber in some embodiments. The NH₃ reacts with the organometallic precursor on the substrate to obtain a reaction product photoresist on the substrate surface. The second precursor also forms self-saturating bonds with the underlying reactive species to provide another self-limiting and saturating second half reaction. A second purge is performed to remove unused reactants and the reaction by-products in some embodiments. Pulses of the first precursor and second precursor are alternated with intervening purge operations until a desired thickness of the photoresist layer is achieved.

[0120] In some embodiments, the first and second compounds or precursors are delivered into the deposition chamber **205** with a carrier gas. The carrier gas, a purge gas, a deposition gas, or other process gas may contain nitrogen, hydrogen, argon, neon, helium, or combinations thereof.

[0121] In some embodiments, the photoresist layer **15** is formed to a thickness of about 5 nm to about 50 nm, and to a thickness of about 10 nm to about 30 nm in other embodiments. A person of ordinary skill in the art will recognize that additional ranges of thicknesses within the explicit ranges above are contemplated and are within the present disclosure. The thickness can be evaluated using non-contact methods of x-ray reflectivity and/or ellipsometry based on the optical properties of the photoresist layers. In some embodiments, each photoresist layer thickness is relatively uniform to facilitate processing. In some embodiments, the variation in thickness of the deposited photoresist layer varies by no more than ±25% from the average

thickness, in other embodiments each photoresist layer thickness varies by no more than $\pm 10\%$ from the average photoresist layer thickness. In some embodiments, such as high uniformity depositions on larger substrates, the evaluation of the photoresist layer uniformity may be evaluated with a 1 centimeter edge exclusion, i.e., the layer uniformity is not evaluated for portions of the coating within 1 centimeter of the edge. A person of ordinary skill in the art will recognize that additional ranges within the explicit ranges above are contemplated and are within the present disclosure.

[0122] In some embodiments, the organometallic compound includes tin (Sn), antimony (Sb), bismuth (Bi), indium (In), and/or tellurium (Te) as the metal component, however, the disclosure is not limited to these metals. In other embodiments, additional suitable metals include titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), cobalt (Co), molybdenum (Mo), tungsten (W), aluminum (Al), gallium (Ga), silicon (Si), germanium (Ge), phosphorus (P), arsenic (As), yttrium (Y), lanthanum (La), cerium (Ce), lutetium (Lu), or combinations thereof. The additional metals can be used as alternatives to or in addition to the Sn, Sb, Bi, In, and/or Te.

[0123] The particular metal used may significantly influence the absorption of radiation. Therefore, the metal component can be selected based on the desired radiation and absorption cross section. Tin, antimony, bismuth, tellurium, and indium provide strong absorption of extreme ultraviolet light at 13.5 nm. Hafnium provides good absorption of electron beam and extreme UV radiation. Metal compositions including titanium, vanadium, molybdenum, or tungsten have strong absorption at longer wavelengths, to provide, for example, sensitivity to 248 nm wavelength ultraviolet light.

[0124] In some embodiments, the resist layer **15** is formed by mixing the organometallic compound in a solvent to form a resist composition and dispensing the resist composition onto the substrate **10**. To aid in the mixing and dispensing of the photoresist, the solvent is chosen at least in part based upon the materials chosen for the metallic resist. In some embodiments, the solvent is chosen such that the organometallic is evenly dissolved into the solvent and dispensed upon the layer to be patterned.

[0125] In some embodiments, the resist solvent is an organic solvent, and includes any suitable solvent such as propylene glycol methyl ether acetate (PGMEA), propylene glycol monomethyl ether (PGME), 1-ethoxy-2-propanol (PGEE), γ -butyrolactone (GBL), cyclohexanone (CHN), ethyl lactate (EL), methanol, ethanol, propanol, n-butanol, acetone, dimethylformamide (DMF), isopropanol (IPA), tetrahydrofuran (THF), methyl isobutyl carbinol (MIBC), n-butyl acetate (nBA), 2-heptanone (MAK), formic acid, acetic acid, propanoic acid, butanoic acid, or the like.

[0126] As one of ordinary skill in the art will recognize, the materials listed and described above as examples of materials that may be used for the solvent component of the photoresist are merely illustrative and are not intended to limit the embodiments. Rather, any suitable material that dissolves the metallic photoresist material may be used to help mix and apply the photoresist. All such materials are fully intended to be included within the scope of the embodiments.

[0127] The resist layer deposition apparatus **200** illustrated in FIG. **19** is also used to apply the floating additive

composition to the substrate **10**, BARC layer **20**, or photoresist layer **15** in some embodiments. A floating additive composition supply **260** and carrier gas supply **265** are connected to an inlet **275** in the chamber via a supply line **270**. In some embodiments, the inlet **275** is configured to deliver the floating additive composition as a liquid spray or as an atomized vapor. In some embodiments, a purge gas supply **280** is connected a purge gas inlet **290** via a gas supply line **285**. In some embodiments, the chamber **205** is purged with the purge gas before the floating additive composition is introduced into the chamber **205**. In some embodiments, the floating additive composition is introduced into the chamber **205** before the photoresist layer is formed, and in other embodiments, the floating additive composition is added after the photoresist layer **15** is formed. In other embodiments, the floating additive composition is introduced into the chamber **205** substantially simultaneously with the introduction of the photoresist components, and the floating additive composition is applied directly to the photoresist layer **15** while the photoresist layer **15** is being formed. In some embodiments, the flow rate of the floating additive composition, carrier gas, or purge gas are also controlled by the controller **260** configured to control each of these parameters, along with the flow rate of the precursor gases and carrier/purge gases, evacuation of excess reactants and reaction byproducts, pressure inside the vacuum chamber **205**, and temperature of the vacuum chamber **205** or wafer support stage **210**.

[0128] The floating additive composition and photoresist composition are applied onto the substrate **10** to form the base composition treated photoresist layer **15**, as shown in FIGS. **2**, **3A**, **4A**, and **4B** in some embodiments. In some embodiments, the floating additive composition and the photoresist composition are applied using a process such as a spin-on coating process, a dip coating method, an air-knife coating method, a curtain coating method, a wire-bar coating method, a gravure coating method, a lamination method, an extrusion coating method, CVD, ALD, PVD, combinations of these, or the like. In some embodiments, the photoresist layer **15** thickness ranges from about 10 nm to about 300 nm.

[0129] After the photoresist layer **15** has been formed on the substrate **10** pre-exposure baking and cooling operations **S140** are performed, as discussed herein (see FIG. **1**) in some embodiments, and the photoresist layer **15** is selectively exposed to form an exposed region **50** and an unexposed region **52**, as discussed herein, and shown in FIGS. **1**, **5A** and **5B**. In some embodiments, the exposure to radiation is carried out by placing the photoresist coated substrate in a photolithography tool. In the embodiments illustrated in FIGS. **5A** and **5B**, the photolithography tool includes a photomask **30**, **65** optics, an exposure radiation source to provide the radiation **45**, **97** for exposure, and a movable stage for supporting and moving the substrate under the exposure radiation.

[0130] The selectively exposed photoresist layer **15** is subsequently post exposure baked/cooled and then developed, as shown in FIG. **6**. In some embodiments of the disclosure, the developer composition **57**, includes an ammonium compound. In some embodiments, suitable bases include tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, and tetrabutylammonium hydroxide, and combinations thereof; or inorganic bases selected from the group consist-

ing of ammonium hydroxide, ammonium sulfamate, ammonium carbamate, NaOH, KOH, LiOH, Ca(OH)₂, Ba(OH)₂, Na₂CO₃,

[0131] NH₄OH, Mg (OH) 2, RbOH, CsOH, Sr (OH) 2 and combinations thereof or inorganic bases selected from the group consisting of ammonia, ammonium hydroxide, ammonium sulfamate, ammonium carbamate, and combinations thereof. In some embodiments, the concentration of the base is about 1 ppm to about 30 wt. % based on a total weight of the developer composition.

[0132] In some embodiments, the developer composition includes water or ethylene glycol at a concentration of about 0.001 wt. % to about 30 wt. % based on a total weight of the developer composition.

[0133] In some embodiments, the photoresist developer composition includes a surfactant in a concentration range of from about 0.001 wt. % to about less than 5 wt. % based on a total weight of the developer composition to increase the solubility and reduce the surface tension on the substrate. In other embodiments, the concentration of the surfactant ranges from about 0.01 wt. % to about 1 wt. % based on the total weight of the developer composition.

[0134] At concentrations of the developer composition components outside the disclosed ranges, developer composition performance and development efficiency may be reduced, leading to increased photoresist residue and scum in the photoresist pattern, and increased line width roughness and line edge roughness.

[0135] In some embodiments, the developer 57 is applied to the photoresist layer 15 using a spin-on process. In the spin-on process, the developer 57 is applied to the photoresist layer 15 from above the photoresist layer 15 while the photoresist coated substrate is rotated, as shown in FIG. 7. In some embodiments, the developer 57 is supplied at a rate of between about 5 ml/min and about 800 ml/min, while the photoresist coated substrate 10 is rotated at a speed of between about 100 rpm and about 2000 rpm. In some embodiments, the developer is at a temperature of between about 20° C. and about 75° C. during the development operation. The development operation continues for between about 10 seconds to about 10 minutes in some embodiments.

[0136] While the spin-on operation is one suitable method for developing the photoresist layer 15 after exposure, it is intended to be illustrative and is not intended to limit the embodiment. Rather, any suitable development operations, including dip processes, puddle processes, and spray-on methods, may alternatively be used. All such development operations are included within the scope of the embodiments.

[0137] During the development process, the developer composition 57 dissolves the photoresist regions exposed to radiation, the upper floating additive layer 22, and expose portions of the lower floating additive layer 20, exposing the surface of the substrate 10, as shown in FIG. 7, and leaving behind well-defined unexposed photoresist regions 52, having improved definition when compared with conventional photolithographic techniques.

[0138] After the developing operation S170, remaining developer is removed from the patterned photoresist covered substrate. The remaining developer is removed using a spin-dry process in some embodiments, although any suitable removal technique may be used. After the photoresist layer 15 is developed, and the remaining developer is

removed, additional processing is performed while the patterned photoresist layer 50 is in place. For example, an etching operation, using dry or wet etching, is performed in some embodiments, to transfer the pattern of the photoresist layer 50 to the underlying substrate 10, forming recesses 55' as shown in FIG. 8. The substrate 10 has a different etch resistance than the photoresist layer 15. In some embodiments, the etchant is more selective to the substrate 10 than the photoresist layer 15.

[0139] In some embodiments, the controller 260 is a computer system. FIGS. 20A and FIG. 20B illustrate a computer system 260 for controlling a deposition apparatus 200 and its components in accordance with various embodiments of the disclosure. FIG. 20A is a schematic view of the computer system 260 that controls the deposition apparatus 200 and its components. In some embodiments, the computer system 260 is programmed to monitor and control the flow rate of the precursor gases and carrier/purge gases, evacuation of excess reactants and reaction byproducts, pressure inside the vacuum chamber 205, temperature of the vacuum chamber 205 or wafer support stage 210, and the flow rate of the base composition.

[0140] As shown in FIG. 20A, the computer system 260 is provided with a computer 1001 including an optical disk read only memory (e.g., CD-ROM or DVD-ROM) drive 1005 and a magnetic disk drive 1006, a keyboard 1002, a mouse 1003 (or other similar input device), and a monitor 1004 in some embodiments.

[0141] FIG. 20B is a diagram showing an internal configuration of the computer system 260. In FIG. 20B, the computer 1001 is provided with, in addition to the optical disk drive 1005 and the magnetic disk drive 1006, one or more processors 1011, such as a micro-processor unit (MP) or a central processing unit (CPU); a read-only memory (ROM) 1012 in which a program, such as a boot up program is stored; a random access memory (RAM) 1013 that is connected to the processors 1011 and in which a command of an application program is temporarily stored, and a temporary electronic storage area is provided; a hard disk 1014 in which an application program, an operating system program, and data are stored; and a data communication bus 1015 that connects the processors 1011, the ROM 1012, and the like. Note that the computer 1001 may include a network card (not shown) for providing a connection to a computer network such as a local area network (LAN), wide area network (WAN) or any other useful computer network for communicating data used by the computer system 260 and the deposition apparatus 200. In various embodiments, the controller 260 communicates via wireless or hardwired connection to the deposition apparatus 200 and its components.

[0142] The programs for causing the computer system 260 to execute the method for controlling the deposition apparatus 200 and its components are stored in an optical disk 1021 or a magnetic disk 1022, which is inserted into the optical disk drive 1005 or the magnetic disk drive 1006, and transmitted to the hard disk 1014. Alternatively, the programs are transmitted via a network (not shown) to the computer system 500 and stored in the hard disk 1014. At the time of execution, the programs are loaded into the RAM 1013. The programs are loaded from the optical disk 1021 or the magnetic disk 1022, or directly from a network in various embodiments.

[0143] The stored programs do not necessarily have to include, for example, an operating system (OS) or a third-party program to cause the computer 1001 to execute the methods disclosed herein. The program may only include a command portion to call an appropriate function (module) in a controlled mode and obtain desired results in some embodiments. In various embodiments described herein, the controller 260 is in communication with the deposition apparatus 200 to control various functions thereof.

[0144] The controller 260 is coupled to the deposition apparatus 200 in various embodiments. The controller 260 is configured to provide control data to those system components and receive process and/or status data from those system components. For example, in some embodiments, the controller 260 comprises a microprocessor, a memory (e.g., volatile or non-volatile memory), and a digital I/O port capable of generating control voltages sufficient to communicate and activate inputs to the processing system, as well as monitor outputs from the deposition apparatus 200. In addition, a program stored in the memory is utilized to control the aforementioned components of the deposition apparatus 200 according to a process recipe. Furthermore, the controller 260 is configured to analyze the process and/or status data, to compare the process and/or status data with target process and/or status data, and to use the comparison to change a process and/or control a system component. In addition, the controller 260 is configured to analyze the process and/or status data, to compare the process and/or status data with historical process and/or status data, and to use the comparison to predict, prevent, and/or declare a fault or alarm.

[0145] As set forth above, the executed program causes the processor or computer 260 to measure the pressure in the coolant or cooling fluid line or conduit, determine a pressure difference between the coolant or cooling fluid inflow line and outflow line, determine whether the pressure difference is greater than a threshold value, and adjust a valve to change the coolant or cooling fluid flowrate to reduce the pressure difference when the pressure difference is greater than the stored threshold value. In some embodiments, the executed program causes the processor or computer 500 to measure the pressure in the coolant or cooling fluid line or conduit periodically, for example, every second, 10 seconds, 20 seconds, or 30 seconds.

[0146] In some embodiments, a layer to be patterned (target layer) 60 is disposed over the substrate prior to forming the photoresist layer 15 or the floating additive layers 20, 22, as shown in FIGS. 21, 22A, 22B, 23A, and 23B. Pre-exposure baking/cooling operations S140 are performed, to dry and cure the photoresist layer 15 discussed herein in reference to FIGS. 1-4 in some embodiments. In some embodiments, the target layer 60 is a metallization layer or a dielectric layer, such as a passivation layer, disposed over a metallization layer. In embodiments where the target layer 60 is a metallization layer, the target layer 60 is formed of a conductive material using metallization processes, and metal deposition techniques, including chemical vapor deposition, atomic layer deposition, and physical vapor deposition (sputtering). Likewise, if the target layer 60 is a dielectric layer, the target layer 60 is formed by dielectric layer formation techniques, including thermal oxidation, CVD, ALD, and PVD.

[0147] The photoresist layer 15 is subsequently selectively exposed to actinic radiation 45, 97 in operation S150 to form

exposed regions 50 and unexposed regions 52 in the photoresist layer, as shown in FIGS. 24A and 24B, and described herein in relation to FIGS. 5A and 5B.

[0148] As shown in FIG. 21, post exposure baking/cooling operations S160 are subsequently performed, as described herein.

[0149] As shown in FIG. 25, the selectively exposed photoresist layer 50, 52 is subsequently developed by dispensing developer 57 from a dispenser 62 in operation S170 to form a pattern of photoresist openings 55, as shown in FIG. 26. The development operation is similar to that explained with reference to FIGS. 6 and 7, herein.

[0150] Then, as shown in FIG. 27, the pattern 55 in the photoresist layer 15 is transferred to the target layer 60 using an etching operation and the photoresist layer is removed, as explained with reference to FIG. 8 to form pattern 55' in the target layer 60.

[0151] Other embodiments include other operations before, during, or after the operations described above. In some embodiments, the disclosed methods include forming fin field effect transistor (FinFET) structures. In some embodiments, a plurality of active fins are formed on the semiconductor substrate. Such embodiments, further include etching the substrate through the openings of a patterned hard mask to form trenches in the substrate; filling the trenches with a dielectric material; performing a chemical mechanical polishing (CMP) process to form shallow trench isolation (STI) features; and epitaxy growing or recessing the STI features to form fin-like active regions. In some embodiments, one or more gate electrodes are formed on the substrate. Some embodiments include forming gate spacers, doped source/drain regions, contacts for gate/source/drain features, etc. In other embodiments, a target pattern is formed as metal lines in a multilayer interconnection structure. For example, the metal lines may be formed in an inter-layer dielectric (ILD) layer of the substrate, which has been etched to form a plurality of trenches. The trenches may be filled with a conductive material, such as a metal; and the conductive material may be polished using a process such as chemical mechanical planarization (CMP) to expose the patterned ILD layer, thereby forming the metal lines in the ILD layer. The above are non-limiting examples of devices/structures that can be made and/or improved using the method described herein.

[0152] In some embodiments, active components such diodes, field-effect transistors (FETs), metal-oxide semiconductor field effect transistors (MOSFET), complementary metal-oxide semiconductor (CMOS) transistors, bipolar transistors, high voltage transistors, high frequency transistors, sheet FETs such as nanosheet FETs, FinFETs, gate all around FETs (GAA FETs), other three-dimensional (3D) FETs, other memory cells, and combinations thereof are formed, according to embodiments of the disclosure.

[0153] The novel floating additive layer application techniques and semiconductor manufacturing methods according to the present disclosure provide higher semiconductor device feature density with reduced defects in a higher efficiency process than conventional methods. The novel techniques and methods provide a floating additive layer that satisfies the following functions: (1) a thin, about 5 nm thickness, phase separated layer, (2) improved OOB (out of band) radiation absorbance, (3) high glass transition temperature (T_g), (4) high developer dissolution, (5) high sen-

sitivity to extreme ultraviolet (EUV) and e-beam radiation, (6) high etch resistance, and (7) a high molecular weight.

[0154] The floating additive layer according to the present disclosure is useful in sub-28 nm technology. In ArF immersion techniques, it can be used in water isolate shielding, dissolution controlling, and profile modification. In EUV techniques, the floating additive layer acts as a sacrificial layer that provides improved after development inspection (ADI), local critical dimension uniformity (LCDU), and line width roughness (LWR). In some embodiments, the floating additive layer provides improved LWR/LCDU stability. In some embodiments, the LCDU is improved by greater than about 3%. In some embodiments, the variation in LWR and LCDU is reduced to less than about 5%. The floating additive layer of the present disclosure can also allow the use of a lower exposure dose to achieve the reduced LWR and LCDU variation. Thus, providing a cost savings and increased device yield.

[0155] An embodiment of the disclosure is a method of manufacturing a semiconductor device including forming a photoresist layer including a photoresist composition over a substrate and forming a floating additive layer including a floating additive polymer. The floating additive polymer includes a pendant fluorine substituted organic group and one or more of a pendant acid generating group, a pendant base group, a pendant acid labile group, a pendant chromophore group, a pendant developer solubility promoter group, and a pendant acid diffusion control group. The photoresist layer is selectively exposed to actinic radiation to form a latent pattern. The selectively exposed photoresist layer is developed to form a pattern in the photoresist layer. In an embodiment, the photoresist layer is formed in a vacuum chamber. In an embodiment, the floating additive polymer is added to the photoresist composition before forming the photoresist layer. In an embodiment, a floating additive layer including the floating additive polymer is formed over the photoresist layer before the selectively exposing the photoresist layer to actinic radiation. In an embodiment, the method includes forming a photoresist underlayer over the substrate before forming the photoresist layer, wherein the photoresist underlayer includes the floating additive polymer. In an embodiment, the photoresist composition includes a metallic resist. In an embodiment, the method includes heating the photoresist layer at a temperature ranging from 40° C. to 300° C. before selectively exposing the photoresist layer to actinic radiation. In an embodiment, the pendant fluorine substituted organic group includes a fluoroalcohol group. In an embodiment, the floating additive polymer includes the pendant acid generating group and the pendant acid labile group. In an embodiment, the floating additive polymer includes the pendant chromophore group. In an embodiment, the floating additive polymer includes the pendant developer solubility promoter group.

[0156] Another embodiment of the disclosure is a method of manufacturing a semiconductor device, including forming a photoresist layer comprising a photoresist composition over a substrate. The photoresist composition includes a first polymer; a photoactive compound; and a second polymer including a pendant fluorine substituted organic group and one or more of a pendant acid generating group, a pendant base group, a pendant acid labile group, a pendant chromophore group, a pendant developer solubility promoter group, and a pendant acid diffusion control group. The

second polymer is floated over the first polymer and the photoactive compound to form a floating layer over the photoresist layer. The photoresist layer is selectively exposed to actinic radiation through the floating layer to form a latent pattern in the photoresist layer. The latent pattern is developed to form a pattern in the photoresist layer. In an embodiment, the floating the second polymer includes rotating the substrate while forming the photoresist layer or after forming the photoresist layer. In an embodiment, the method includes heating the photoresist layer at a temperature ranging from 40° C. to 300° C. before selectively exposing the photoresist layer to actinic radiation. In an embodiment, the first polymer includes the pendant acid labile group. In an embodiment, the floating layer is removed during the developing the latent pattern. In an embodiment, the second polymer includes the pendant acid generating group and the pendant acid labile group.

[0157] Another embodiment of the disclosure is a photoresist composition including a photoresist polymer, a photoactive compound, and a floating additive polymer. The floating additive polymer includes a pendant fluorine substituted organic group and one or more of a pendant acid generating group, a pendant base group, a pendant acid labile group, a pendant chromophore group, a pendant developer solubility promoter group, and a pendant acid diffusion control group. The floating additive polymer and the photoresist polymer are different polymers. In an embodiment, the photoresist polymer includes the pendant acid labile group. In an embodiment, the pendant fluorine substituted organic group includes a fluoroalcohol group. In an embodiment, the floating additive polymer includes the pendant acid labile group. In an embodiment, the floating additive polymer includes the pendant chromophore group. In an embodiment, the floating additive polymer includes the pendant developer solubility promoter group. In an embodiment, the floating additive polymer includes the pendant acid diffusion control group. In an embodiment, the floating additive polymer includes a polystyrene or poly(meth)acrylate backbone. In an embodiment, the floating additive polymer includes the pendant acid labile group, the pendant acid generating group, and the pendant fluorine substituted organic group, wherein the pendant fluorine substituted organic group is a fluoroalcohol group. In an embodiment, the floating additive polymer includes the pendant acid diffusion control group, the pendant chromophore group, the pendant developer solubility promoter group, and the pendant fluorine substituted organic group, wherein the pendant fluorine substituted organic group is a fluoroalcohol group.

[0158] Another embodiment of the disclosure is a method of manufacturing a semiconductor device, including forming a photoresist underlayer over a substrate, and forming a first floating layer over the photoresist underlayer. The first floating layer includes a first floating polymer having a pendant fluorine substituted organic group and one or more of a pendant acid generating group, a pendant base group, a pendant acid labile group, a pendant chromophore group, a pendant developer solubility promoter group, and a pendant acid diffusion control group. A photoresist layer is formed over the first floating layer. A second floating layer is formed over the photoresist layer. The second floating layer includes a second floating polymer having a pendant fluorine substituted organic group and one or more of a pendant acid generating group, a pendant base group, a pendant acid

labile group, a pendant chromophore group, a pendant developer solubility promoter group, and a pendant acid diffusion control group. The photoresist layer is selectively exposed to actinic radiation to form a latent pattern, and the latent pattern is developed to form a pattern in the photoresist layer. In an embodiment, the second floating layer is removed during the developing the latent pattern. In an embodiment, the photoresist layer includes a photoresist polymer, and the photoresist polymer, the first floating polymer, and the second floating polymer are different polymers.

[0159] Another embodiment of the disclosure is a composition including a polymer including a pendant fluorine substituted organic group, and one or more of a pendant acid generating group, a pendant base group, a pendant acid labile group, a pendant developer solubility promoter group, a pendant chromophore group, and a pendant acid diffusion control group; and a solvent. In an embodiment, the pendant fluorine substituted organic group includes a fluoroalcohol group. In an embodiment, the polymer includes the pendant acid generating group and the pendant acid labile group. In an embodiment, the polymer includes the pendant chromophore group. In an embodiment, the polymer includes the pendant developer solubility promoter group. In an embodiment, the polymer includes a polystyrene or a poly(meth)acrylate backbone. In an embodiment, the polystyrene or the poly(meth)acrylate backbone includes iodine as a substituent.

[0160] Another embodiment of the disclosure is a polymer including a polymer backbone including a pendant fluorine substituted organic group and one or more of a pendant acid generating group, a pendant base group, a pendant acid labile group, a pendant chromophore group, a pendant acid diffusion control group, and a pendant developer solubility promoter group, wherein the polymer backbone includes a polystyrene or a poly(meth)acrylate. In an embodiment, the polymer includes the pendant fluorine substituted organic group, the pendant acid generating group, and the pendant acid labile group, wherein the pendant fluorine substituted organic group is a fluoroalcohol group. In an embodiment, the polymer includes the pendant fluorine substituted organic group, the pendant acid diffusion control group, the pendant chromophore group, and the pendant developer solubility promoter group.

[0161] Another embodiment of the disclosure is a stacked structure, including a photoresist layer disposed over a substrate and a floating additive layer disposed over the photoresist layer. The photoresist layer includes a photoresist polymer and a photoactive compound. The floating additive layer includes a floating additive polymer. The floating additive polymer includes a pendant fluorine substituted organic group and one or more of a pendant acid generating group, a pendant base groups, a pendant acid labile group, a pendant chromophore group, a pendant developer solubility promoter group, and a pendant acid diffusion control group. The floating additive polymer and the photoresist polymer are different polymers. In an embodiment, the stacked structure includes a photoresist underlayer disposed between the substrate and the photoresist layer, and the photoresist underlayer includes the floating additive polymer. In an embodiment, the photoresist polymer includes a pendant acid labile group, and the pendant fluorine substituted organic group includes a fluoroalcohol group.

[0162] The foregoing outlines features of several embodiments or examples so that those skilled in the art may better understand the aspects of the present disclosure. Those skilled in the art should appreciate that they may readily use the present disclosure as a basis for designing or modifying other processes and structures for carrying out the same purposes and/or achieving the same advantages of the embodiments or examples introduced herein. Those skilled in the art should also realize that such equivalent constructions do not depart from the spirit and scope of the present disclosure, and that they may make various changes, substitutions, and alterations herein without departing from the spirit and scope of the present disclosure.

What is claimed is:

1. A method of manufacturing a semiconductor device, comprising:
 - forming a photoresist layer comprising a photoresist composition over a substrate;
 - forming a floating additive layer comprising a floating additive polymer,
 - wherein the floating additive polymer includes a pendant fluorine substituted organic groups and one or more of a pendant acid generating group, a pendant base group, a pendant acid labile group, a pendant chromophore group, a pendant developer solubility promoter group, and a pendant acid diffusion control group;
 - selectively exposing the photoresist layer to actinic radiation to form a latent pattern; and
 - developing the selectively exposed photoresist layer to form a pattern in the photoresist layer.
2. The method according to claim 1, wherein the photoresist layer is formed in a vacuum chamber.
3. The method according to claim 1, wherein the floating additive polymer is added to the photoresist composition before forming the photoresist layer.
4. The method according to claim 1, wherein a floating additive layer comprising the floating additive polymer is formed over the photoresist layer before the selectively exposing the photoresist layer to actinic radiation.
5. The method according to claim 1, further comprising forming a photoresist underlayer over the substrate before forming the photoresist layer, wherein the photoresist underlayer comprises the floating additive polymer.
6. The method according to claim 1, wherein the photoresist composition comprises a metallic resist.
7. The method according to claim 1, further comprising heating the photoresist layer at a temperature ranging from 40° C. to 300° C. before selectively exposing the photoresist layer to actinic radiation.
8. The method according to claim 1, wherein the pendant fluorine substituted organic group includes a fluoroalcohol group.
9. The method according to claim 1, wherein the floating additive polymer comprises the pendant acid generating group and the pendant acid labile group.
10. The method according to claim 1, wherein the floating additive polymer comprises the pendant chromophore group.
11. The method according to claim 1, wherein the floating additive polymer comprises the pendant developer solubility promoter group.
12. A method of manufacturing a semiconductor device, comprising:

forming a photoresist layer comprising a photoresist composition over a substrate,

wherein the photoresist composition comprises:

a first polymer;

a photoactive compound; and

a second polymer including a pendant fluorine substituted organic group and one or more of a pendant acid generating group, a pendant base group, a pendant acid labile group, a pendant chromophore group, a pendant developer solubility promoter group, and a pendant acid diffusion control group;

floating the second polymer over the first polymer and the photoactive compound to form a floating layer over the photoresist layer;

selectively exposing the photoresist layer to actinic radiation through the floating layer to form a latent pattern in the photoresist layer; and

developing the latent pattern to form a pattern in the photoresist layer.

13. The method according to claim **12**, wherein the floating the second polymer comprises rotating the substrate while forming the photoresist layer or after forming the photoresist layer.

14. The method according to claim **12**, further comprising heating the photoresist layer at a temperature ranging from 40° C. to 300° C. before selectively exposing the photoresist layer to actinic radiation.

15. The method according to claim **12**, wherein the first polymer includes a pendant acid labile group.

16. The method according to claim **12**, wherein the floating layer is removed during the developing the latent pattern.

17. The method according to claim **12**, wherein the second polymer comprises the pendant acid generating group and the pendant acid labile group.

18. A stacked structure, comprising:

a photoresist layer disposed over a substrate; and

a floating additive layer disposed over the photoresist layer,

wherein the photoresist layer comprises a photoresist polymer and

a photoactive compound; and

the floating additive layer comprises a floating additive polymer,

wherein the floating additive polymer includes a pendant fluorine substituted organic group and one or more of a pendant acid generating group, a pendant base groups, a pendant acid labile group, a pendant chromophore group, a pendant developer solubility promoter group, and a pendant acid diffusion control group,

wherein the floating additive polymer and the photoresist polymer are different polymers.

19. The stacked structure of claim **18**, further comprising a photoresist underlayer disposed between the substrate and the photoresist layer, wherein the photoresist underlayer comprises the floating additive polymer.

20. The stacked structure of claim **18**, wherein the photoresist polymer includes a pendant acid labile group, and the pendant fluorine substituted organic group includes a fluoroalcohol group.

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