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Weng et al.

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(54) **METHOD FOR PERFORMING LITHOGRAPHY PROCESS WITH POST TREATMENT**

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G03F 7/40 (2006.01)
H01L 21/027 (2006.01)

(Continued)

(52) **U.S. Cl.**

CPC ***G03F 7/40*** (2013.01); ***H01L 21/0273*** (2013.01); ***H01L 21/0274*** (2013.01); *G03F 7/20* (2013.01); *G03F 7/30* (2013.01)

(58) **Field of Classification Search**

None

See application file for complete search history.

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Primary Examiner — Kathleen Duda

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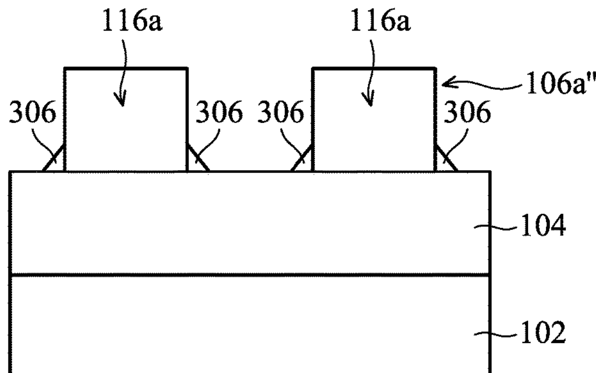
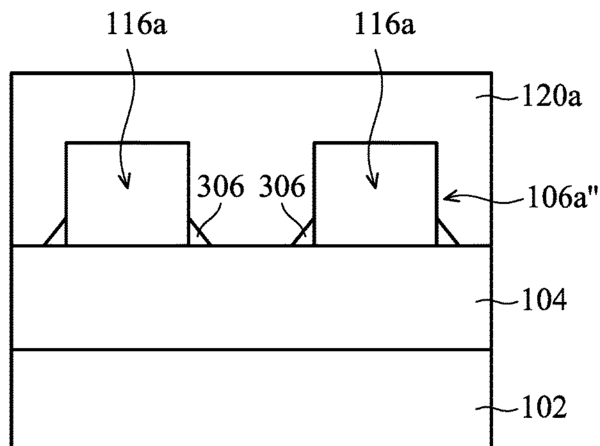
(57) **ABSTRACT**

Methods for performing a lithography process are provided. The method for performing a lithography process includes forming a resist layer over a substrate and exposing a portion of the resist layer to form an exposed portion between unexposed portions. The method for performing a lithography process further includes developing the resist layer to remove the exposed portion of the resist layer such that an opening is formed between the unexposed portions and forming a post treatment coating material in the opening and over the unexposed portions of the resist layer. The method for performing a lithography process further includes reacting a portion of the unexposed portions of the resist layer with the post treatment coating material by performing a post treatment process and removing the post treatment coating material.

18 Claims, 11 Drawing Sheets





Related U.S. Application Data

(60) Provisional application No. 62/549,607, filed on Aug. 24, 2017.

(51) **Int. Cl.**

G03F 7/30	(2006.01)
G03F 7/20	(2006.01)

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FIG. 1A

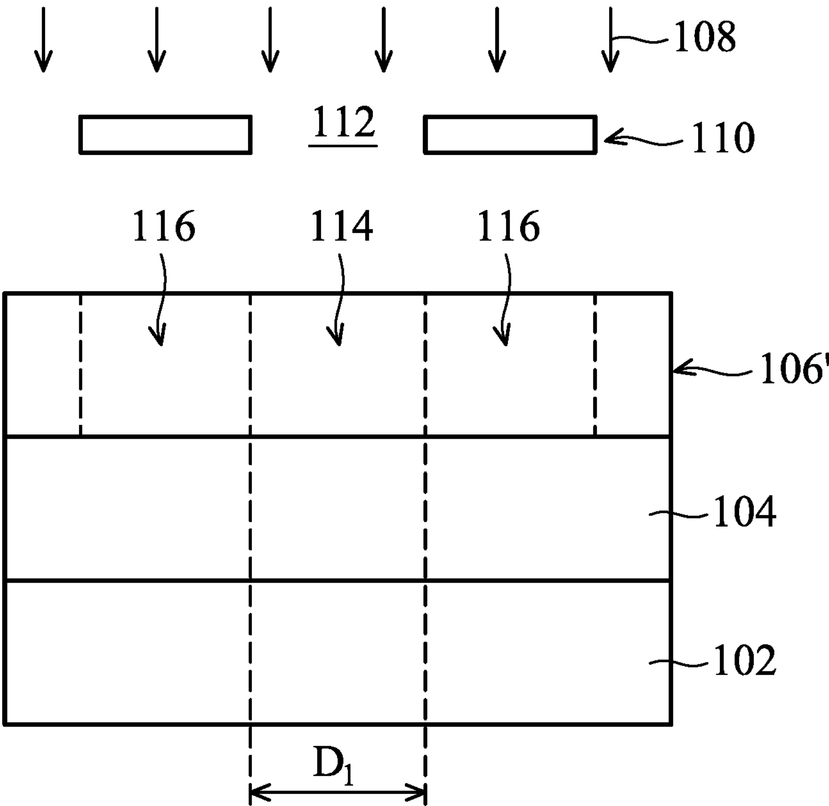


FIG. 1B

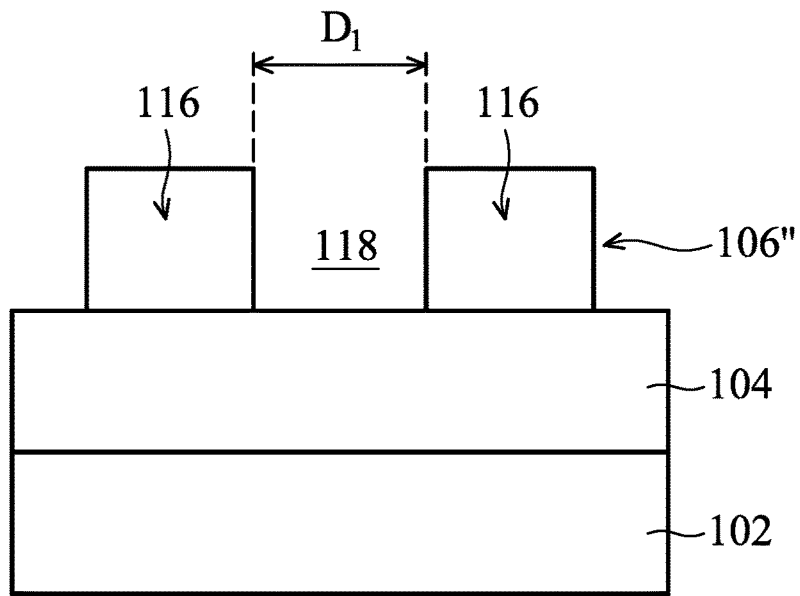


FIG. 1C

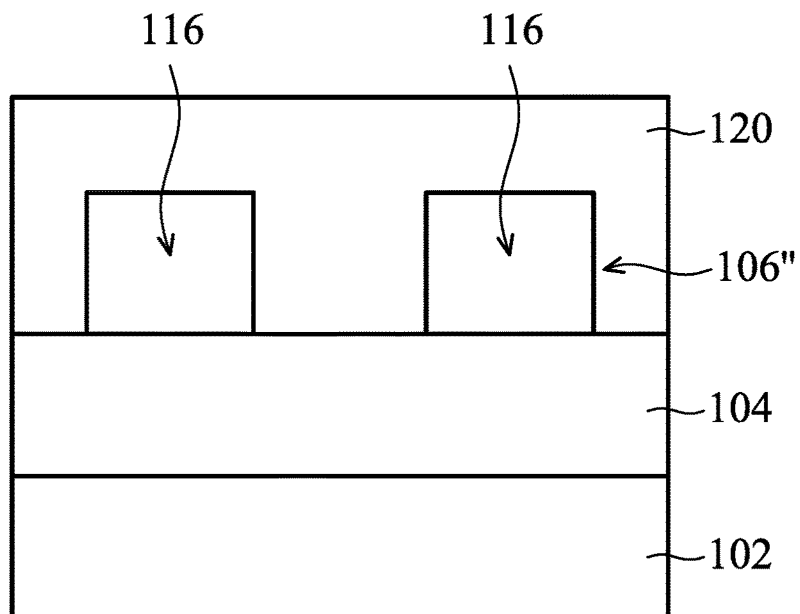


FIG. 1D

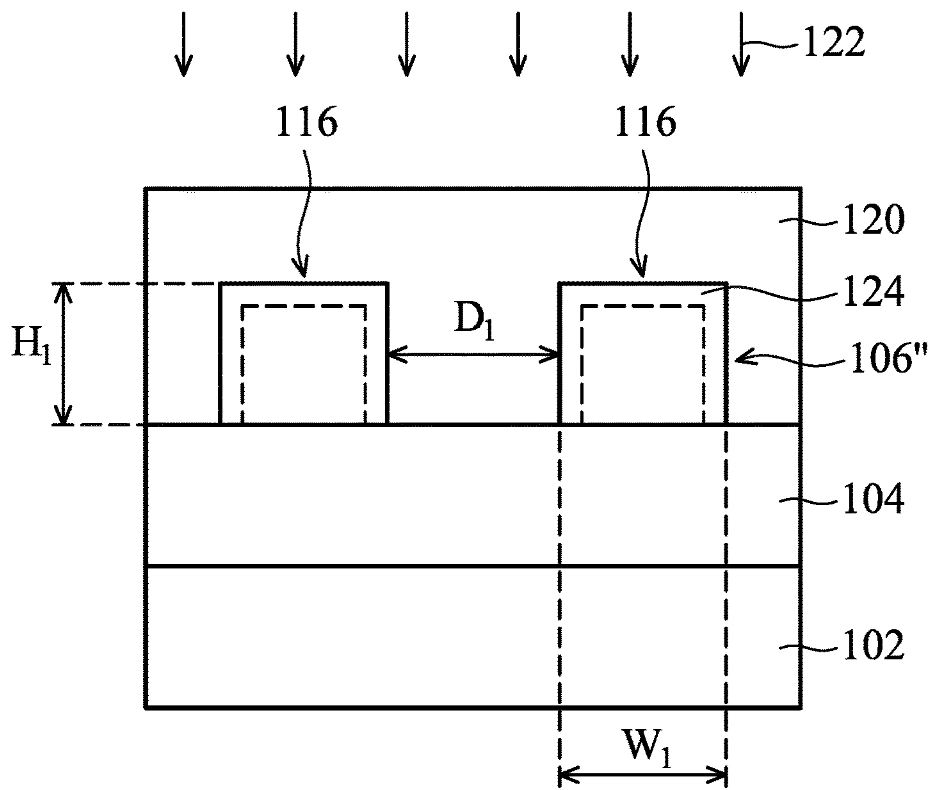


FIG. 1E

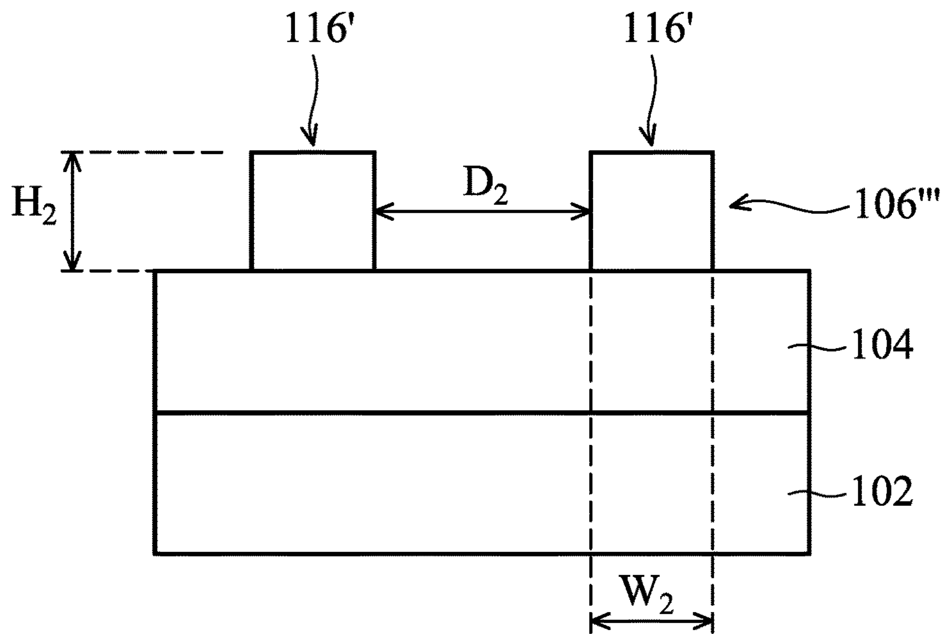


FIG. 1F

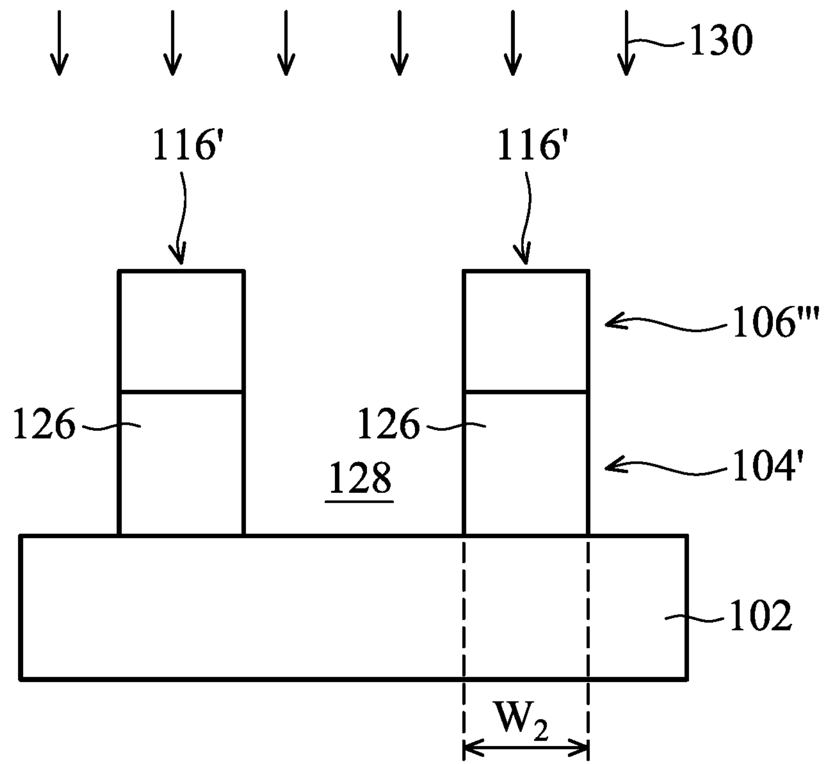


FIG. 1G

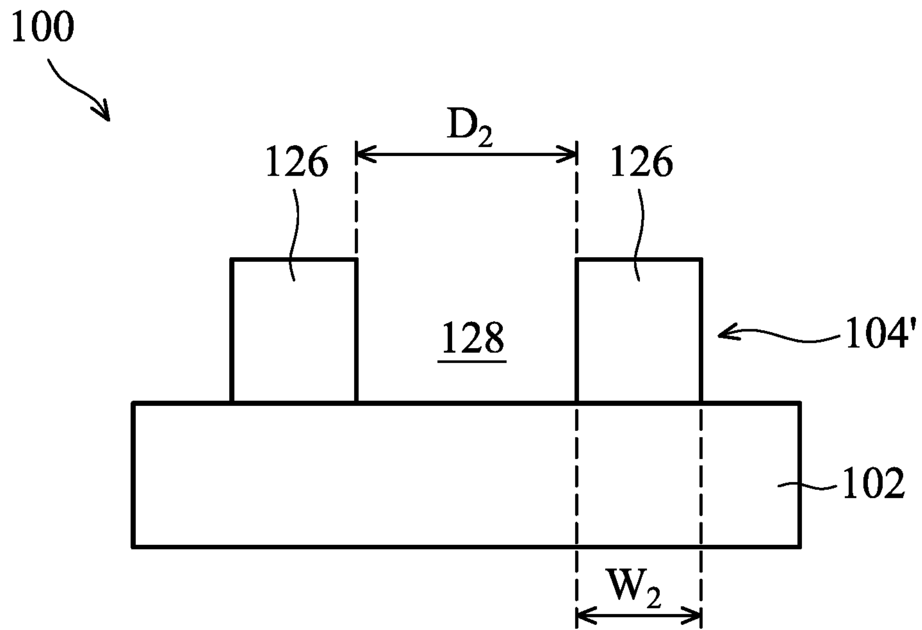


FIG. 1H

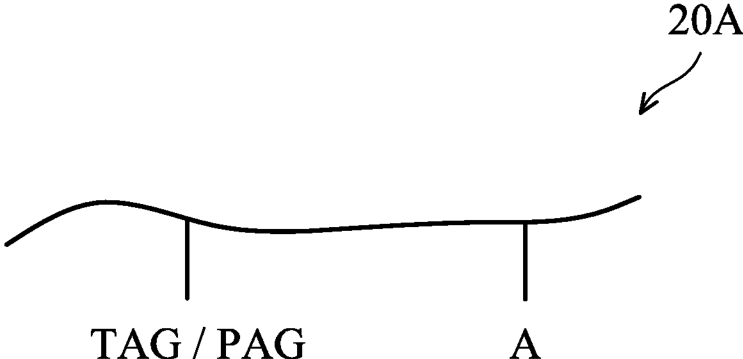


FIG. 2A

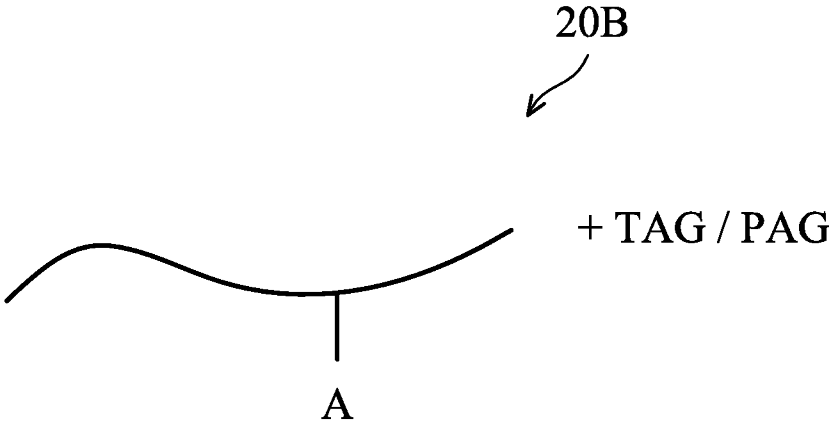


FIG. 2B

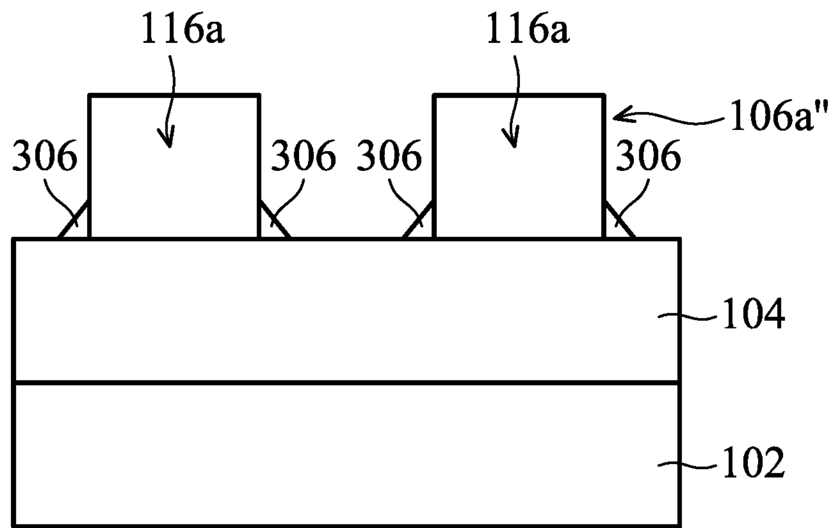


FIG. 3A

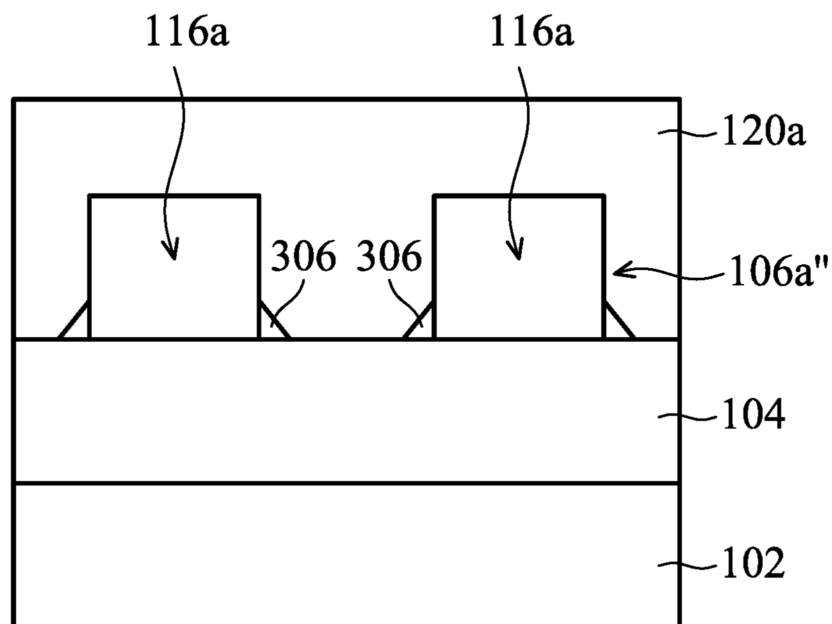


FIG. 3B

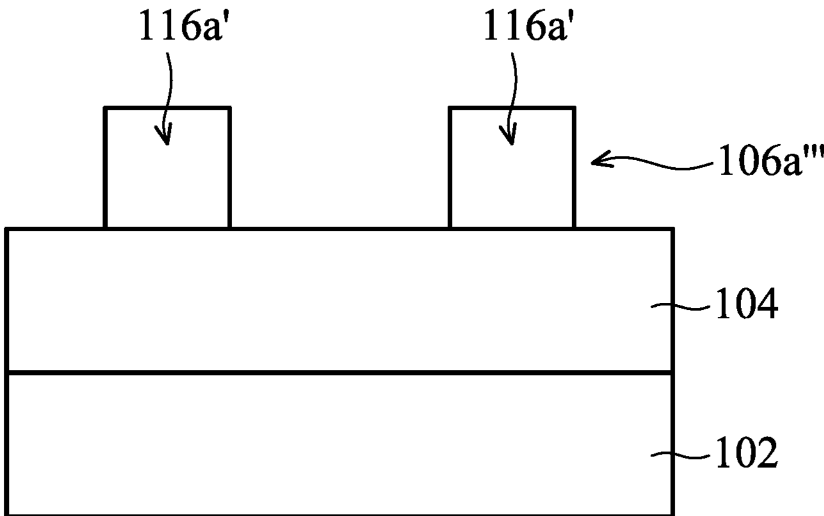


FIG. 3C

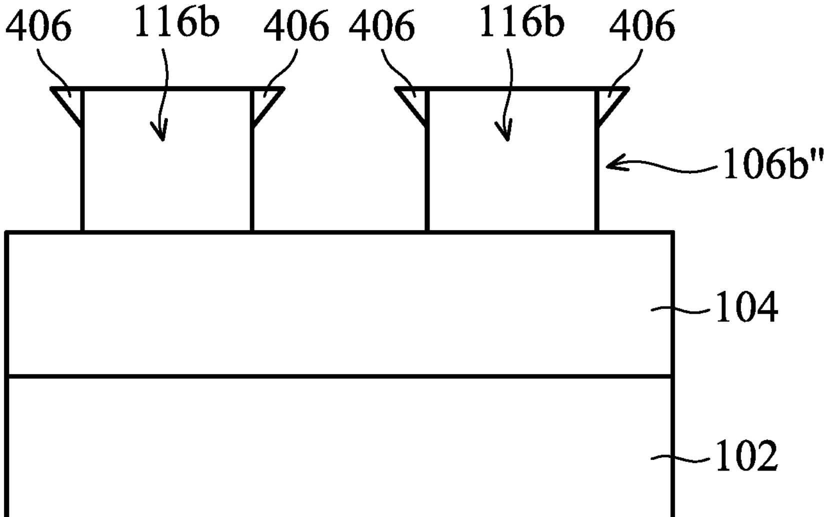


FIG. 4A

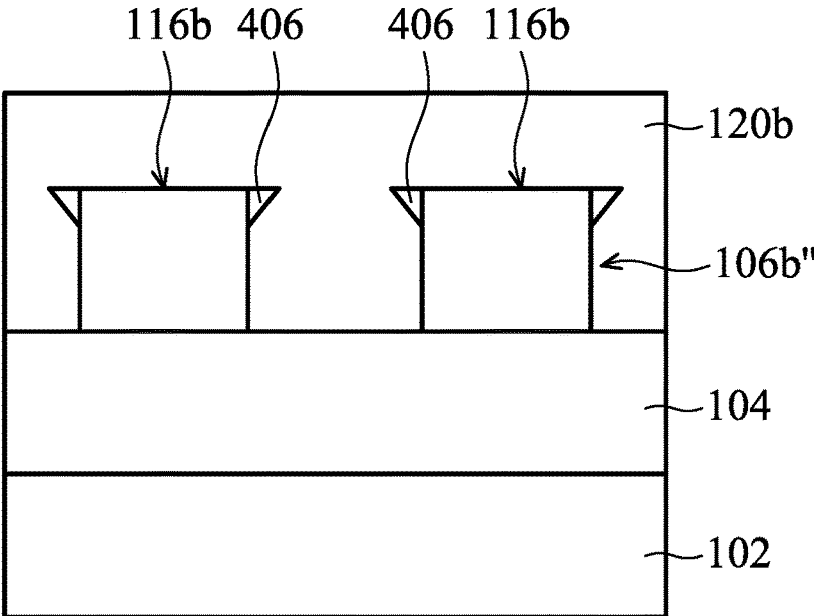


FIG. 4B

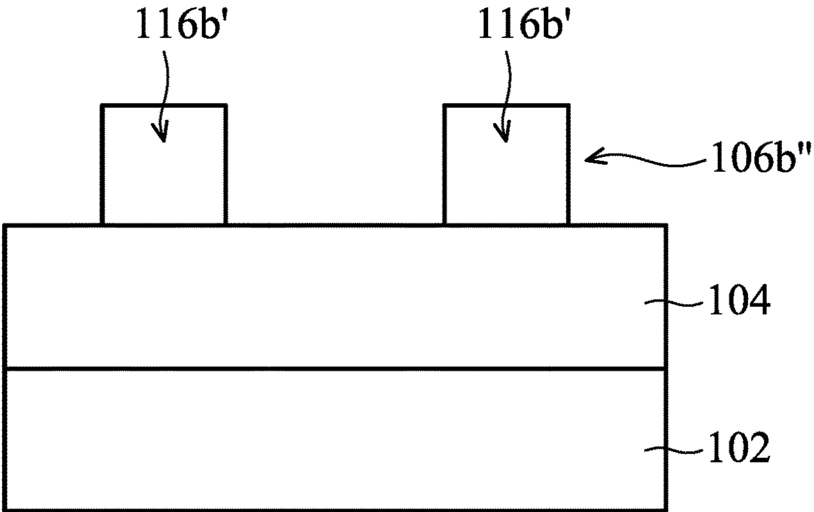


FIG. 4C

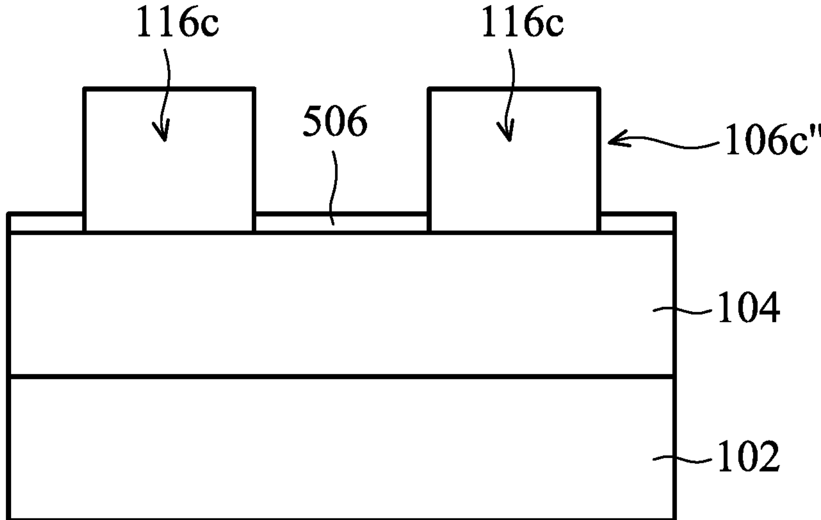


FIG. 5A

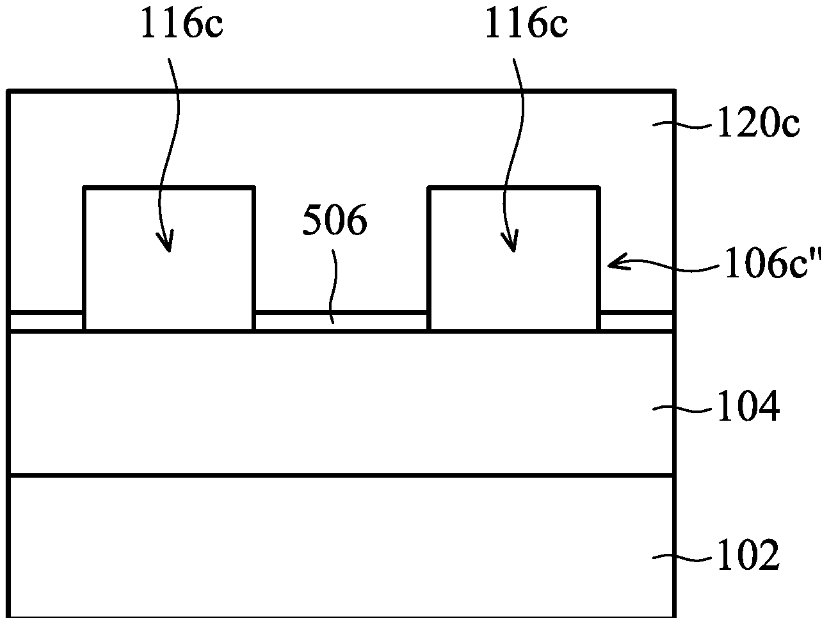


FIG. 5B

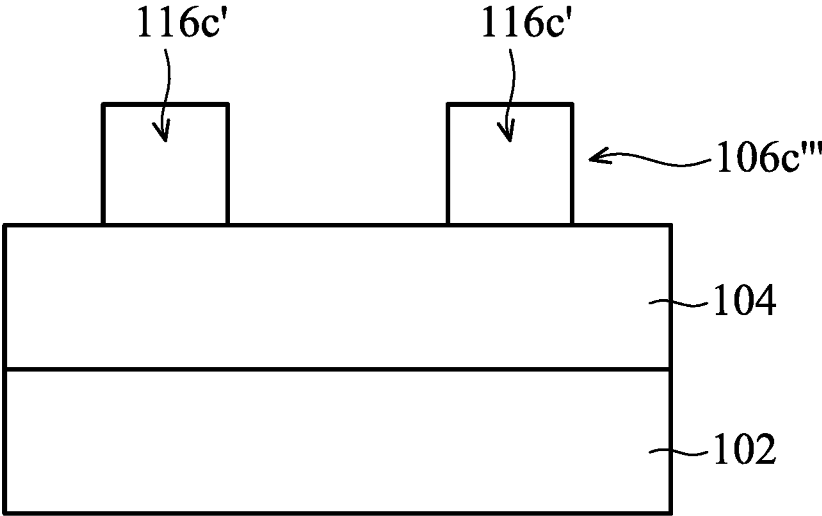


FIG. 5C

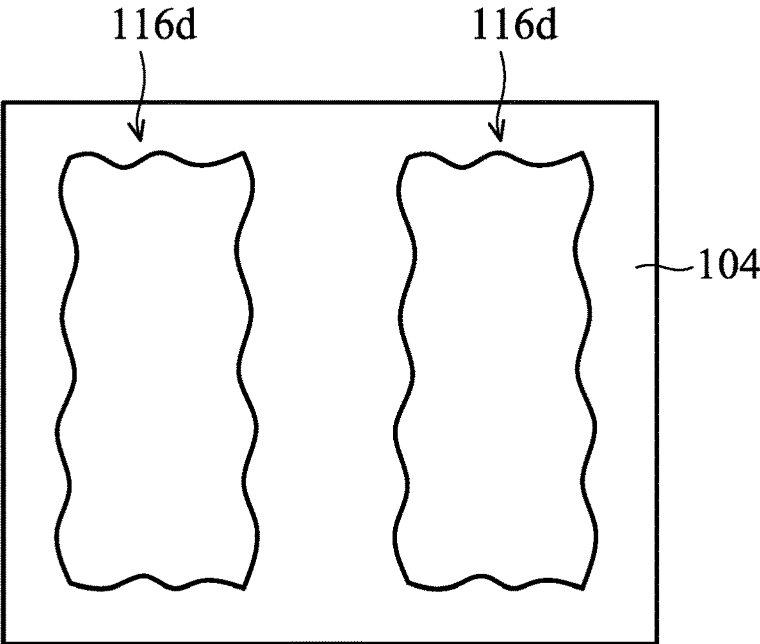


FIG. 6A

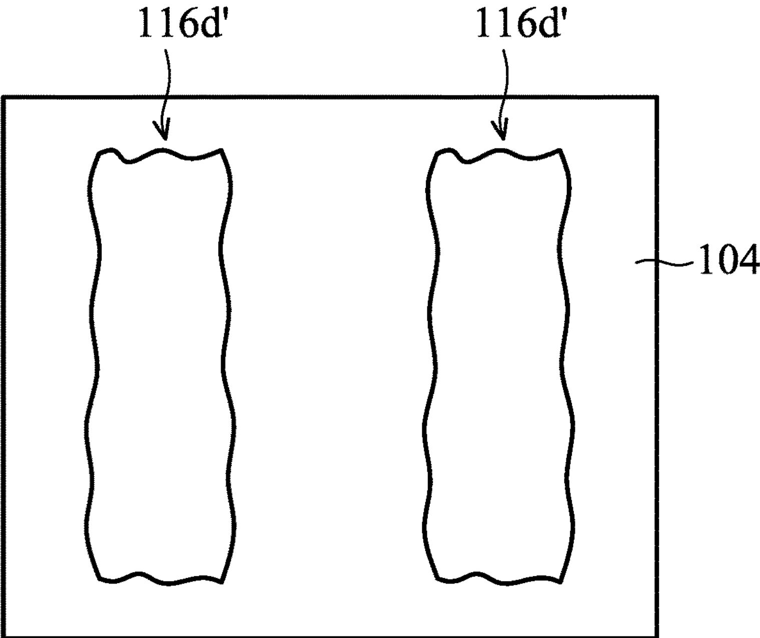


FIG. 6B

METHOD FOR PERFORMING LITHOGRAPHY PROCESS WITH POST TREATMENT

PRIORITY CLAIM AND CROSS-REFERENCE

This application is a Continuation application of U.S. patent application Ser. No. 15/940,107, filed on Mar. 29, 2018, the entirety of which is incorporated by reference herein. The U.S. patent application Ser. No. 15/940,107 claims the benefit of U.S. Provisional Application No. 62/549,607, filed on Aug. 24, 2017, the entirety of which is incorporated by reference herein.

BACKGROUND

Semiconductor devices are used in a variety of electronic applications, such as personal computers, cell phones, digital cameras, and other electronic equipment. Semiconductor devices are typically fabricated by sequentially depositing insulating or dielectric layers, conductive layers, and semiconductor layers of material over a semiconductor substrate, and patterning the various material layers using lithography to form circuit components and elements thereon.

One of the important drivers for increased performance in a semiconductor structure is the higher level of integration of circuits. This is accomplished by miniaturizing or shrinking device sizes on a given chip. However, as the device sizes shrink, lithography processes used to form the devices also become more and more challenging.

BRIEF DESCRIPTION OF THE DRAWINGS

Aspects of the present disclosure are best understood from the following detailed description when read with the accompanying figures. It should be noted that, in accordance with standard practice in the industry, various features are not drawn to scale. In fact, the dimensions of the various features may be arbitrarily increased or reduced for clarity of discussion.

FIGS. **1**A to **1**H show cross-sectional representations of various stages of forming a semiconductor structure including performing a lithography process in accordance with some embodiments.

FIG. **2**A illustrates a polymer in the post treatment coating material that has PAG/TAGs bonding to the polymer in accordance with some embodiments.

FIG. **2**B illustrates a polymer and PAG/TAGs mixing in the post treatment coating material in accordance with some embodiments.

FIGS. **3**A to **3**C show cross-sectional representations of various stages of performing a lithography process in accordance with some embodiments.

FIGS. **4**A to **4**C show cross-sectional representations of various stages of performing a lithography process in accordance with some embodiments.

FIGS. **5**A to **5**C show cross-sectional representations of various stages of performing a lithography process in accordance with some embodiments.

FIGS. **6**A and **6**B illustrate the top views of unexposed portions of a patterned resist layer before and after the post treatment process is performed in accordance with some embodiments.

DETAILED DESCRIPTION

The following disclosure provides many different embodiments, or examples, for implementing different features of the subject matter provided. Specific 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, 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 between the first and second features, such that the first and second features may not be in direct contact. In addition, the present disclosure may repeat reference numerals and/or letters in the various examples. This repetition is for the purpose of simplicity and clarity and does not in itself dictate a relationship between the various embodiments and/or configurations discussed.

The advanced lithography process, method, and materials described in the current disclosure can be used in many applications, including fin-type field effect transistors (FinFETs). For example, the fins may be patterned to produce a relatively close spacing between features, for which the above disclosure is well suited. In addition, spacers used in forming fins of FinFETs can be processed according to the above disclosure.

Furthermore, 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 apparatus may be otherwise oriented (rotated 90 degrees or at other orientations) and the spatially relative descriptors used herein may likewise be interpreted accordingly. It should be understood that additional operations can be provided before, during, and after the method, and some of the operations described can be replaced or eliminated for other embodiments of the method.

Embodiments of methods for performing a lithography process are provided. The lithography process may include forming a resist layer over a substrate and performing an exposure process and a first developing process to the resist layer. Next, a post treatment coating material is formed over the resist layer and a post treatment process is performed. Afterwards, the post treatment coating material is removed. By forming the post treatment coating material and performing the post treatment process, the resolution of the resulting pattern in the resist layer may be improved, and the energy required to be consumed for the lithography process may be reduced.

FIGS. **1**A to **1**H show cross-sectional representations of various stages of forming a semiconductor structure **100** including performing a lithography process in accordance with some embodiments. As shown in FIG. **1**A, a substrate **102** is received in accordance with some embodiments. The substrate **102** may be a semiconductor wafer such as a silicon wafer. Alternatively or additionally, the substrate **102** may include elementary semiconductor materials, compound semiconductor materials, and/or alloy semiconductor materials. Examples of the elementary semiconductor materials may include, but are not limited to, crystal silicon, polycrystalline silicon, amorphous silicon, germanium, and diamond. Examples of the compound semiconductor materials may include, but are not limited to, silicon carbide, gallium arsenic, gallium phosphide, indium phosphide, indium arsenide, and indium antimonide. Examples of the

alloy semiconductor materials may include, but are not limited to, SiGe, GaAsP, AlInAs, AlGaAs, GaInAs, GaInP, and GaInAsP.

In some embodiments, the substrate **102** includes structures such as doped regions including wells and source/drain regions, isolation features including shallow trench isolation (STI), inter-level dielectric (ILD) layers, and/or conductive features including gate electrodes, metal lines, vias, and contacts.

A material layer **104** is formed over the substrate **102**, as shown in FIG. **1**A in accordance with some embodiments. The material layer **104** is configured to be patterned in subsequent manufacturing processes. The material layer **104** may be one or more material layers. In some embodiments, the material layer **104** is a dielectric layer. In some embodiments, the material layer **104** is made of metal oxides, metal nitrides, metal silicates, transition metal-oxides, transition metal-nitrides, transition metal-silicates, or oxynitrides of metals. Examples of materials used to form the material layer **104** include, but are not limited to, titanium oxide, titanium nitride, hafnium oxide (HfO_2), hafnium silicon oxide (HfSiO), hafnium silicon oxynitride (HfSiON), hafnium tantalum oxide (HfTaO), hafnium titanium oxide (HfTiO), hafnium zirconium oxide (HfZrO), silicon nitride, silicon oxynitride, zirconium oxide, titanium oxide, aluminum oxide, hafnium dioxide-alumina (HfO_2—Al_2O_3) alloy, or other applicable dielectric materials. In some embodiments, the material layer **104** is made of low-k dielectric materials. In some embodiments, the material layer **104** is made of silicon oxide, silicon nitride, silicon oxynitride, phosphosilicate glass (PSG), borophosphosilicate glass (BPSG), and/or other applicable low-k dielectric materials. In some embodiments, the material layer **104** is formed by performing a chemical vapor deposition (CVD) process, a physical vapor deposition (PVD) process, an atomic layer deposition (ALD) process, a spin-on coating process, or other applicable processes.

After the material layer **104** is formed, a resist layer **106** is formed over the material layer **104**, as shown in FIG. **1**A in accordance with some embodiments. In some embodiments, the resist layer **106** is formed by coating a resist material over the material layer **104**. In some embodiments, the resist material used to form the resist layer **106** includes photosensitive polymers, photo-acid generators (PAG), quenchers, and a solvent. The photosensitive polymers may release electrons as being exposed to a radiation, and the electrons may induce the PAG to release acids to form an acidic environment. Next, acid labile functional groups at the photosensitive polymers may then be released in the acidic environment, and the acid labile functional group of the photosensitive polymer may be transformed into acid groups (e.g. deprotected). Accordingly, the photosensitive polymers may be insoluble in a developer used in a developing process before performing an exposure process but become soluble in the developer after performing an exposure process.

After the resist layer **106** is formed, an exposure process **108** is performed on the resist layer **106** to form a patterned resist layer **106'**, as shown in FIG. **1**B in accordance with some embodiments. More specifically, a mask structure **110** having an opening **112** is positioned over the resist layer **106** during the exposure process **108** to form an exposed portion **114** and unexposed portions **116**. In some embodiments, the exposed portion **114** is located between the unexposed portions **116**.

In some embodiments, the exposure process **108** includes exposing the exposed portion **114** to a radiation. In some embodiment, the radiation has a wavelength smaller than 250 nm. In some embodiments, the radiation includes KrF, ArF, EUV, or E-beam. More specifically, the photosensitive polymers in the exposed portion **114** of the patterned resist layer **106'** will release electrons as being exposed to the radiation during the exposure process, and the electrons will induce the PAG to release acids, resulting in an acidic environment. Accordingly, acid labile functional groups at the photosensitive polymers will be released in the acidic environment, and therefore the photosensitive polymers will become soluble in the developer used afterwards. After the exposure process **108** is performed, the mask structure **110** is removed.

In some embodiments, the patterned resist layer **106'** is baked (e.g. heated) after the exposure process **108** is performed. In some embodiments, the amount of acid groups (e.g. —COOH group) in the exposed portion **114** of the patterned resist layer **106'** increases after the patterned resist layer **106'** is baked, so that the exposed portion **114** become more soluble than before it is baked.

Next, a first developing process is performed on the patterned resist layer **106'** to remove the exposed portions **114**, such that an opening **118** is formed between the unexposed portions **116**, as shown in FIG. **1**C in accordance with some embodiments. More specifically, the exposed portions **116** of the patterned resist layer **106"** are dissolved in a first developer used in the first developing process and are removed with the first developer. As described previously, the acid groups of the exposed portion **114** of the patterned resist layer **106'** are de-protected in the acidic environment and therefore the exposed portion **114** become soluble in the first developer used in the first developing process. On the other hand, the unexposed portions **116** are not exposed to a radiation during the exposure process **108**, and the unexposed portions **116** of the patterned resist layer **106'** remains insoluble in the first developer during the first developing process. In some embodiments, the first developer includes tetramethylammonium hydroxide (TMAH).

After the first developing process is performed, a post treatment coating material **120** is formed in the opening **118** and over the unexposed portions **116**, as shown in FIG. **1**D in accordance with some embodiments. In addition, the opening **118** is fully filled with the post treatment coating material **120** in accordance with some embodiments. The post treatment coating material **120** may be a precursor for releasing acids, so that the acids produced by the post treatment coating material **120** may react with the peripheral portion of the unexposed portions **116**. In some embodiments, the post treatment coating material **120** includes photo-acid generator (PAG) and thermal acid generator (TAG). Details of the post treatment coating material **120** will be described afterwards.

After the post treatment coating material **120** is formed, a post treatment process **122** is performed onto the post treatment coating material **120**, as shown in FIG. **1**E in accordance with some embodiments. The post treatment process **122** is configured to induce the formation of acids in the post treatment coating material **120**, so that the acids may react with the peripheral portion **124** of the unexposed portions **116**. In some embodiments, the acids released during the post treatment process **122** has a pKa value less than about 3. In addition, the post treatment process **122** may be configured to control the diffusion distance of the post treatment coating material **120**, so that the size of the resulting unexposed portions may be formed as designed (Details will be described later.)

In some embodiments, the post treatment process **122** is a thermal baking process. As described above, the post treatment coating material **120** may include thermal acid generators which tend to release acids when the post treatment coating material **120** is heated. Accordingly, the post treatment process **122** may be a thermal baking process, so that the thermal acid generators may be decomposed during the post treatment process **122** to release acids in the post treatment coating material **120**.

In some embodiments, the post treatment process **122** includes heating the post treatment coating material **120** under a temperature in a range of about 60° C. to about 200° C. In some embodiments, the post treatment coating material **120** is heated for about 5 sec to about 300 sec. The temperature and the time for performing the post treatment process **122** is controlled to be high/long enough to trigger the reaction between the post treatment coating material **120** and the unexposed portion **116**. On the other hand, the temperature and the time for performing the post treatment process **122** should not be too high/long, or intermixing/diffusion between the post treatment coating material **120** and the unexposed portions may become too much.

In some embodiments, the post treatment process **122** is a radiation curing process. In some embodiments, the radiation curing process includes exposing the post treatment coating material **120** to a radiation. In some embodiment, the radiation has a wavelength smaller than 365 nm. In some embodiments, the radiation includes i-line, KrF, ArF, EUV, or E-beam.

As described above, the post treatment coating material **120** may include photo-acid generators which tend to release acids when the post treatment coating material **120** reacts with radiation. Accordingly, the post treatment process **122** may be a radiation curing process, so that the photo-acid generators may be decomposed during the post treatment process **122** to release acids in the post treatment coating material **120**.

In some embodiments, the post treatment coating material **120** may diffuse from the top surface and the sidewalls of the unexposed portions **116** toward the center of the exposed portions **116**, and the post treatment coating material **120** will release acids, so that the acids will react with the unexposed portions **116** of the patterned resist layer **106** during the post treatment process **122**. For example, the acids may react with the peripheral portion **124** of the unexposed portion **116** of the patterned resist layer **106"**.

In some embodiments, the peripheral portion **124** of the unexposed portion **116** of the patterned resist layer **106"** has a thickness in a range from about 1 nm to about 50 nm. The peripheral portion **124** of the unexposed portion **116** of the patterned resist layer **106"** may be defined as the portion of the unexposed portion **116** reacting with the acids released from the post treatment coating material **120**.

After the post treatment process **122** is performed, a second developing process is performed to remove the post treatment coating material **120**, as shown in FIG. **1**F in accordance with some embodiments. In addition, the peripheral portions **124** of the unexposed portions **116** are also removed by the second developing process in accordance with some embodiments.

More specifically, a second developer is used in the second developing process, and both the post treatment coating material and the peripheral portions **124** of the unexposed portions **116** are dissolved in the second developer in accordance with some embodiments. In some embodiments, the second developer used in the second developing process is the same as the first developer used in the first developing process described above. In some embodiments, the second developer includes tetramethylammonium hydroxide (TMAH). In some embodiments, the second developer includes 2.38% of TMAH or less than 2.38% of TMAH solution.

Since the peripheral portions **124** of the unexposed portions **116** are removed by the second developing process, the size of the unexposed portion **116'** of the patterned resist layer **106'''** shown in FIG. **1**F is smaller than the size of the unexposed portion **116** of the patterned resist layer **106"** shown in FIG. **1**E in accordance with some embodiments. That is, the distance D_2 between the unexposed portions **116'** shown in FIG. **1**F is greater than the distance D_1 between the unexposed portion **116** shown in FIG. **1**E.

In some embodiments, the width W_1 of the unexposed portion **116** of the patterned resist layer **106"** shown in FIG. **1**E is greater than the width W_2 of the unexposed portion **116'** of the patterned resist layer **106'''** shown in FIG. **1**F. In some embodiments, the difference between the width W_1 and the width W_2 is in a range from about 1 nm to about 50 nm. Since the width W_1 of the unexposed portion **116** can be reduced by performing the post treatment process, the energy used in the exposure process **108** may be reduced (Details will be described later.)

In some embodiments, the height H_1 of the unexposed portion **116** of the patterned resist layer **106"** shown in FIG. **1**E is greater than the height H_2 of the unexposed portion **116'** of the patterned resist layer **106'''** shown in FIG. **1**F. In some embodiments, the difference between the height H_1 and the height H_2 is in a range from about 1 nm to about 50 nm. Since the height H_2 of the unexposed portion **116** can be reduced by performing the post treatment process, the aspect ratio of the unexposed portion **116** may also be reduced. Therefore, risks of bending or cracking of the resist layer due to the high aspect ratio (or large height) may also be reduced.

Next, an etching process **124** is performed to etch the material layer **104** using the unexposed portions **116'** as masks, as shown in FIG. **1**G in accordance with some embodiments. In some embodiments, the etching process **124** is a dry etching process, such as a plasma etching process. After the etching process **124** is performed, the material layer **104** is patterned to form patterns **126** of the patterned material layer **104'**. In addition, an opening **128** is formed between the patterns **126** of the patterned material layer **104'**, as shown in FIG. **1**G in accordance with some embodiments.

After the etching process **124** is performed, the unexposed portions **116'** of the patterned resist layer **106'''** are removed, as shown in FIG. **1**H in accordance with some embodiments. The patterns **126** may have a width substantially equal to the width W_2 of the unexposed portion **116'** shown in FIG. **1**E. In addition, the distance between the patterns **126** in the patterned material layer **104'** may be substantially equal to the distance D_2 between the unexposed portions **116'** shown in FIG. **1**E.

As described previously, the method for manufacturing the semiconductor structure **100** includes performing a lithography process using the post treatment coating material **120** and performing the post treatment process **122** in accordance with some embodiments. More specifically, the post treatment coating material **120** is formed over the patterned resist layer **106'** and the post treatment process **122** is performed afterwards. In addition, the post treatment coating material **120** is configured to be a precursor for releasing acids, so that the acids produced by the post

treatment coating material **120** may react with the peripheral portions **124** of the unexposed portions **116**.

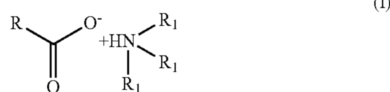
In some embodiments, the post treatment coating material **120** includes a polymer, a photo-acid generator (PAG) and/or a thermal acid generator (TAG), and a solvent. The solvent may be chosen so that it will not intermix with the resist layer **106**. That is, the resist layer **106** should be insoluble to the solvent of the post treatment coating material **120**. In some embodiments, the solvent is alcohol, ether, ester, or the like. In some embodiments, the solvent is H_2O, methanol, ethanol, propanol, butanol, isopropyl alcohol (IPA), ethylene glycol, methyl isobutyl carbinol (MIBC), diisopentyl ether (DIAE), dimethyl ether, diethyl ether, dipropyl ether, dibutyl ether, normal butyl acetate (NBA), or combinations thereof.

The polymer in the post treatment coating material **120** may include PAG and/or TAGs bonding thereto or may be blended with PAG and/or TAGs. FIG. **2**A illustrates a polymer **20**A in the post treatment coating material **120** that has PAG/TAGs bonding to the polymer in accordance with some embodiments.

As shown in FIG. **2**A, the polymer **20**A has a main chain and at least two functional groups bonding to the main chain. The first functional group A is configured to adjust the solubility of the polymer **20**A and the second functional group is configured to release acids in the post treatment coating material **120**.

In particular, the polymer is designed to be soluble in the solvent but the resist layer **106** should be in-soluble to the solvent. In some embodiments, the first functional group A is a moiety of a monomer A with acidity. In some embodiments, the pKa value of the monomer A is less than 4.5. In some embodiments, the first functional group A is a moiety of mathacrylic acid (MAA), methyl methacrylate (MMA), vinyl alcohol, hydroxystyrene (HS), 4-styrenesulfonic acid, fluoro-alcohol substituted alkane, or a fluorine substituted alkane. In some embodiments, the first functional group A is a fluoro-alcohol substituted alkyl group or a fluorine substituted alkyl group. In some embodiments, the first functional group A is a fluorine-substituted C_1-C_{10} alkyl group.

In some embodiments, the second functional group is a moiety of PAG or TAG. For example, the PAG/TAG may be bonded to the main chain of the polymer **20**A through a covalent bond. In some embodiments, the second functional group is a moiety of the following formula (I):

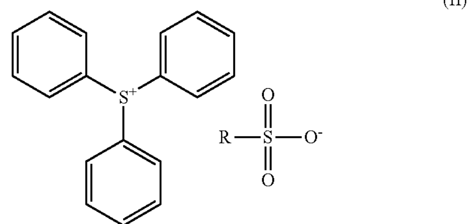


(I)

In some embodiments, R in formula (I) is C_1-C_{10} alkyl, C_3-C_{10} alkenyl, C_3-C_{10} alkynyl, or C_1-C_{10} alkoxy, and R_1 in formula (I) is hydrogen, C_1-C_{10} alkyl, C_3-C_{10} alkenyl, C_3-C_{10} alkynyl, or C_1-C_{10} alkoxy. In some embodiments, R in formula (I) is a fluorine-substituted alkyl group, such as a fluorine-substituted C_1-C_{10} alkyl group. In some embodiments, the molecular weight of R in formula (I) is greater than 15. In some embodiments, the molecular weight of R in formula (I) is in a range from about 15 to about 500. The molecular weight of the R group should be great enough to limit the diffusion of the polymer. In some embodiments, a carbon in the R group of the compound shown in formula (I) is bonded to the main chain of the polymer **20**A through a covalent bond.

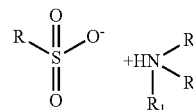
In some embodiments, the second functional group is a moiety of the following formula (II):

(II)



In some embodiments, R in formula (II) is C_1-C_{10} alkyl, C_3-C_{10} alkenyl, C_3-C_{10} alkynyl, or C_1-C_{10} alkoxy. In some embodiments, R in formula (II) is a fluorine-substituted alkyl group, such as a fluorine-substituted C_1-C_{10} alkyl group. In some embodiments, the molecular weight of R in formula (II) is greater than 15. In some embodiments, the molecular weight of R in formula (II) is in a range from about 15 to about 500. The molecular weight of the R group should be great enough to limit the diffusion distance of the polymer. In some embodiments, a carbon in the R group of the compound shown in formula (II) is bonded to the main chain of the polymer **20**A through a covalent bond.

In some embodiments, the second functional group is a moiety of the following formula (III):



In some embodiments, R in formula (III) is C_1-C_{10} alkyl, C_3-C_{10} alkenyl, C_3-C_{10} alkynyl, or C_1-C_{10} alkoxy. In some embodiments, R in formula (III) is a fluorine-substituted alkyl group, such as a fluorine-substituted C_1-C_{10} alkyl group. R_1 in formula (III) is hydrogen, C_1-C_{10} alkyl, C_3-C_{10} alkenyl, C_3-C_{10} alkynyl, or C_1-C_{10} alkoxy. In some embodiments, the molecular weight of R in formula (III) is greater than 15. In some embodiments, the molecular weight of R in formula (III) is in a range from about 15 to about 500. The molecular weight of the R group should be great enough to limit the diffusion of the polymer. In some embodiments, a carbon in the R group of the compound shown in formula (III) is bonded to the main chain of the polymer **20**A through a covalent bond.

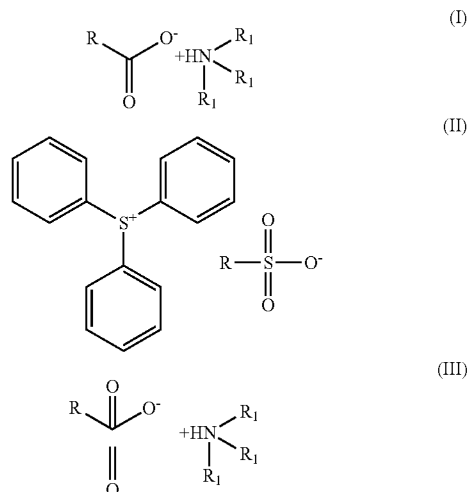
In some embodiments, the polymer **20**A has a weight average molecular weight in a range from about 2000 to about 500000. As described above, the size (i.e. molecular weight) of the polymer **20**A may be controlled so that the diffusion distance of post treatment coating material **120** may be easier to control.

In some embodiments, the mole ratio of the first functional group to the second functional group is in a range from about 1 to about 100. As described above, the first functional group may be seen as a solubility controller, and the second functional group may be seen as an acid generator. More specifically, the first functional group A is configured to adjust the solubility of the polymer **20**A and the second functional group is configured to release acids in the post treatment coating material **120**. Therefore, the ratio of the first functional group to the second functional group may

be controlled so that a proper amount of the acids can be released from the polymer A and the polymer A can be soluble in the solvent in the post treatment coating material.

In some other embodiments, the polymer in the post treatment coating material **120** is blended with PAG and/or TAG. FIG. **2**B illustrates a polymer **20**B and PAG/TAGs mixing in the post treatment coating material **120** in accordance with some embodiments. As shown in FIG. **2**B, the polymer **20**B has a main chain and the first functional group A bonding to the main chain. The first functional group A is configured to adjust the solubility of the polymer **20**A. Examples of the first functional group A shown in FIG. **2**B may be similar to, or the same as, those of the first functional group A shown in FIG. **2**A and described above and are not repeated herein.

As shown in FIG. **2**B, PAG/TAG is not chemically bonded to the polymer **20**B but is mixed with the polymer **20**B in accordance with some embodiments. In some embodiments, the PAG/TAG has the following formula (I), (II), or (III):



In some embodiments, R in formula (I), (II), and (III) are independently selected from C_1-C_{10} alkyl, C_3-C_{10} alkenyl, C_3-C_{10} alkynyl, and C_1-C_{10} alkoxy. In some embodiments, R in formula (II) is a fluorine-substituted alkyl group, such as a fluorine-substituted C_1-C_{10} alkyl group. R_1 in formula (I) and (III) are independently selected from hydrogen, C_1-C_{10} alkyl, C_3-C_{10} alkenyl, C_3-C_{10} alkynyl, and C_1-C_{10} alkoxy. In some embodiments, the molecular weight of R in formula (I), (II), and (III) is greater than 15. In some embodiments, the molecular weight of R in formula (I), (II), and (III) is in a range from about 15 to about 500. In some embodiments, the PAG has a molecular weight in a range from about 300 to about 1000. In some embodiments, the TAG has a molecular weight in a range from about 60 to about 600. Similar to the PAG/TAG shown in FIG. **2**A and described above, the PAG/TAG in the mixture of the polymer **20**B and PAG/TAG is configured to release acids in the post treatment coating material **120**.

In some embodiments, the amount of TAG/PAG is greater than 0.1 wt %. In some embodiments, the amount of TAG/PAG is in a range from about 1 wt % to about 30 wt %. In some embodiments, the amount of TAG/PAG is in a range from about 1 wt % to about 70 wt %.

As described above, the post treatment coating material **120** covers the top surfaces and the sidewalls of the unexposed portions **116** (e.g. FIG. **1**D). After the post treatment coating material **120** is formed, the post treatment process **122** is performed (e.g. FIG. **1**E) to produced acids in the post treatment coating material **120**.

In some embodiments, the post treatment coating material **120** includes PAG, and therefore a radiation curing process is performed as the post treatment process **122**, so that acids are formed in the post treatment coating material **120** in accordance with some embodiments. In some other embodiments, the post treatment coating material **120** includes TAG, and therefore a thermal baking process is performed as the post treatment process **122**, so that acids are formed in the post treatment coating material **120**.

As described previously, the resist layer **106** may be made of photosensitive polymers and the photosensitive polymers may include acid labile functional groups. Therefore, when the acids are formed in the post treatment coating material **120** during the post treatment process **122**, the acids will react with the unexposed portions **116** of the patterned resist layer **106"**, such that the acid labile functional groups in the unexposed portions **116** of the patterned resist layer **106"** will be released in the acidic environment and will be transformed into acid groups (e.g. —COOH). That is, the portions of the unexposed portions **116** of the patterned resist layer **106"** reacting with the acids released by the post treatment coating material **120** may become soluble in a developer (e.g. the second developer) while the portions of the unexposed portions **116** not react with the acids remain insoluble to the developer.

In some embodiments, the post treatment coating material **120** diffuses into the peripheral portions **124** of the unexposed portions **116**, so that the peripheral portions **124** of the unexposed portions **116** can react with the acids released in the post treatment material **120** and be dissolved in the second developer. Therefore, the peripheral portions **124** of the unexposed portions **116** can be removed during the second developing process.

Accordingly, the distance D_2 between the unexposed portions **116'** shown in FIG. **1**F is greater than the distance D_1 between the unexposed portions **116** that is formed by the exposure process **108** and the first developing process shown in FIG. **1**C. Therefore, although the final opening **128** between the patterns **126** of the patterned material layer **104'** has the distance D_2, the energy (e.g. radiation) used in the manufacturing process only need to expose the exposed portion **114** shown in FIG. **1**B that has the distance D_1, which is shorter than D_2. That is, the energy required to form the patterns **126** may be reduced.

It should be noted that although the exposed portions **116'** of the patterned resist layer **106'''** are used as masks in the etching process **124** for patterning the material layer **104**, the exposed portions **116'** of the patterned resist layer **106'''** may be used for different purposes in other embodiments. For example, the exposed portions **116'** of the patterned resist layer **106'''** may be used as masks in an implantation process to implant dopants in the portions of material layer not covered by the exposed portions **116'**.

FIGS. **3**A to **3**C show cross-sectional representations of various stages of performing a lithography process in accordance with some embodiments. The lithography process shown in FIGS. **3**A to **3**C may be similar to the lithography process shown in FIGS. **1**A to **1**H, except some portions of the exposed portions of the resist layer remain on the material layer **104** after the first developing process is performed. Some materials and processes of the lithography

process shown in FIGS. **3**A to **3**C may be similar to, or the same as, those shown in FIGS. **1**A to **1**H and are not repeated herein.

In particular, an exposure process similar to those shown in FIGS. **1**A and **1**B may be performed, and a first developing process may be performed to remove the exposed portions of the patterned resist layer **106***a*", as shown in FIG. **3**A in accordance with some embodiments. However, unlike those shown in FIG. **1**C, the exposed portions of the patterned resist layer **106***a*" are only partially removed by the first developing process. As shown in FIG. **3**A, remaining portions **306** of the exposed portions of the patterned resist layer **106***a*" remain at the bottom portion of the sidewalls of the unexposed portions **116***a* in accordance with some embodiments. In some embodiments, the remaining portions **306** of the exposed portions of the patterned resist layer **106***a*" also cover a portion of the material layer **104** over the substrate **102**.

After the first developing process is performed to at least partially remove the exposed portions, a post treatment coating material **120***a* is formed to cover the patterned resist layer **106***a*", as shown in FIG. **3**B in accordance with some embodiments. In some embodiments, the post treatment coating material **120***a* is directly formed on the top surface and the sidewalls of the unexposed portions **116***a* and on the remaining portions **306** of the exposed portions of the patterned resist layer **106***a*". The materials for forming the post treatment coating material **120***a* may be similar to, or the same as, the materials for forming the post treatment coating material **120** described previously and are not repeated herein.

After the post treatment coating material **120***a* is formed, a post treatment process is performed first and a second developing process is performed afterwards to remove the post treatment coating material **120***a*, as shown in FIG. **3**C in accordance with some embodiments. In addition, the remaining portions **306** of the exposed portions are also removed in the second developing process. The post treatment process and the second developing process may be similar to, or the same as, the post treatment process **122** and the second developing process shown in FIGS. **1**A to **1**H described previously.

More specifically, the post treatment coating material **120** releases acids during the post treatment process, so that the remaining portions **306** of the exposed portions of the patterned resist layer **106***a*" react with the acids and become soluble in the second developer used in the second developing process in accordance with some embodiments. In addition, the periphery portion of the unexposed portions **116***a* may also react with the acids and become soluble in the second developer used in the second developing process. That is, both the remaining portions **306** of the exposed portions and the periphery portion of the unexposed portions **116***a* are dissolved in the second developer in the second developing process in accordance with some embodiments.

Accordingly, the size of the resulting unexposed portions **116***a*' of the patterned resist layer **106***a*''' shown in FIG. **3**C is smaller than the size of the unexposed portion **116***a* shown in FIG. **3**A in accordance with some embodiments. The differences of their heights and widths between the unexposed portions **116***a*' and the unexposed portion **116***a* may be similar to, or the same as, those between the unexposed portions **116**' shown in FIG. **1**F and the unexposed portion **116** shown in FIG. **1**E described previously and are not repeated herein.

As described previously, the patterned resist layer **106***a*''' may be used as masks for patterning the material layer **104** therebelow. Therefore, if the remaining portions **306** of the exposed portions are not removed, the resolution of the resulting pattern of the material layer **104** may be reduced. Accordingly, by applying the post treatment coating material **120***a* and the post treatment process, the resolution of the lithography process may be improved.

FIGS. **4**A to **4**C show cross-sectional representations of various stages of performing a lithography process in accordance with some embodiments. The lithography process shown in FIGS. **4**A to **4**C may be similar to the lithography process shown in FIGS. **3**A to **3**C, except the remaining portions of the exposed portions of patterned the resist layer is located at the upper portion of the unexposed portions. Some materials and processes of the lithography process shown in FIGS. **4**A to **4**C may be similar to, or the same as, those shown in FIGS. **1**A to **1**H and **3**A to **3**C and are not repeated herein.

In particular, an exposure process similar to those shown in FIGS. **1**A and **1**B may be performed, and a first developing process may be performed to partially remove the exposed portions of the patterned resist layer **106***a*", such that remaining portions **406** of the exposed portions of the patterned resist layer **106***b*" remain at the upper portion of the sidewalls of the unexposed portions **116***b*, as shown in FIG. **4**A in accordance with some embodiments.

Afterwards, a post treatment coating material **120***b* is formed to cover the patterned resist layer **106***b*", as shown in FIG. **4**B in accordance with some embodiments. The materials for forming the post treatment coating material **120***b* may be similar to, or the same as, the materials for forming the post treatment coating material **120** described previously and are not repeated herein.

After the post treatment coating material **120***b* is formed, a post treatment process is performed first and a second developing process is performed afterwards to remove the post treatment coating material **120***b*, as shown in FIG. **4**C in accordance with some embodiments. In addition, both the remaining portions **406** of the exposed portions and the periphery portion of the unexposed portions **116***b* are dissolved in the second developer in the second developing process in accordance with some embodiments. The resulting unexposed portion **116***b* of the patterned resist layer **106***b*''' shown in FIG. **4**C may be similar to, or the same as, the unexposed portion **116***a* shown in FIG. **3**C and therefore details of its structure are not repeated herein.

In some other embodiments, the remaining portions **406** of the exposed portions may form bridges between the unexposed portions, and these bridges may also be removed by applying the post treatment coating material **120***b* and the post treatment process. Accordingly, the resolution of the lithography process may be improved.

FIGS. **5**A to **5**C show cross-sectional representations of various stages of performing a lithography process in accordance with some embodiments. The lithography process shown in FIGS. **5**A to **5**C may be similar to the lithography process shown in FIGS. **1**A to **1**F, except a polymer layer is formed over the material layer after the first developing process is performed. Some materials and processes of the lithography process shown in FIGS. **5**A to **5**C may be similar to, or the same as, those shown in FIGS. **1**A to **1**H and are not repeated herein.

In particular, an exposure process similar to those shown in FIGS. **1**A and **1**B is performed, and a first developing process is performed to remove the exposed portions of the patterned resist layer **106***c*", as shown in FIG. **5**A in accordance with some embodiments. In addition, a polymer layer **506** is formed over the top surface of the material layer **104**

during the first developing process in accordance with some embodiments. The formation of the polymer layer **506** may result from the interfacial adhesion between the material layer **104** and particles/compounds over the material layer **104** during the first developing process. In some embodiments, the polymer layer **506** includes the residues of the exposed portion of the patterned resist layer **106***c*" and the first developer used in the first developing process.

Afterwards, a post treatment coating material **120***c* is formed to cover the patterned resist layer **106***c*", as shown in FIG. **5**B in accordance with some embodiments. In some embodiments, the post treatment coating material **120***c* is directly formed on the top surface and the sidewalls of the unexposed portions **116***c* and on the polymer layer **506**. The materials for forming the post treatment coating material **120***c* may be similar to, or the same as, the materials for forming the post treatment coating material **120** described previously and are not repeated herein.

After the post treatment coating material **120***c* is formed, a post treatment process is performed first and a second developing process is performed afterwards to remove the post treatment coating material **120***c* and the polymer layer **506**, as shown in FIG. **5**C in accordance with some embodiments. In some embodiments, the polymer layer **506** and the top portion of the unexposed portions **116***c* are both dissolved in the second developer in the second developing process. The resulting unexposed portion **116***c* of the patterned resist layer **106***c*"' shown in FIG. **5**C may be similar to, or the same as, the unexposed portion **116** shown in FIG. **1**F and therefore details of its structure are not repeated herein.

As described previously, the size of the unexposed portions of the patterned resist layers (e.g. the unexposed portions **116**, **116***a*, **116***b*, and **116***c*) before the post treatment process is performed is greater than the size of the unexposed portions of the patterned resist layers (e.g. the unexposed portions **116**', **116***a*', **116***b*', and **116***c*') after the post treatment process is performed. In addition, the line/space profile of the patterned resist layer may be trimmed to have improved line width roughness/line edge roughness. FIGS. **6**A and **6**B illustrate the top views of unexposed portions of a patterned resist layer before and after the post treatment process is performed in accordance with some embodiments.

More specifically, FIG. **6**A illustrates the top view of the unexposed portions **116***d* of the patterned resist layers before the post treatment process is performed, and FIG. **6**B illustrates the top view of the unexposed portions **116***d*' of the patterned resist layers after the post treatment process is performed in accordance with some embodiments. When unexposed portion **116***d* reacts with acids during the post treatment process (e.g. the post treatment process **122**), the polymer of the unexposed portion **116***d* may be redistributed and therefore the profile of the unexposed portion **116***d* may be smoothened. Accordingly, the resulting unexposed portions **116***d*' may have an improved line width roughness/line edge roughness.

The unexposed portions **116***d* shown in FIG. **6**A may be similar to the unexposed portions **116**, **116***a*, **116***b*, and **116***c* and the unexposed portions **116***d*' shown in FIG. **6**B may be similar to the unexposed portions **116**', **116***a*', **116***b*', and **116***c*' described previously, and therefore details of these structures are not repeated herein.

Generally, lithography processes, including an exposure process and a developing process, are commonly used in semiconductor manufacturing processes. However, when the lithography processes is performed on a relatively large area, the uniformity of the resulting pattern may become difficult to control. For example, there may be "on-focus" regions and "de-focus" regions when a resist layer is exposed in the exposure process, and the resolution at the "de-focus" regions may be worse than the "on-focus" regions. Accordingly, in some embodiments of the disclosure, the post treatment coating material (e.g. post treatment coating material **120**, **120***a*, **120***b*, **120***c*, and **120***d*) and the post treatment process are applied in the lithography processes, so that residues at the exposed portions (e.g. the remaining portions **306**/**406** and/or the polymer layer **506**) of the resist layer may be removed. Therefore, the resolution of the resulting pattern may be improved, and the uniformity of the lithography process may also be improved.

Furthermore, the energy required for the lithography process may be reduced by performing the post treatment process described above. More specifically, the peripheral portion (e.g. the peripheral portion **124**) of the unexposed portions may react with the post treatment coating material and may be removed by performing the second developing process. Therefore, the size of the unexposed portions (e.g. the unexposed portions **116**', **116***a*', **116***b*', **116***c*', and **116***d*') of the resist layer after the second developing process is performed is smaller than the size of the unexposed portions (e.g. the unexposed portions **116**, **116***a*, **116***b*, **116***c*, and **116***d*) of the resist layer before the second developing process is performed. Since the peripheral portion of the unexposed portions may not need to be exposed in the exposure process, the energy required for the lithography process may be reduced and the cost for performing the lithography process may also be reduced.

Embodiments of methods for performing a lithography process are provided. The method may include performing an exposure process and a developing process on a resist layer to form an opening between the unexposed portions of the resist layer. Next, a post treatment coating material may be formed to cover the unexposed portions of the resist layer and a post treatment process may be performed on the post treatment coating material, so that a peripheral portion of the unexposed portions of the resist layer may be removed. Therefore, the energy required for the lithography process may be reduced and the uniformity of the lithography process may be improved.

In some embodiments, a method for performing a lithography process is provided. The method for performing a lithography process includes forming a resist layer over a substrate and exposing a portion of the resist layer to form an exposed portion between unexposed portions. The method for performing a lithography process further includes developing the resist layer to remove the exposed portion of the resist layer such that an opening is formed between the unexposed portions and forming a post treatment coating material in the opening and over the unexposed portions of the resist layer. The method for performing a lithography process further includes reacting a portion of the unexposed portions of the resist layer with the post treatment coating material by performing a post treatment process and removing the post treatment coating material.

In some embodiments, a method for performing a lithography process is provided. The method for performing a lithography process includes forming a resist layer over a material layer and exposing an exposed portion of the resist layer by performing an exposure process. The method for performing a lithography process further includes dissolving a first portion of the exposed portion of the resist layer in a first developer to form an opening in the resist layer, while a second portion of the exposed portion remains on the

material layer. The method for performing a lithography process further includes forming a post treatment coating material in the opening and over the second portion of the exposed portion of the resist layer and reacting the post treatment coating material with the second portion of the exposed portion of the resist layer. The method for performing a lithography process further includes removing the post treatment coating material and the second portion of the exposed portion of the resist layer.

In some embodiments, a method for performing a lithography process is provided. The method for performing a lithography process includes forming a resist layer over a substrate and exposing a portion of the resist layer to a radiation to form an exposed portion between unexposed portions of the resist layer. The method for performing a lithography process further includes dissolving the exposed portion of the resist layer in a first developer to form an opening between the unexposed portions of the resist layer and forming a post treatment coating material in the opening and over the unexposed portions of the resist layer. The method for performing a lithography process further includes performing a post treatment process on the post treatment coating material to release acids in the post treatment coating material and removing the post treatment coating material and a peripheral portion of the unexposed portions.

The foregoing outlines features of several embodiments 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 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 for performing a lithography process, comprising:

forming a resist layer over a substrate;

exposing a portion of the resist layer to form an exposed portion and an unexposed portion;

dissolving a bottom portion of the exposed portion while an upper portion of the exposed portion covers an upper sidewall of the unexposed portion;

forming a post treatment coating material covering the upper portion of the exposed portion and the unexposed portion of the resist layer, wherein a portion of the post treatment coating layer extends under the upper portion of the exposed portion;

reacting a portion of the unexposed portion of the resist layer with the post treatment coating material by performing a post treatment process; and

removing the post treatment coating material.

2. The method for performing a lithography process as claimed in claim **1**, wherein the portion of the unexposed portion of the resist layer reacting with the post treatment coating material are removed with the post treatment coating material.

3. The method for performing a lithography process as claimed in claim **2**, wherein the upper portion of the exposed portion is removed with the post treatment coating material and the portion of the unexposed portion of the resist layer reacted with the post treatment coating material.

4. The method for performing a lithography process as claimed in claim **1**, wherein the post treatment coating material comprises a photo-acid generator, a thermal acid generator, or a combination thereof.

5. The method for performing a lithography process as claimed in claim **4**, wherein the photo-acid generator has a molecular weight in a range from about 300 to about 1000, and the thermal acid generator has a molecular weight in a range from about 60 to about 600.

6. The method for performing a lithography process as claimed in claim **1**, wherein the post treatment coating material comprises a polymer that comprises a first functional group, and the first functional group is a moiety of methacrylic acid (MAA), methyl methacrylate (MMA), vinyl alcohol, hydroxystyrene (HS), 4-styrenesulfonic acid, fluoro-alcohol substituted alkane, or a fluorine substituted alkane.

7. The method for performing a lithography process as claimed in claim **6**, wherein the polymer further comprises a second functional group, and the second functional group is a moiety of a photo-acid generator or a thermal acid generator.

8. A method for performing a lithography process, comprising:

forming a resist layer over a material layer;

performing an exposure process to form an exposed portion and a first unexposed portion;

partially dissolving the exposed portion in a first developer to form a first remaining portion of the exposed portion at a corner between a sidewall of the first unexposed portion and a top surface of the material layer;

forming a post treatment coating material over the first unexposed portion, the first remaining portion of the exposed portion and the top surface of the material layer;

performing a post treatment process so that the first unexposed portion of the resist layer reacts with the post treatment coating material; and

removing the post treatment coating material and the first remaining portion of the exposed portion of the resist layer.

9. The method for performing a lithography process as claimed in claim **8**, further comprising:

forming a second unexposed portion during the exposure process,

wherein a second remaining portion of the exposed portion is formed at a corner between a sidewall of the second unexposed portion and the top surface of the material layer, and the first remaining portion is not in direct contact with the second remaining portion.

10. The method for performing a lithography process as claimed in claim **9**, a portion of the post treatment coating material is sandwiched between the first remaining portion and the second remaining portion.

11. The method for performing a lithography process as claimed in claim **10**, wherein the post treatment coating material and the first remaining portion of the exposed portion are removed by dissolving the post treatment coating material and the first remaining portion of the exposed portion in a second developer, and the second developer is different from the first developer.

12. The method for performing a lithography process as claimed in claim **10**, wherein the post treatment process is a radiation curing process or a thermal baking process.

13. The method for performing a lithography process as claimed in claim 10, wherein acids are released during the post treatment process, and a pKa value of the acids is less than 3.

14. The method for performing a lithography process as claimed in claim 10, wherein a radiation curing process is performed on the post treatment coating material to produce acids that reacts with the first remaining portion of the exposed portion of the resist layer.

15. A method for performing a lithography process, comprising:

forming a resist layer over a material layer;

exposing a portion of the resist layer to a radiation to form an exposed portion between unexposed portions of the resist layer;

dissolving the exposed portion of the resist layer to form an opening between the unexposed portions of the resist layer and to form a polymer layer between the unexposed portions of the resist layer;

forming a post treatment coating material in the opening, over the polymer layer, and over the unexposed portions of the resist layer;

reacting the post treatment coating material with a peripheral portion of the unexposed portions; and

removing the post treatment coating material and the peripheral portion of the unexposed portions.

16. The method for performing a lithography process as claimed in claim 15, further comprising:

removing the polymer layer with the post treatment coating material and the peripheral portion of the unexposed portions.

17. The method for performing a lithography process as claimed in claim 15, wherein intersections between the unexposed portions and a top surface of the material layer are covered by the polymer layer.

18. The method for performing a lithography process as claimed in claim 15, wherein the polymer layer is sandwiched between the top surface of the material layer and the post treatment coating material.

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