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(54) Title: DOUBLE-DEPROTECTED CHEMICALLY AMPLIFIED PHOTORESISTS

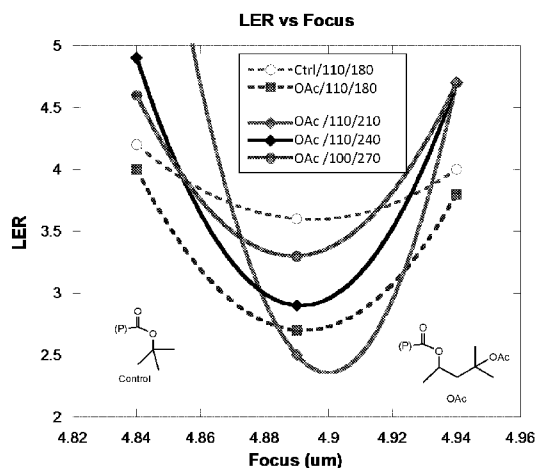
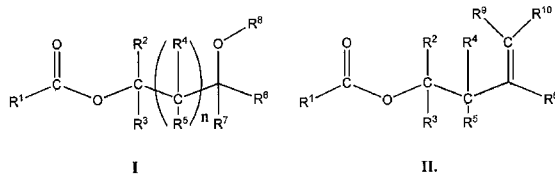


FIG. 3

(57) Abstract: There are disclosed compositions requiring two acid-catalyzed steps for deprotection. The compositions are of formula I or formula II. Also disclosed are polymers formed from these compositions, and methods of using these compositions in, for example, photolithography.





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DOUBLE-DEPROTECTED CHEMICALLY AMPLIFIED PHOTORESISTS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority benefit of U.S. Provisional Patent Application Serial No. 62/142,524, filed April 3, 2015, the disclosure of which is hereby incorporated by reference herein in its entirety.

BACKGROUND OF THE INVENTION

Technical Field

[0002] The present invention generally relates to compositions and methods for blocking polymer-bound carboxylic acids in photoresists and other relevant applications.

Background Information

[0003] A photoresist is a material used in photolithography that undergoes a chemical transformation when it is exposed to radiation, for instance, visible light, ultraviolet light, extreme ultraviolet light, electron beam, or ion beam. A typical photolithographic procedure begins by applying a layer of photoresist to the top of a substrate and then drying the photoresist material in place. A photomask is then placed between a radiation source and the layer of photoresist; the photomask will have a pattern printed on it such that some areas are opaque to the radiation and some are transparent. Those portions of the photoresist layer not covered by the opaque areas of the photomask are then exposed to radiation from the radiation source. In some cases, this exposure step is followed by a post-exposure bake (PEB), which precedes the development step, wherein the entire photoresist layer is chemically treated. The chemical changes to the exposed and unexposed areas of photoresist result in the removal of a portion of the photoresist on the substrate. Those areas of the top layer of the substrate which are uncovered as a result of the development step are etched away, and the remaining photoresist is removed to leave exposed substrate.

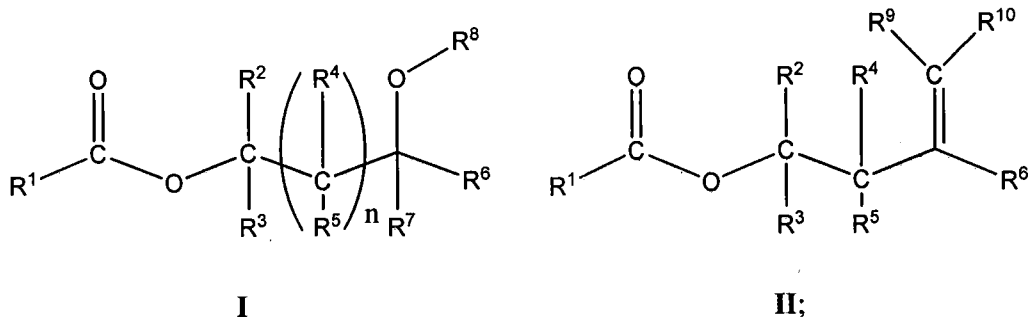
[0004] Circuits are being required to be physically smaller. One way to enable the formation of these smaller circuits includes the use of light of shorter wavelengths.

However, because a photoresist material should not absorb light too strongly at the wavelength used, different materials are needed for new photoresists. For example, phenolic materials are generally not suitable for use as photoresists for light of 193 nm, since phenolic materials tend to absorb 193 nm light. Similarly, materials which may be useful at 193 nm light may not be appropriate for other wavelength ranges.

[0005] Nearly all photoresists used by the microelectronics industry in recent years are positive-tone Chemically Amplified Photoresists (CAMP). This technology has been the driving force behind successes in deep UV (248 nm), Argon Fluoride laser (ArF, 193 nm), and EUV (13.5 nm) lithography. Exposure through a mask converts photoacid generators (PAGs) into catalytic acid in concentrations that are approximately proportional to the absorbed dose in each volume in space. As light passes through a mask of dense line patterns of opaque and transparent lines, the aerial image (light intensity over distance) is a sine wave. Since the amount of acid generated during exposure is approximately proportional to the absorbed dose, the concentration of acid in the film will also be in a sine-wave pattern. During a post-exposure bake (PEB), the acid catalyzes the transformation of an ester side group on a polymer to a carboxylic acid; since the conversion of the protected ester to the carboxylic acid is first-order in catalytic acid, the concentration of the carboxylic acid is also a sine wave pattern. The carboxylic acid increases the solubility of the resist film in 13.4 pH developer. Therefore, the greater the concentration of carboxylic acids, the greater the dissolution rate of the photoresist.

SUMMARY OF THE INVENTION

[0006] The present invention provides, in a first aspect, a compound of formula I or II:



wherein

R¹ is a (C₂₋₃) alkene;

R² is (C₁₋₂₀)hydrocarbon optionally substituted with halogen;

R³, R⁴, R⁵, and R⁷ are selected independently in each instance from the group consisting of hydrogen and (C₁₋₂₀)hydrocarbon, wherein said (C₁₋₂₀)hydrocarbon may in each instance be substituted independently with halogen, and wherein a –CH₂– in the (C₁₋₂₀)hydrocarbon may be replaced by –Si(CH₃)₂–, –N(C=O)–, –O–, or –S–;

R⁶ is selected from the group consisting of hydrogen; –OR⁶⁰; and (C₁₋₂₀)hydrocarbon optionally substituted with halogen;

R⁶⁰ is (C₁₋₂₀)hydrocarbon;

R⁸ is selected from the group consisting of hydrogen; (C₁₋₂₀)hydrocarbon optionally substituted with one or more substituents selected from halogen, dioxane, and dioxolane; –C(=O)R⁸⁰; –C(=O)C(=O)–O–R⁸⁰; –C(=O)OR⁸⁰; and –C(=O)NHR⁸⁰;

R⁸⁰ is (C₁₋₂₀)hydrocarbon optionally substituted with halogen;

R⁹ and R¹⁰ are selected independently in each instance from the group consisting of hydrogen, (C₁₋₆)alkyl, and phenyl;

n is selected from 0, 1, or 2;

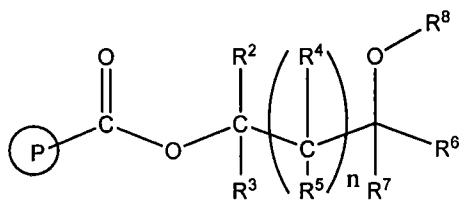
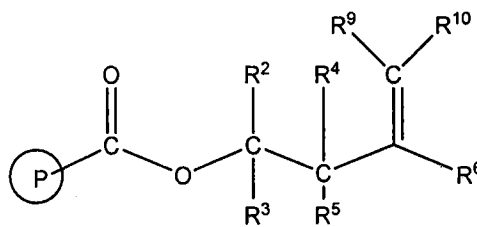
or, alternatively, a plurality of R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R⁶⁰, and R⁸⁰, together with the atoms to which they are attached, may form a monocyclic ring or a polycyclic ring system; and wherein a –CH₂– in the monocyclic ring or polycyclic ring system may be replaced by –Si(CH₃)₂–, –N(C=O)–, –O–, or –S–;

wherein:

when n is 0, at least one of R⁶ and R⁷ must be an aliphatic (C₂₋₂₀)hydrocarbon; and

when n is 2, the two R⁵ substituents, together with the carbons to which they are attached, form a cyclopropyl ring.

[0007] The present invention provides, in a second aspect, a polymer of formula Ip or Iip:

**Ip****Iip;**

wherein

P is a polymer chain;

R² is (C₁₋₂₀)hydrocarbon optionally substituted with halogen;

R³, R⁴, R⁵, and R⁷ are selected independently in each instance from the group consisting of hydrogen and (C₁₋₂₀)hydrocarbon, wherein said (C₁₋₂₀)hydrocarbon may in each instance be substituted independently with halogen, and wherein a –CH₂– in the (C₁₋₂₀)hydrocarbon may be replaced by –Si(CH₃)₂–, –N(C=O)–, –O–, or –S–;

R⁶ is selected from the group consisting of hydrogen; –OR⁶⁰; and (C₁₋₂₀)hydrocarbon optionally substituted with halogen;

R⁶⁰ is (C₁₋₂₀)hydrocarbon;

R⁸ is selected from the group consisting of hydrogen; (C₁₋₂₀)hydrocarbon optionally substituted with one or more substituents selected from halogen, dioxane, and dioxolane; –C(=O)R⁸⁰; –C(=O)C(=O)–O–R⁸⁰; –C(=O)OR⁸⁰; and –C(=O)NHR⁸⁰;

R⁸⁰ is (C₁₋₂₀)hydrocarbon optionally substituted with halogen;

R⁹ and R¹⁰ are selected independently in each instance from the group consisting of hydrogen, (C₁₋₆)alkyl, and phenyl;

n is selected from 0, 1, or 2;

or, alternatively, a plurality of R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R⁶⁰, and R⁸⁰, together with the atoms to which they are attached, may form a monocyclic ring or a polycyclic ring system; and wherein a –CH₂– in the monocyclic ring or polycyclic ring system may be replaced by –Si(CH₃)₂–, –N(C=O)–, –O–, or –S–;

wherein:

when n is 0, at least one of R⁶ and R⁷ must be an aliphatic (C₂₋₂₀)hydrocarbon; and

when n is 2, the two R⁵ substituents, together with the carbons to which they are attached, form a cyclopropyl ring.

[0008] The present invention provides, in a third aspect, a composition for photolithography comprising a polymer disclosed herein.

[0009] The present invention provides, in a fourth aspect, a photoresist composition comprising a polymer disclosed herein.

[0010] The present invention provides, in a fifth aspect, a photoresist substrate which is coated with a photoresist composition disclosed herein.

[0011] The present invention provides, in a sixth aspect, a method for preparing a substrate for photolithography, comprising coating the substrate with a photoresist composition disclosed herein.

[0012] The present invention provides, in a seventh aspect, a method for conducting photolithography on a substrate, comprising (a) providing a substrate, (b) coating the substrate with a photoresist composition disclosed herein, and (c) irradiating the coated substrate through a photomask.

[0013] These, and other objects, features and advantages of this invention will become apparent from the following detailed description of the various aspects of the invention taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 depicts the relative concentrations of carboxylic acid starting with a sine-wave under control conditions vs. the improved acid profile resulting from an embodiment of the invention.

[0015] FIG. 2 depicts the relationship between post-exposure bake and line edge roughness for embodiments of the invention.

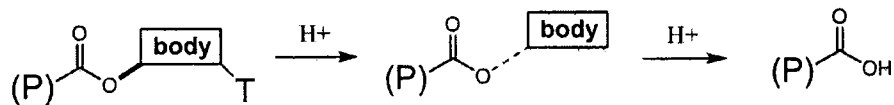
[0016] FIG. 3 illustrates a graph resulting from the plot of focus vs. line edge roughness (LER) utilizing embodiments of the invention.

[0017] FIG. 4 shows SEM results for an embodiment of the invention.

[0018] FIG. 5 depicts a graph resulting from the plot of focus vs. line edge roughness (LER) utilizing embodiments of the invention.

DETAILED DESCRIPTION OF THE INVENTION

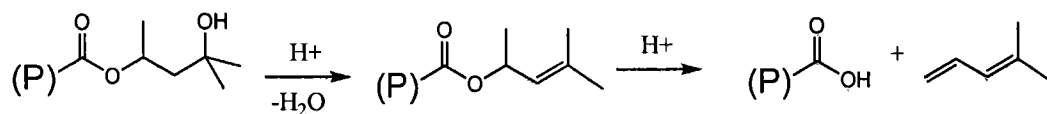
[0019] The current disclosure relates to a method for blocking polymer-bound carboxylic acids in 193nm and EUV resists, as well as those used in deep UV and e-beam lithography. Previous acid amplifiers utilize one acid-catalyzed step to deprotect the compound. This method, in contrast to previous methods, requires two acid-catalyzed steps for deprotection, as shown below ("P" represents a link to a polymer):



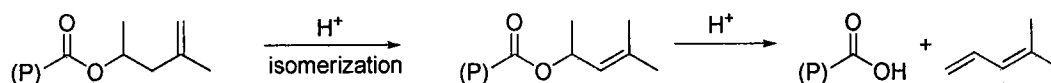
Since two reactions are needed for deprotection, this can be represented by "*Double Deprotected-Chemically AMplified Photoresist*" or "DD-CAMP". By design, if the second step is equivalent in speed, or is slightly slower than the first step, the kinetic rate law will be approximately second-order in acid. (Experimental results have shown the kinetic rate to be slightly less than second-order, at 1.84.) The resulting concentration of carboxylic acid that will be generated after the post-exposure bake should form a pattern that is proportional to approximately the *square* of the absorbed dose, as shown in FIG. 1. FIG. 1 shows the relative concentrations of carboxylic acid starting with a sine-wave under control conditions vs. the improved acid profile resulting from DD-CAMP. The shape of the carboxylic acid concentration shown in FIG. 1 in the DD-CAMP curve is dramatically better than the conventional profile, for a number of reasons. The slope at the mask edge is steeper in the DD-CAMP curve than in the control curve, resulting in lines with better line edge roughness (LER). The width at half-maximum is 39% narrower in the DD-CAMP curve than in the control, which translates to 39% better resolution. Finally, the unexposed regions of the DD-CAMP curve are very flat, causing smoother, flatter tops of the resist lines. All of these characteristics are desirable for photoresists.

[0020] The reaction below shows one example of a DD-CAMP blocking group that could react in the way proposed in FIG. 1. Catalytic acid would be generated by photolysis of a PAG molecule. This catalytic acid protonates and removes the tertiary

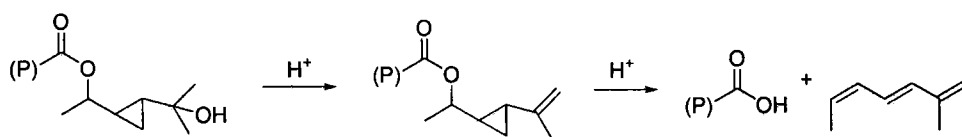
alcohol, converting it to an olefin. This olefin would then make the carbon-oxygen bond in the ester allylic, and easier to remove during the second acidolysis step. Since at the beginning of the reaction, the C-O bond in the ester is only a secondary ester, it will not be removed until it is allylic; therefore, the reaction will require two catalytic steps in order to produce the carboxylic acid. An example of the mechanism of the decomposition of a polymer of formula Ip is shown below:



An example of the mechanism of the decomposition of a polymer of formula Iip is shown below:

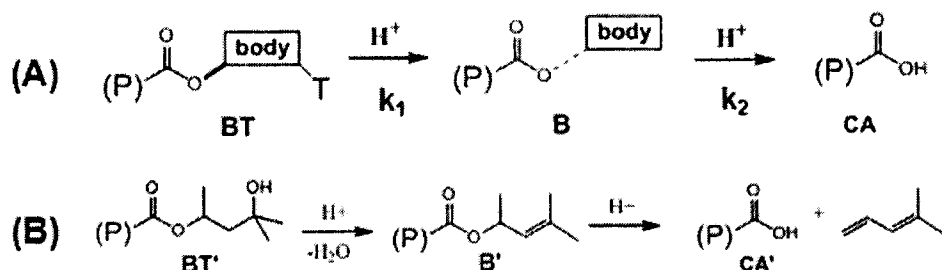


In some embodiments described herein, a cyclopropyl may be present within the polymer. The mechanism of decomposition of such an example is shown below:



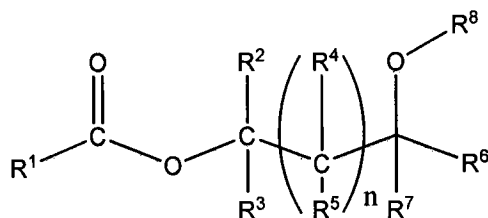
[0021] Acid amplifiers (AAs) may be conceptualized as having three components: a trigger, a body and an acid precursor. The trigger is an acid sensitive group that, when activated under acid, allows the compound to decompose to create a double bond allylic to the carboxyl. The resulting allylic ester decomposes thermally, producing an acid.

[0022] As shown below, the new blocking groups are composed of a body and a trigger:



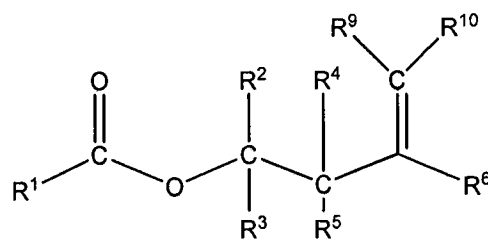
Without being held to any one theory, it is hypothesized that the group protecting the carboxylic acid on the polymer (BT) is unreactive, but the trigger (T) (e.g., a tertiary alcohol) is reactive under the reaction conditions. Once the trigger is “pulled”, a double-bond is created that enables the intermediate blocking group (B) to be removed under acid-catalyzed conditions (k_2), producing a carboxylic acid (CA).

[0023] In some embodiments, the invention relates to a compound of formula I:



I.

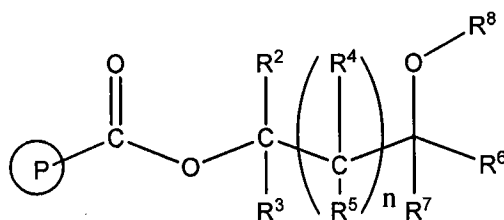
[0024] In other embodiments, the invention relates to a compound of formula II:



II.

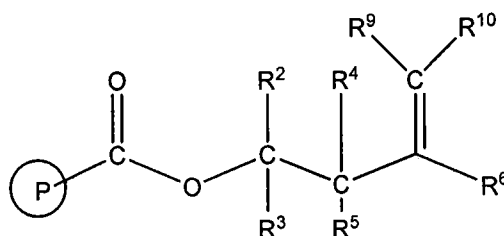
[0025] In some embodiments, R^1 is a (C_{2-3}) alkene. In other embodiments, R^1 is $-C(=C)H$. In still other embodiments, R^1 is $-C(=C)CH_3$.

[0026] In some embodiments, the invention relates to a polymer of formula Ip:



Ip.

[0027] In some embodiments, the invention relates to a polymer of formula IIp:



IIp.

[0028] In some embodiments, P is a polymer chain in which the polymer is a polyolefin. In some embodiments, P is a polyacrylate. In still other embodiments, P is a polymethacrylate. In some embodiments P is a copolymer of two or more monomers chosen from a styrene, an acrylate, and a methacrylate.

[0029] In some embodiments, R² is (C₁₋₂₀)hydrocarbon optionally substituted with halogen. In some embodiments, the halogen is fluorine. In other embodiments, R² is (C₁₋₁₀)hydrocarbon optionally substituted with fluorine. In still other embodiments, R² is methyl. In some embodiments, R² is phenyl.

[0030] In some embodiments, R³, R⁴, R⁵, and R⁷ are selected independently in each instance from hydrogen or (C₁₋₂₀)hydrocarbon. In some of these embodiments, the (C₁₋₂₀)hydrocarbon may in each instance be substituted independently with halogen. In some embodiments, the halogen is fluorine. In other embodiments, a -CH₂- moiety of the (C₁₋₂₀)hydrocarbon may be replaced by -Si(CH₃)₂-. In still other embodiments, a -CH₂- moiety of the (C₁₋₂₀)hydrocarbon may be replaced by -N(C=O)-. In yet other embodiments, a -CH₂- moiety of the (C₁₋₂₀)hydrocarbon may be replaced by -O-. In some embodiments, more than one -CH₂- moiety of the (C₁₋₂₀)hydrocarbon may be replaced by -O-. In some embodiments, a -CH₂- moiety of the (C₁₋₂₀)hydrocarbon

may be replaced by-S-. In some embodiments, R^3 is hydrogen. In other embodiments, R^3 is methyl. In still other embodiments, R^4 is hydrogen. In yet other embodiments, R^5 is hydrogen. In other embodiments, R^5 is methyl. In some embodiments, R^4 is hydrogen and R^5 is hydrogen or methyl. In yet other embodiments, R^7 is hydrogen. In still other embodiments, R^7 is methyl. In other embodiments, R^7 is phenyl.

[0031] In some embodiments, R^6 is hydrogen. In other embodiments, R^6 is $-OR^{60}$. In still other embodiments, R^6 is (C_{1-20}) hydrocarbon optionally substituted with halogen. In some embodiments, the halogen is fluorine. In yet other embodiments, R^6 is (C_{1-10}) hydrocarbon. In some embodiments, R^6 is methyl.

[0032] In some embodiments, R^{60} is (C_{1-20}) hydrocarbon.

[0033] In some embodiments, R^8 is hydrogen. In other embodiments, R^8 is (C_{1-20}) hydrocarbon optionally substituted with one or more substituents selected from halogen, dioxane, and dioxolane. In some embodiments, R^8 is (C_{1-6}) alkyl. In other embodiments, R^8 is phenyl. In still other embodiments, R^8 is $-C(=O)R^{80}$. In some embodiments, R^8 is $-C(=O)C(=O)-O-R^{80}$. In other embodiments, R^8 is $-C(=O)OR^{80}$. In yet other embodiments, R^8 is $-C(=O)NHR^{80}$. In some embodiments, the halogen is fluorine.

[0034] In some embodiments, R^{80} is (C_{1-20}) hydrocarbon optionally substituted with halogen. In some embodiments, the halogen is fluorine. In other embodiments, R^{80} is (C_{1-4}) alkyl optionally substituted with halogen. In still other embodiments, R^{80} is (C_{1-4}) alkyl optionally substituted with fluorine. In other embodiments, R^{80} is phenyl optionally substituted with halogen. In yet other embodiments, R^{80} is phenyl optionally substituted with fluorine. In some embodiments, R^{80} is $-CH_2$ -adamantyl. In other embodiments, R^{80} is adamantyl.

[0035] In some embodiments, R^8 is $-C(=O)OR^{80}$, and R^{80} is (C_{1-4}) alkyl optionally substituted with halogen. In some embodiments, R^8 is $-C(=O)OR^{80}$, and R^{80} is (C_{1-4}) alkyl optionally substituted with fluorine. In some embodiments, R^8 is $-C(=O)OR^{80}$, and R^{80} is phenyl optionally substituted with halogen. In some embodiments, R^8 is $-C(=O)OR^{80}$, and R^{80} is phenyl optionally substituted with fluorine. In some embodiments, R^8 is $-C(=O)OR^{80}$, and R^{80} is $-CH_2$ -adamantyl. In some embodiments, R^8 is $-C(=O)OR^{80}$, and R^{80} is adamantyl.

[0036] In some embodiments, R^8 is $-C(=O)R^{80}$, and R^{80} is phenyl optionally substituted with halogen. In other embodiments, R^8 is $-C(=O)R^{80}$, and R^{80} is phenyl optionally substituted with fluorine. In some embodiments, R^8 is $-C(=O)R^{80}$, and R^{80} is (C_{1-4}) alkyl optionally substituted with halogen. In other embodiments, R^8 is $-C(=O)R^{80}$, and R^{80} is (C_{1-4}) alkyl optionally substituted with fluorine.

[0037] In some embodiments, R^9 is hydrogen. In other embodiments, R^9 is (C_{1-6}) alkyl. In some embodiments, R^9 is phenyl.

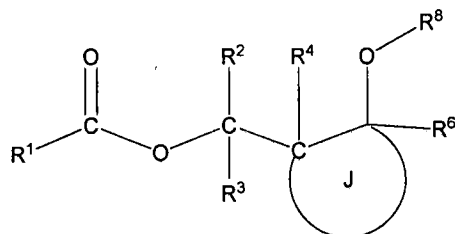
[0038] In some embodiments, R^{10} is hydrogen. In other embodiments, R^{10} is (C_{1-6}) alkyl. In some embodiments, R^{10} is phenyl.

[0039] In some embodiments, n is 0. In these instances, the ester and trigger are two carbons apart (1,2 arrangements). In other embodiments, n is 1. In these instances, the trigger and ester are essentially spaced three carbons apart (1,3 arrangements). In still other embodiments, n is 2. In these instances, the trigger and ester are essentially spaced four carbons apart (1,4 arrangements).

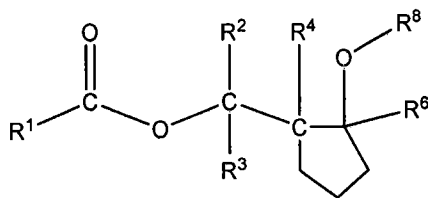
[0040] In some embodiments, a plurality of R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{60} , and R^{80} , together with the atoms to which they are attached, may form a monocyclic ring or a polycyclic ring system. A "plurality", for purposes of this disclosure, indicates two or more of R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{60} , and R^{80} . For instance, in some embodiments, R^5 and R^7 , together with the carbons to which they are attached, may form cyclohexyl, while in other embodiments R^2 , R^3 , R^5 and R^7 , together with the carbons to which they are attached, may form adamantane. To be perfectly clear, these ring systems may be formed in compounds of formula I or formula II, or in polymers of formula Ip or formula IIp. More than one of these ring systems may be formed by these substituent pairings at one time; for instance a ring system may be formed by R^5 and R^7 and by R^8 and R^{60} at the same time in the same compound or polymer. In some of these embodiments, a $-CH_2-$ in the monocyclic ring or polycyclic ring system may be replaced by $-Si(CH_3)_2-$, $-N(C=O)-$, $-O-$, or $-S-$.

[0041] In some embodiments, R^5 is present (that is, n is not 0), and R^5 and R^7 , together with the carbons to which they are attached, form a 3- to 6-membered monocyclic ring. In some embodiments, R^5 is present (that is, n is not 0), and R^5 and R^7 , together with the carbons to which they are attached, form a 7- to 10-membered

bicyclic ring system. An example of formula I, when R^5 and R^7 form a ring, represented by ring J, is shown below:

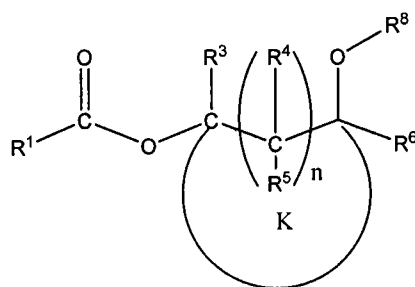


A more specific example is shown below:

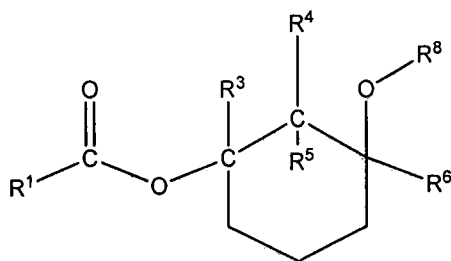


In some embodiments, a $-CH_2-$ in the monocyclic ring or bicyclic ring system may be replaced by $-Si(CH_3)_2-$, $-O-$, $-NC(=O)-$, or $-S-$.

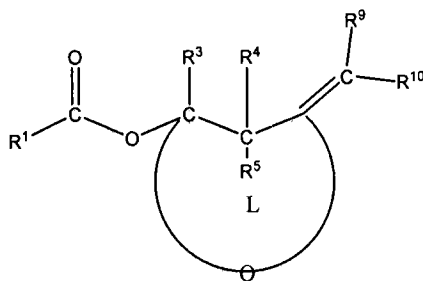
[0042] In some embodiments, R^2 and R^6 (when R^6 is a (C_{1-20}) hydrocarbon optionally substituted with halogen), or R^2 and R^7 , together with the carbons to which they are attached, form a 3- to 6-membered monocyclic carbocycle. In some embodiments, R^2 and R^6 (when R^6 is a (C_{1-20}) hydrocarbon optionally substituted with halogen), or R^2 and R^7 , together with the carbons to which they are attached, form a 7- to 10-membered bicyclic carbocycle. An example of formula I when R^2 and R^7 form a ring, represented by ring K, is shown below:



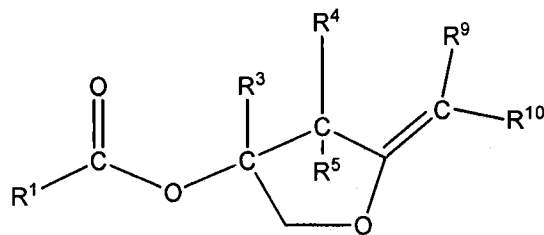
A more specific example is shown below:



[0043] In some embodiments, R^2 and R^{60} (when R^6 is $-OR^{60}$), together with the atoms to which they are attached, form a 5- or 6-membered oxygen-containing heterocycle. An example of formula II when R^2 and R^{60} form a ring, represented by ring L, is shown below:



A more specific example is shown below:



[0044] In some embodiments, R^2 and R^5 , together with the carbons to which they are attached, form a monocyclic. In some embodiments, R^2 and R^5 , together with the carbons to which they are attached, form a bicyclic carbocycle.

[0045] In some embodiments, R^2 and R^3 , together with the carbons to which they are attached, form a 3- to 6-membered monocyclic carbocycle. In some embodiments, R^2 and R^3 , together with the carbons to which they are attached, form a 7- to 10-membered polycyclic carbocycle.

[0046] In some embodiments, R^4 and R^5 , together with the carbons to which they are attached, form a 3- to 6-membered monocyclic carbocycle. In some embodiments,

R⁴ and R⁵, together with the carbons to which they are attached, form a 7- to 10-membered polycyclic carbocycle.

[0047] In some embodiments, R⁶ and R⁷, together with the carbons to which they are attached, form a 3- to 6-membered monocyclic carbocycle. In another embodiment, R⁶ and R⁷, together with the carbons to which they are attached, form a 7- to 10-membered polycyclic carbocycle.

[0048] In some embodiments, R⁸ and R⁶⁰ form a dioxane. In another embodiment, R⁸ and R⁶⁰ form dioxolane. The dioxane or dioxolane may be substituted with one or two methyl groups.

[0049] In some embodiments, R⁵ and R⁷ form a ring and R⁸ and R⁶⁰ form a dioxane or dioxolane optionally substituted with one or two methyl groups. In another embodiment, R² and R⁷ form a ring and R⁸ and R⁶⁰ form a dioxane or dioxolane optionally substituted with one or two methyl groups.

[0050] In some embodiments, R⁶ is hydrogen or (C₁₋₁₀)hydrocarbon and R⁷ is hydrogen. In other embodiments, R⁶ is hydrogen or (C₁₋₁₀)hydrocarbon and R⁷ is methyl. In still other embodiments, R⁶ is hydrogen or (C₁₋₁₀)hydrocarbon and R⁷ is phenyl.

[0051] In some embodiments when the compound is of formula II, both R⁹ and R¹⁰ are hydrogen.

[0052] In some embodiments when the compound is of formula IIp, both R⁹ and R¹⁰ are hydrogen.

[0053] In some embodiments when the compound is of formula II, R⁶ and R⁹, together with the carbons to which they are attached, form an unsaturated 3- to 6-membered monocyclic carbocycle. In other embodiments, R⁶ and R⁹, together with the carbons to which they are attached, form an unsaturated 7- to 10-membered bicyclic carbocycle.

[0054] In some embodiments when the polymer is of formula IIp, R⁶ and R⁹, together with the carbons to which they are attached, form an unsaturated 3- to 6-membered monocyclic carbocycle. In other embodiments, R⁶ and R⁹, together with

the carbons to which they are attached, form an unsaturated 7- to 10-membered bicyclic carbocycle.

[0055] In some embodiments when the polymer is of formula II, R⁶ is hydrogen. In some embodiments when the polymer is of formula II, R⁶ is methyl.

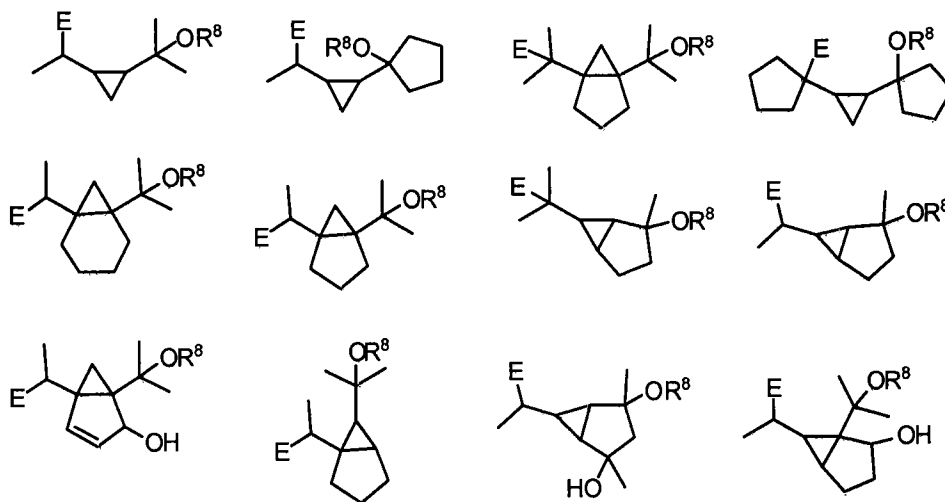
[0056] In some embodiments when the polymer is of formula IIp, R⁶ is hydrogen. In some embodiments when the polymer is of formula IIp, R⁶ is methyl.

[0057] In some embodiments, n is 0 and at least one of R⁶ and R⁷ is an aliphatic (C₁₋₂₀)hydrocarbon.

[0058] In some embodiments, n is 0 and R² and R⁷ form a 3- to 6-membered monocyclic carbocycle. In other embodiments, n is 0 and R² and R⁷ form a 5- to 6-membered monocyclic carbocycle. In still other embodiments, n is 0 and R² and R⁷ form a 7- to 10-membered bicyclic carbocycle. In some of these embodiments, R⁸ and R⁶⁰ form a dioxane or dioxolane optionally substituted with one or two methyl groups.

[0059] In some embodiments when n is 0, at least one of R² and R³ is (C₁₋₆)alkyl, and at least one of R⁶ and R⁷ is (C₁₋₆)alkyl. In some embodiments, n is 0, at least one of R² and R³ is methyl, and at least one of R⁶ and R⁷ is (C₁₋₃)alkyl. In some of these embodiments, R⁸ and R⁶⁰ form a dioxane or dioxolane optionally substituted with one or two methyl groups.

[0060] In some embodiments, n is 2 and the two R⁵ substituents, together with the carbons to which they are attached, form a cyclopropyl ring. Some examples are shown below:



[0061] In some embodiments, the halogen is fluorine.

[0062] In some embodiments, R^2 is (C_{1-10}) hydrocarbon optionally substituted with fluorine and R^3 is hydrogen. In some embodiments, R^2 is (C_{1-10}) hydrocarbon optionally substituted with fluorine and R^3 is methyl.

[0063] All of the compounds falling within the foregoing parent genera and their subgenera are useful for photolithography. It may be found upon examination that compounds that have been included in the claims are not patentable to the inventors in this application. In this event, subsequent exclusions of species from the compass of applicants' claims are to be considered artifacts of patent prosecution and not reflective of the inventors' concept or description of their invention; the invention encompasses all of the members of the genera described above that are not already in the possession of the public. The invention also encompasses the use of a broader genus of compounds in photoresists.

[0064] Most, but not all, of the compounds disclosed herein are novel, and thus, there are provided in some embodiments of the invention, the molecules *per se*, as well as methods for preparing these molecules.

[0065] In the context of the present disclosure, alkyl is intended to include linear or branched saturated hydrocarbon structures and combinations thereof.

[0066] Cycloalkyl includes cyclic hydrocarbon groups of from 3 to 8 carbon atoms. Examples of cycloalkyl groups include *c*-propyl, *c*-butyl, *c*-pentyl, norbornyl and the like.

[0067] Hydrocarbon refers to a substituent comprised of hydrogen and carbon as the only elemental constituents, and therefore includes, for instance, alkyl, cycloalkyl, polycycloalkyl, alkenyl, alkynyl, aryl and combinations thereof. Examples include benzyl, phenyl, ethyl, phenethyl, cyclohexylmethyl, adamantyl, and naphthylethyl. To be perfectly clear, (C₁-C₈)hydrocarbon refers to a moiety that includes 1, 2, 3, 4, 5, 6, 7 or 8 carbons and the appropriate number of hydrogen atoms to satisfy valency. The term “carbocycle” is intended to include ring systems consisting entirely of carbon but of any oxidation state. Thus (C₃-C₁₂) carbocycle refers to such systems as cyclopropane, benzene, adamantyl, and cyclohexene; (C₈-C₁₂) carbopolycycle refers to such systems as norbornane, decalin, indane and naphthalene.

[0068] Acyl refers to groups of from 1 to 8 carbon atoms of a straight, branched, cyclic configuration, saturated, unsaturated and aromatic and combinations thereof, attached to the parent structure through a carbonyl functionality. Acyl also refers to formyl, which has only a hydrogen attached to the parent structure through a carbonyl functionality. One or more carbons in the acyl residue may be replaced by nitrogen, oxygen or sulfur as long as the point of attachment to the parent remains at the carbonyl. Examples include acetyl, benzoyl, propionyl, isobutyryl, *t*-butoxycarbonyl, benzyloxycarbonyl and the like. Lower-acyl refers to groups containing one to four carbons.

[0069] Aliphatic refers to non-aromatic hydrocarbon substituents. Aliphatic substituents may be cyclic (such as cyclopentane or adamantyl) or acyclic, and may contain saturated or unsaturated bonds (i.e., they may be straight or branched alkanes, alkenes or alkynes).

[0070] The terms “monocycle” and “bicycle” or “monocyclic” and “bicyclic” refer to carbocycles and heterocycles having one or two rings respectively. Preferred monocycles are 3, 4, 5, 6 or 7-membered rings, which may be aromatic, saturated or partially unsaturated. Non-limiting examples include cyclopropane, cyclopentane, cyclohexane, pyran, furan, tetrahydrofuran, tetrahydropyran, oxepane and phenyl.

Preferred bicycles are those having from 8 to 12 ring atoms in total. Non-limiting examples include chroman, tetralin, naphthalene, benzofuran, indole, octahdropentalene and tetrahydrobenzo[b]oxepine. A particular embodiment comprises fused 5:6 and 6:6 systems. A "polycyclic" ring system includes bicyclic ring systems, such as norbornyl; tricyclic ring systems, such as adamantane; as well as other ring systems with more than three rings.

[0071] Aryl and heteroaryl mean a 5- or 6-membered aromatic or heteroaromatic ring containing 0-3 heteroatoms selected from O, N, or S; a bicyclic 9- or 10-membered aromatic or heteroaromatic ring system containing 0-3 heteroatoms selected from O, N, or S; or a tricyclic 13- or 14-membered aromatic or heteroaromatic ring system containing 0-3 heteroatoms selected from O, N, or S: The aromatic 6- to 14-membered carbocyclic rings include, *e.g.*, benzene, naphthalene, indane, tetralin, and fluorene and the 5- to 10-membered aromatic heterocyclic rings include, *e.g.*, imidazole, pyridine, indole, thiophene, benzopyranone, thiazole, furan, benzimidazole, quinoline, isoquinoline, quinoxaline, pyrimidine, pyrazine, tetrazole and pyrazole.

[0072] Arylalkyl refers to a substituent in which an aryl residue is attached to the parent structure through alkyl. Examples are benzyl, phenethyl and the like. Heteroarylalkyl refers to a substituent in which a heteroaryl residue is attached to the parent structure through alkyl. Examples include, *e.g.*, pyridinylmethyl, pyrimidinylethyl and the like.

[0073] Heterocycle means a cycloalkyl or aryl residue in which from one to three carbons is replaced by a heteroatom selected from the group consisting of N, O and S. The nitrogen and sulfur heteroatoms may optionally be oxidized, and the nitrogen heteroatom may optionally be quaternized. Examples of heterocycles that fall within the scope of the invention include pyrrolidine, pyrazole, pyrrole, indole, quinoline, isoquinoline, tetrahydroisoquinoline, benzofuran, benzodioxan, benzodioxole (commonly referred to as methylenedioxyphenyl, when occurring as a substituent), tetrazole, morpholine, thiazole, pyridine, pyridazine, pyrimidine, thiophene, furan, oxazole, oxazoline, isoxazole, dioxane, tetrahydrofuran and the like. It is to be noted that heteroaryl is a subset of heterocycle in which the heterocycle is aromatic. Examples of heterocyclyl residues additionally include piperazinyl, 2-oxopiperazinyl,

2-oxopiperidinyl, 2-oxo-pyrrolidinyl, 2-oxoazepinyl, azepinyl, 4-piperidinyl, pyrazolidinyl, imidazolyl, imidazoliny, imidazolidinyl, pyrazinyl, oxazolidinyl, isoxazolidinyl, thiazolidinyl, isothiazolyl, quinuclidinyl, isothiazolidinyl, benzimidazolyl, thiadiazolyl, benzopyranyl, benzothiazolyl, tetrahydrofuryl, tetrahydropyranyl, thienyl, benzothienyl, thiamorpholinyl, thiamorpholinylsulfoxide, thiamorpho-linylsulfone, oxadiazolyl, triazolyl and tetrahydroquinolinyl. An oxygen heterocycle is a heterocycle containing at least one oxygen in the ring; it may contain additional oxygens, as well as other heteroatoms. A sulphur heterocycle is a heterocycle containing at least one sulphur in the ring; it may contain additional sulphurs, as well as other heteroatoms. Oxygen heteroaryl is a subset of oxygen heterocycle; examples include furan and oxazole. Sulphur heteroaryl is a subset of sulphur heterocycle; examples include thiophene and thiazine. A nitrogen heterocycle is a heterocycle containing at least one nitrogen in the ring; it may contain additional nitrogens, as well as other heteroatoms. Examples include piperidine, piperazine, morpholine, pyrrolidine and thiomorpholine. Nitrogen heteroaryl is a subset of nitrogen heterocycle; examples include pyridine, pyrrole and thiazole.

[0074] As used herein, the term “optionally substituted” may be used interchangeably with “unsubstituted or substituted”. The term “substituted” refers to the replacement of one or more hydrogen atoms in a specified group with a specified radical. For example, substituted alkyl, aryl, cycloalkyl, heterocyclyl etc. refer to alkyl, aryl, cycloalkyl, or heterocyclyl wherein one or more H atoms in each residue are replaced with halogen, haloalkyl, alkyl, acyl, alkoxyalkyl, hydroxyloweralkyl, carbonyl, phenyl, heteroaryl, benzenesulfonyl, hydroxy, loweralkoxy, haloalkoxy, oxaalkyl, carboxy, alkoxycarbonyl [$-C(=O)O\text{-alkyl}$], cyano, acetoxy, nitro, mercapto, alkylthio, alkylsulfinyl, alkylsulfonyl, aryl, benzyl, oxaalkyl, and benzyloxy. “Oxo” is also included among the substituents referred to in “optionally substituted”; it will be appreciated by persons of skill in the art that, because oxo is a divalent radical, there are circumstances in which it will not be appropriate as a substituent (e.g. on phenyl). In one embodiment, 1, 2 or 3 hydrogen atoms are replaced with a specified radical. In the case of alkyl, cycloalkyl and aryl, more than three hydrogen atoms can be replaced by fluorine; indeed, all available hydrogen atoms could be replaced by fluorine.

[0075] The term "halogen" means fluorine, chlorine, bromine or iodine.

[0076] Photoresist polymers, i.e polymers suitable for use with photoacid generators and/or acid amplifiers in making photoresists are well-known in the art. In the context of the present disclosure, any polymer or polymer chain arising from an olefin polymerization may be utilized. In some embodiments, styrene, acrylate, methacrylate, or mixtures thereof may be used.

[0077] As used herein, the term "photoresist polymer" refers to a polymer which may serve as the primary component in a photoresist.

[0078] As used herein, the term "photoresist substrate" refers to an article, such as a silicon wafer, which is suitable for use as a substrate in photolithography or other similar processes, and thus may have a photoresist applied thereto as part of the photolithography process.

[0079] As used herein, the term "photoresist composition" refers to a composition which may be used in connection with photolithography.

[0080] When the term "an integer between" two numbers is used, it is meant to include any single integer between and including the two named numbers. For instance, the term "an integer between 1 and 4" indicates that any integer selected from 1, 2, 3, or 4 is meant to be included.

[0081] Some of the compounds described herein contain one or more asymmetric centers and may thus give rise to enantiomers, diastereomers, and other stereoisomeric forms that may be defined, in terms of absolute stereochemistry, as (R)- or (S)-. Unless indicated otherwise, the present invention is meant to include all such possible isomers, as well as, their racemic and optically pure forms. Optically active (R)- and (S)-, or (D)- and (L)- isomers may be prepared using chiral synthons or chiral reagents, or resolved using conventional techniques. When the compounds described herein contain olefinic double bonds or other centers of geometric asymmetry, and unless specified otherwise, it is intended that the compounds include both E and Z geometric isomers. Likewise, all tautomeric forms are also intended to be included.

[0082] The configuration of any carbon-carbon double bond other than an endocyclic double bond appearing herein is selected for convenience only and is not intended to designate a particular configuration; thus a carbon-carbon double bond depicted arbitrarily herein as *trans* may be *cis*, *trans*, or a mixture of the two in any proportion.

[0083] Terminology related to "protecting", "deprotecting" and "protected" functionalities occurs in some places in this application. Such terminology is well understood by persons of skill in the art and is used in the context of processes which involve sequential treatment with a series of reagents. In that context, a protecting group refers to a group which is used to mask a functionality during a process step in which it would otherwise react, but in which reaction is undesirable. The protecting group prevents reaction at that step, but may be subsequently removed to expose the original functionality. The removal or "deprotection" occurs after the completion of the reaction or reactions in which the functionality would interfere. Thus, when a sequence of reagents is specified, as it is in the processes of the invention, the person of ordinary skill can readily envision those groups that would be suitable as "protecting groups".

[0084] The following abbreviations and terms have the indicated meanings throughout:

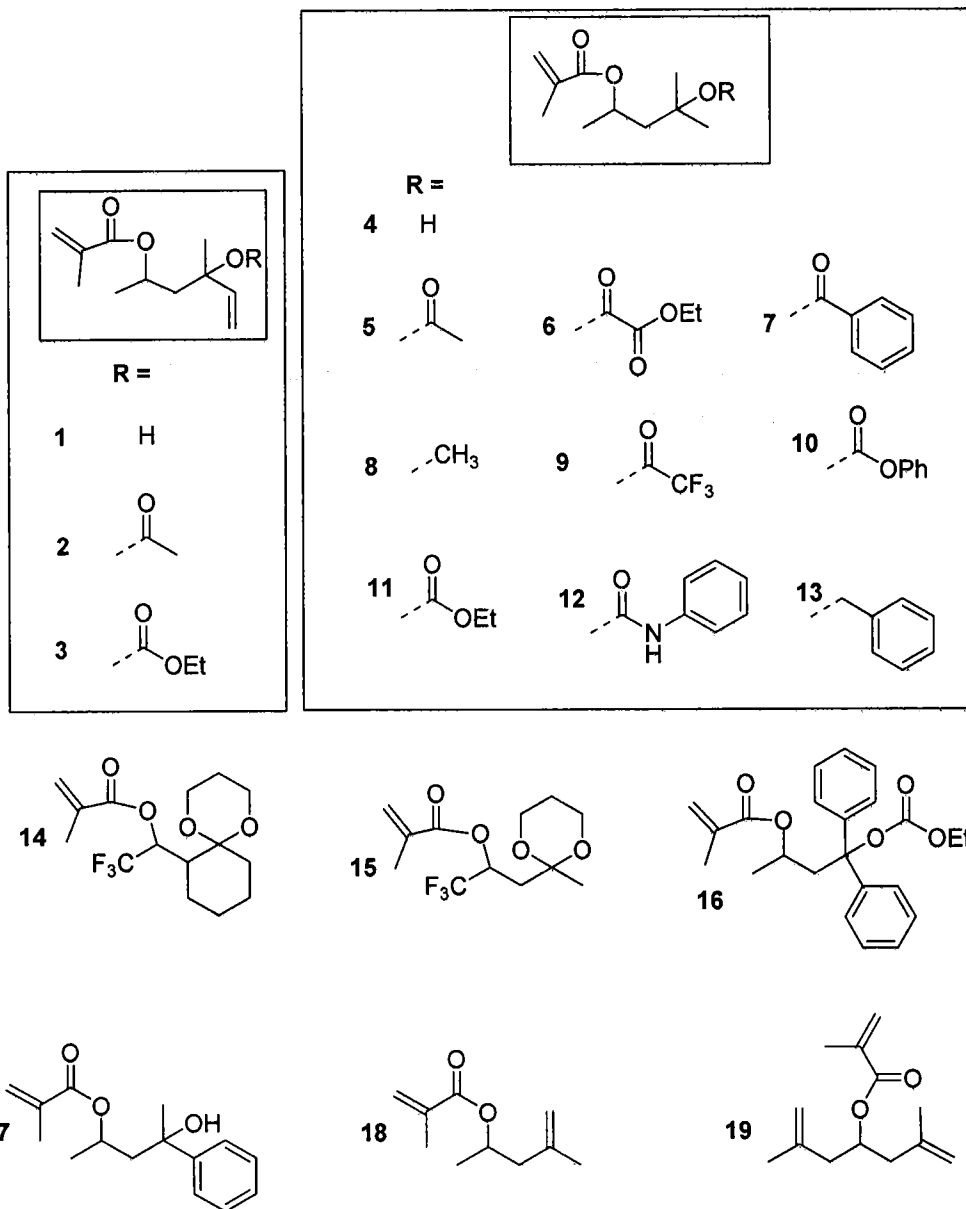
Ac	=	acetyl
Bu	=	butyl
c-	=	cyclo
Et	=	ethyl
EUV	=	extreme ultraviolet
LER	=	line edge roughness
Me	=	methyl
PAG	=	photo acid generator
PEB	=	post-exposure bake
Ph	=	phenyl
rt	=	room temperature
sat'd	=	saturated
s-	=	secondary
t-	=	tertiary

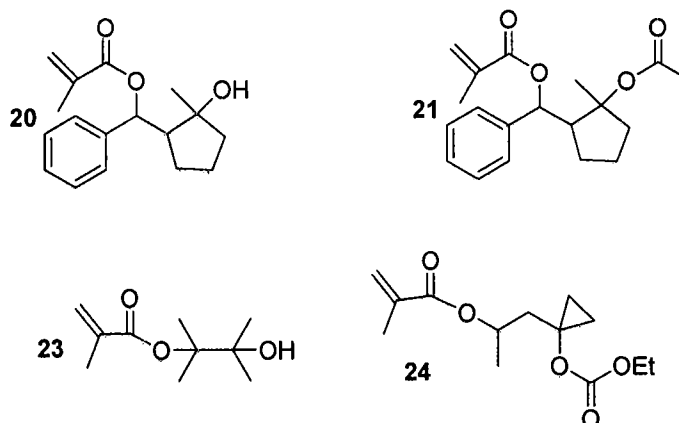
[0085] A comprehensive list of abbreviations utilized by organic chemists (i.e. persons of ordinary skill in the art) appears in the first issue of each volume of the

Journal of Organic Chemistry. The list, which is typically presented in a table entitled “Standard List of Abbreviations” is incorporated herein by reference.

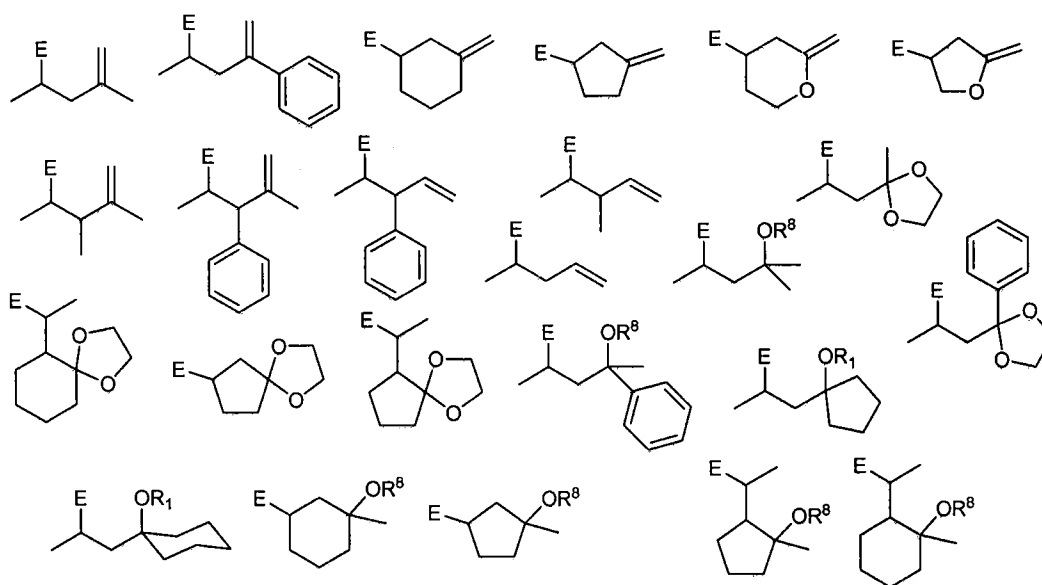
[0086] Examples

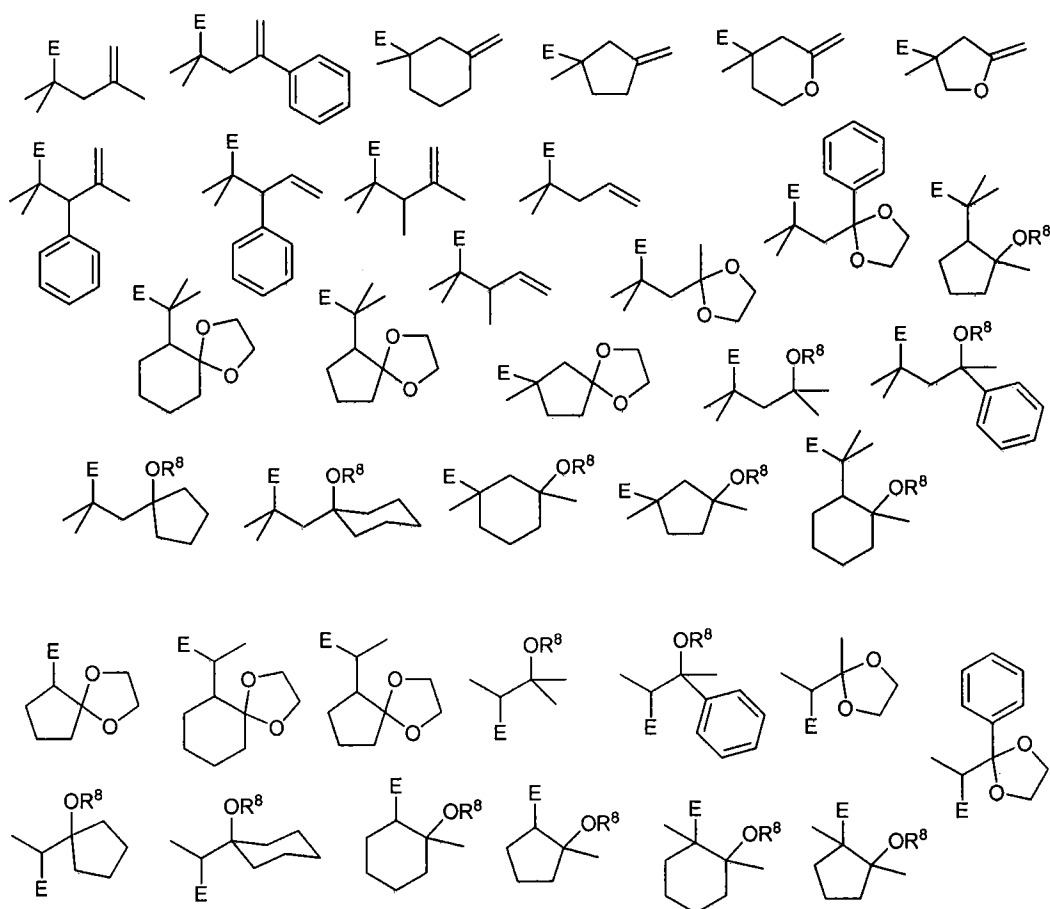
[0087] The following compounds have been synthesized. These compounds may be used with EUV (13.5 nm) radiation. Compound numbers are listed next to the substituent (R), where applicable:



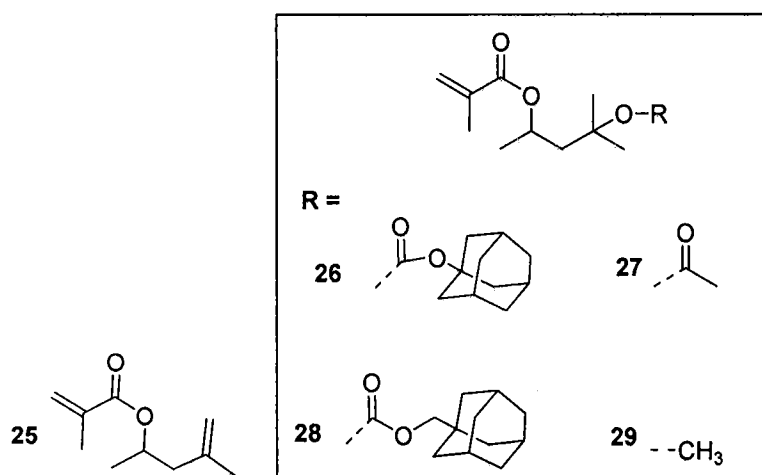


[0088] Other compounds that fall within the genus described herein include those shown below, although these examples are not exhaustive. These compounds are useful for EUV wavelengths. In the examples below, E represents (P)CO₂-, where (P) is a polymer chain or a (C₂₋₃)alkene, and R⁸ is as defined in the claims:



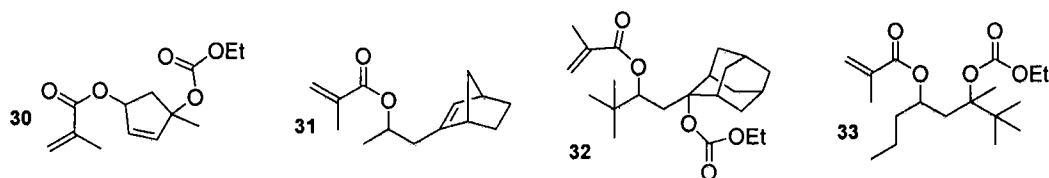


[0089] The compounds below have been synthesized and may be used for photolithography using 193 nm wavelength:

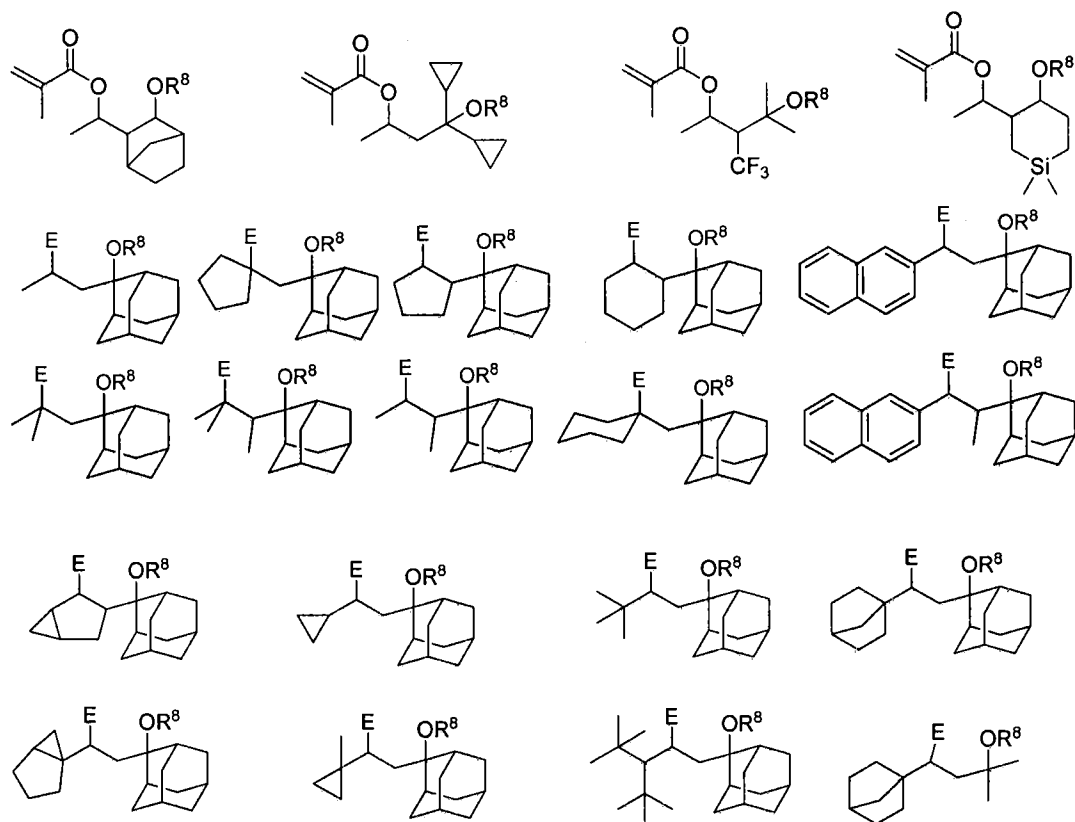


[0090] Other compounds that fall within the genus described herein include those shown below, although these examples are not exhaustive. These compounds are

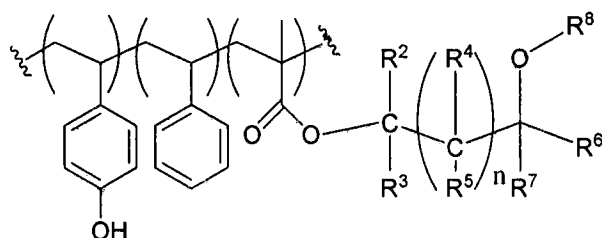
useful for 193 nm wavelengths. Compound numbers are listed next to the compound, where applicable:



In the examples below, E represents (P)CO₂-, where (P) is a polymer chain or a (C₂-₃)alkene, and R⁸ is as defined in the claims:



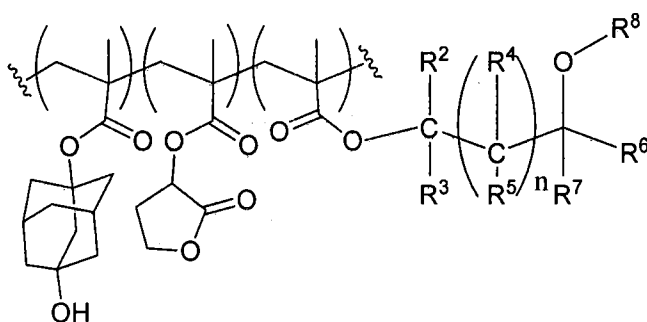
[0091] A non-limiting example of a polymer of the genus disclosed herein for use in EUV photolithography is shown below:



EUV Polymer
60/20/20 (OHStyr/Styr/DD-CAMP)

This is a random terpolymer of hydroxystyrene, styrene, and a methacrylate DD-CAMP monomer.

[0092] A non-limiting example of a polymer of the genus disclosed herein for use in photolithography using 193 nm wavelength is shown below:



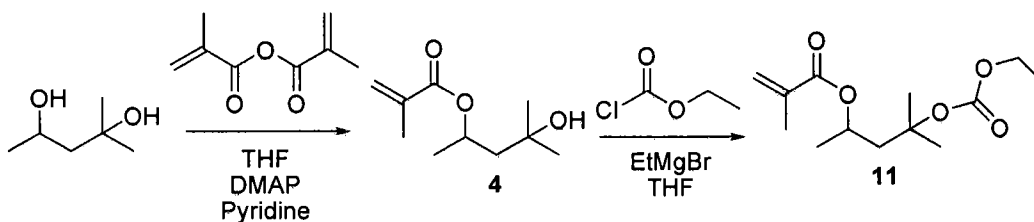
193-nm polymer
20/40/40 (HadMA/GBLMA/DD-CAMP)

This is a random terpolymer of HadMA, GBLMA, and a methacrylate monomer of DD-CAMP.

Syntheses

[0093] In general, compounds *per se* or for use in accordance with embodiments of present invention may be prepared by the methods illustrated in the general reaction schemes as, for example, described below, or by modifications thereof, using readily available starting materials, reagents and conventional synthesis procedures. In these reactions, it is also possible to make use of variants that are in themselves known, but are not mentioned here.

[0094] **Methacrylate Monomers.** Monomers were synthesized using procedures adapted from the literature. A specific synthetic procedure is described for Monomer 11 and spectroscopic data is listed in Table 1.

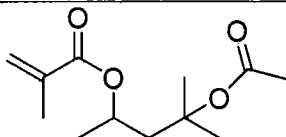
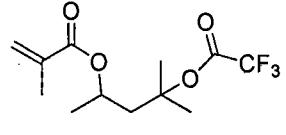
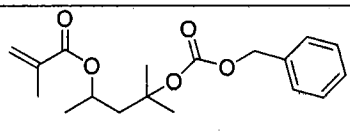
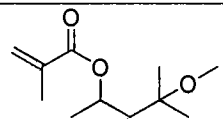
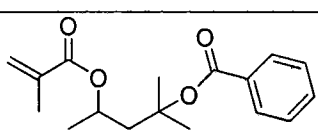
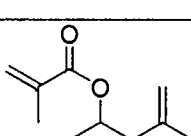


[0095] **Synthesis of Intermediate 4 (4-hydroxy-4-methylpentan-2-yl methacrylate):** To a solution of 2-methylpentane-2,4-diol (20.5g, 173 mmol) in 100 ml of THF, 4-(dimethylamino)pyridine (DMAP) (4.2g, 34.6 mmol) was added followed by pyridine (27.4g, 346 mmol) and methacrylic anhydride (21.25g, 208 mmol). A constant flow of nitrogen was kept through the reaction vessel. The reaction was to stir for 14 hours at room temperature. 40 ml of a 1% aqueous solution of NaHCO_3 was added to the reaction mixture. The mixture was stirred for 10 minutes and then extracted with ethyl acetate (3x40 ml). The organic layers were combined and dried with sodium sulfate, filtered and concentrated under vacuum. Chromatography on silica gel eluting with 1:1 ether : hexane yielded 4 (15.6g 48%) as a colorless oil. ^1H NMR (400 MHz, Chloroform- d) δ 6.06 (s, 1H), 5.53 (s, 1H), 5.19 (dq, J = 9.4, 6.3, 6.3, 6.2, 3.1 Hz, 1H), 2.1 (m, 1H), 1.91-1.87 (m, 1H), 1.91 (s, 3H), 1.66 (dd, J = 14.9, 3.3 Hz, 1H), 1.27 (d, J = 6.2 Hz, 3H), 1.20 (s, 6H),

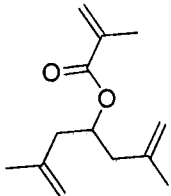
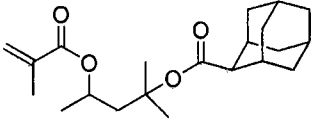
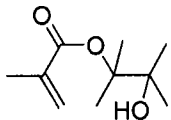
[0096] **Synthesis of Monomer 11 (4-(ethoxycarbonyloxy)-4-methylpentan-2-yl methacrylate):** Methylmagnesium bromide (1 M in THF) (13.2 ml, 13.2 mmol) was added to a solution of 4-hydroxy-4-methylpentan-2-yl methacrylate (4) (2.25g, 13.2 mmol) in THF (40 ml) at -78°C . The reaction was stirred at -78°C for 1 hour, then ethylchloroformate (1.14g, 10.5 mmol) was added dropwise. The reaction was then slowly warmed to room temperature and kept at room temperature for 1 hour. The reaction mixture was poured into a cold solution of saturated aqueous sodium bicarbonate. The mixture was stirred for 5 min. then extracted with ethyl acetate, dried with sodium sulfate, filtered and concentrated to an oil. Purification was done using silica gel chromatography. The compound was eluted with 2:1 hexane: ether to yield 2.6g (59%) of 11 as a colorless oil. ^1H NMR (400 MHz, Chloroform- d) ^1H

NMR (400 MHz, Chloroform-*d*) δ 6.05 (s, 1H), 5.51 (s, 1H), 5.17 (dq, J = 8.6, 6.3, 6.3, 6.3, 3.1 Hz, 1H), 4.18-4.06 (m, 2H), 2.25-2.18 (m, 1H), 2.01 (dd, J = 15.0, 8.5 Hz, 1H), 1.95 (s, 3H), 1.51 (s, 6H), 1.35-1.2 (m, 6H).

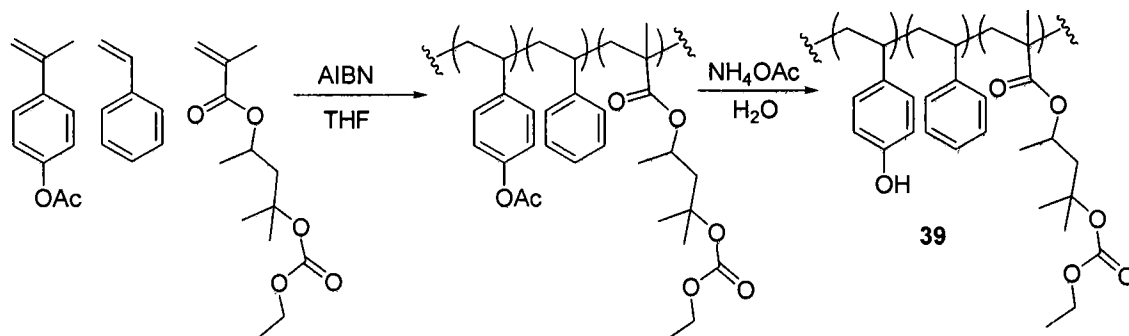
Table 1.

Structure	Name	¹ H NMR (400 MHz, CDCl ₃)
	4-acetoxy-4-methylpentan-2-yl methacrylate Example 5	δ 6.05 (s, 1H), 5.51 (s, 1H), 5.17 (dq, J = 8.6, 6.3, 6.3, 6.3, 3.1 Hz, 1H), 2.18 (dd, J = 15.0, 8.5 Hz, 1H), 1.98 (dd, J = 15.0, 3.1 Hz, 1H), 1.90 (s, 3H), 1.43 (s, 3H), 1.41 (s, 3H), 1.23 (d, J = 6.3 Hz, 3H).
	4-methyl-4-(2,2,2-trifluoroacetoxy)pentan-2-yl methacrylate Example 9	δ 6.04 (s, 1H), 5.53 (s, 1H), 5.17 (dtd, J = 12.4, 6.3, 6.2, 3.2 Hz, 1H), 2.33 (dd, J = 15.2, 8.5 Hz, 1H), 2.01 (dd, J = 15.2, 3.2 Hz, 1H), 1.89 (s, 3H), 1.55 (s, 6H), 1.26 (d, J = 6.3 Hz, 3H).
	4-(benzyloxycarbonyloxy)-4-methylpentan-2-yl methacrylate Example 35	δ 7.36 – 7.27 (m, 5H), 6.04 (s, 1H), 5.48 (s, 1H), 5.23 – 5.12 (m, 1H), 5.03 (q, J = 12.1, 12.1, 12.1 Hz, 2H), 2.27 (dd, J = 15.1, 8.8 Hz, 1H), 2.04 – 1.96 (m, 1H), 1.88 (s, 1H), 1.46 (s, 3H), 1.23 (d, J = 2.2 Hz, 3H).
	4-methoxy-4-methylpentan-2-yl methacrylate Example 29	δ 6.04 (s, 1H), 5.49 (s, 1H), 5.21 – 5.03 (m, 1H), 3.14 (s, 3H), 1.90 (s, 3H), 1.85 (d, J = 7.9 Hz, 1H), 1.66 (dd, J = 14.9, 3.6 Hz, 1H), 1.25 (d, J = 6.2 Hz, 3H), 1.13 (s, 6H).
	4-(methacryloyloxy)-2-methylpentan-2-yl benzoate Example 7	δ 7.96 – 7.86 (m, 2H), 7.57 – 7.42 (m, 1H), 7.36 (dd, J = 8.4, 7.1 Hz, 2H), 5.96 (s, 1H), 5.38 (s, 1H), 5.28 (dq, J = 9.3, 6.3, 6.2, 6.2, 3.0 Hz, 1H), 2.42 (dd, J = 15.1, 8.6 Hz, 1H), 2.19 – 2.05 (m, 1H), 1.79 (s, 3H), 1.58 (s, 6H), 1.27 (d, J = 6.3 Hz, 3H).
	4-methylpent-4-en-2-yl methacrylate Example 25	δ 6.04 (s, 1H), 5.48 (s, 1H), 5.20 – 4.96 (m, 1H), 4.76 (s, 1H), 4.70 (s, 1H), 2.36 (dd, J = 13.9, 7.3 Hz, 1H), 2.18 (dd, J = 13.9, 5.9 Hz, 1H), 1.90 (s, 3H), 1.72 (s, 3H), 1.23 (d, J = 6.4 Hz, 3H).

Structure	Name	¹ H NMR (400 MHz, CDCl ₃)
	(2-hydroxy-2-methylcyclopentyl)(phenyl) methyl methacrylate Example 21	2 major diastereomers (A,B) δ 7.36-7.22 (m, 5H, A,B), 6.20 (s, 0.4H, A), 6.12 (s, 0.6H, B), 5.89 (d, <i>J</i> = 10.3 Hz, .4H, A), 5.70 – 5.44 (m, 1.6H, A, B), 4.12-4.05 (m, 0.6H, B), 2.98-2.10 (m, 0.4H, A), 2.55-2.44 (m, 0.4H, A), 2.24-2.14 (m, 0.6H, B), 2.07-1.64 (m, 3H, A,B), 1.93 (s, 1.2H, A), 1.90 (s, 1.8, B), 1.54-1.12 (m, 3H, A,B), 1.37 (s, 1.8H, B), 1.27 (s, 1.2H, A).
	1-(2-(trifluoromethyl)-1,3-dioxan-2-yl)propan-2-yl methacrylate Example 15	δ 6.13 (s, 1H), 5.91-5.79 (m, 1H), 5.59 (s, 1H), 3.97 – 3.64 (m, 4H), 2.14 (dd, <i>J</i> = 15.0, 9.3 Hz, 1H), 2.04 (dd, <i>J</i> = 15.1, 1.6 Hz, 1H), 1.94 (s, 3H), 1.91 – 1.75 (m, 1H), 1.43-1.32 (m, 1H) 1.40 (s, 3H).
	2,2,2-trifluoro-1-(1,5-dioxaspiro[5.5]undecan-7-yl)ethyl methacrylate Example 14	Diastereomers (A,B) δ 6.25-6.19 (m, 1H, A,B), 6.13 (s, 0.6H, B), 6.10 (s, 0.4H, A), 5.97-5.89 (m, 0.4H, A), 5.56 (s, 0.6H, B), 5.54 (s, 0.4H, A), 4.10-3.47 (m, 4H, A,B) 2.77-2.67 (M, 1H, A,B), 2.12 – 1.48 (m, 6H, A,B), 1.95 (s, 0.6H, B), 1.93 (s, 0.4H, A), 1.32 – 0.99 (m, 4H, A,B),
	(2-acetoxy-2-methylcyclopentyl)(phenyl) methyl methacrylate Example 22	2 major diastereomers (A,B) δ 7.47 – 7.10 (m, 5H, A,B), 6.18 (s, 0.4H, A), 6.09 (s, 0.6H, B), 5.99 (d, <i>J</i> = 10.5 Hz, 0.6H, B), 5.67 (d, <i>J</i> =10.5 Hz, 0.4H, A), 5.55-5.49 (m, 1H, A,B), 2.98 – 2.80 (m, 0.6H, B), 2.42 (ddd, <i>J</i> = 14.6, 7.9, 6.6 Hz, 0.4H, A), 2.03 – 1.05 (m, 6H), 1.90 (s, 0.4H, A), 1.89 (s, 0.6H, B), 1.69 (s, 0.6H, B), 1.48 (s, 0.4H, A).
	ethyl 4-(methacryloyloxy)-2-methylpentan-2-yl oxalate Example 6	δ 6.03 (s, 1H), 5.50 (s, 1H), 5.19 (dq, <i>J</i> = 12.4, 6.3, 6.2, 6.2, 3.3 Hz, 1H), 4.26 (q, <i>J</i> = 7.2, 7.2, 7.1 Hz, 2H), 2.32 (dd, <i>J</i> = 15.1, 8.4 Hz, 1H), 2.02 (dd, <i>J</i> = 15.1, 3.4 Hz, 1H), 1.89 (s, 3H), 1.54 (s, 6H), 1.32 (t, <i>J</i> = 7.2, 7.2 Hz, 3H), 1.27 (d, <i>J</i> = 6.3 Hz, 3H).
	4-methyl-4-(phenylcarbamoyloxy)penta n-2-yl methacrylate Example 12	δ 7.42 – 7.14 (m, 4H), 7.00 (t, <i>J</i> = 7.1, Hz, 1H), 6.45 (s, 1H), 6.05 (s, 1H), 5.44 (s, 1H), 5.26 (ddt, <i>J</i> = 9.9, 6.3, 3.2, 3.2 Hz, 1H), 2.33 (dd, <i>J</i> = 15.1, 8.9 Hz, 1H), 2.01 (dd, <i>J</i> = 15.1, 2.6 Hz, 1H), 1.86 (s, 3H), 1.49 (s, 6H), 1.25 (d, <i>J</i> = 6.3 Hz, 3H).

Structure	Name	¹ H NMR (400 MHz, CDCl ₃)
	2,6-dimethylhepta-1,6-dien-4-yl methacrylate Example 19	δ 6.04 (s, 1H), 5.48 (s, 1H), 5.23 (tt, <i>J</i> = 7.8, 7.8, 5.2, 5.2 Hz, 1H), 4.76 (p, <i>J</i> = 1.6, 1.6, 1.6, 1.6 Hz, 2H), 4.69 (dq, <i>J</i> = 2.3, 1.1, 1.1, 1.1 Hz, 2H), 2.31 (ddd, <i>J</i> = 14.0, 7.8, 1.1 Hz, 2H), 2.23 (ddd, <i>J</i> = 14.1, 5.2, 1.2 Hz, 2H), 1.89 (s, 3H), 1.71 (s, 6H).
	4-methyl-4-(1-adamantyloxy)pentan-2-yl methacrylate Example 39	Rotational isomers A,B δ 6.05 (s, 0.6H, B), 5.97 (s, 0.4H, A), 5.51 (s, 0.6H, B), 5.46 (s, 0.4H, A), 5.20 – 4.98 (m, 1H), 2.19 – 2.01 (m, 2H), 1.96 (bs, 3H), 1.90 (t, <i>J</i> = 1.3 Hz, 1H), 1.86 (t, <i>J</i> = 1.3 Hz, 1H), 1.82 (d, <i>J</i> = 9.5 Hz, 3.6H, B), 1.82 (d, <i>J</i> = 9.5 Hz, 2.4H, A), 1.73 – 1.60
	3-hydroxy-2,3-dimethylbutan-2-yl methacrylate Example 23	¹ H NMR (400 MHz, Chloroform- <i>d</i>) δ 6.01 (s, 1H), 5.03 (s, 1H), 3.41 (s, 1H), 1.98 (s, 3H), 1.51 (s, 6H), 1.20 (s, 6H).

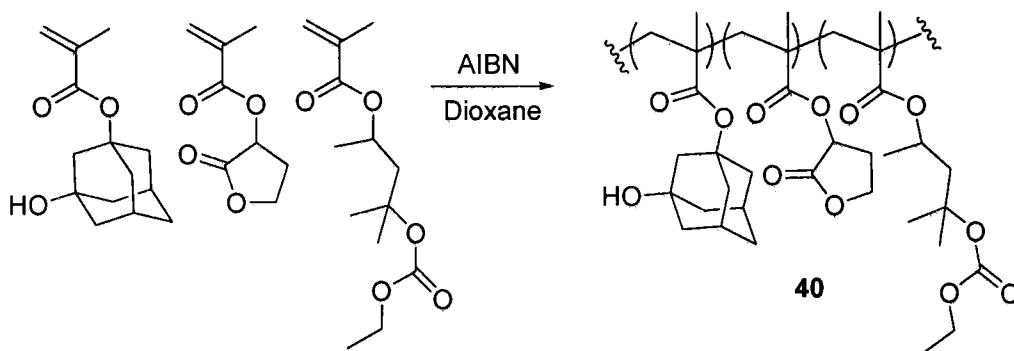
[0097] **SYNTHESIS of an EUV Polymer:**



[0098] **Synthesis of EUV polymer (39) (hydroxystyrene/styrene/4-(ethoxycarbonyloxy)-4-methylpentan-2-yl methacrylate)(60%/20%/20%):** This synthesis is similar to a procedure from Patent 6,042,997 Barclay et al. The three monomers (4-hydroxy styrene (2.33g, 17.4 mmol), Styrene (0.60g, 5.8 mmol), 4-(ethoxycarbonyloxy)-4-methylpentan-2-yl methacrylate (1.5g, 5.8 mmol) were combined in 15 ml of THF. AIBN (0.143g, 0.87 mmol) was added to the solution. Nitrogen was bubbled thru the mixture for 10 min. The mixture was then heated at gentle reflux for 18 hours. The reaction was cooled and 15 ml of hexane was added, after which a gum formed. The solvents were decanted away from the gum. The gum

was dissolved in methylene chloride and added to an equal amount of hexane. The resulting precipitate was filtered, and a polymer **39** was obtained as a white solid 3.4g (78%). GPC MW 11,500

[0099] **SYNTHESIS of an 193-nm Polymer:**



[00100] **Synthesis of 193-nm polymer (40) (HadMA/ GBLMA/4-(ethoxycarbonyloxy)-4-methylpentan-2-yl methacrylate) (20%/40%/40%)**

Synthesis: The three monomers 4-(ethoxycarbonyloxy)-4-methylpentan-2-yl methacrylate (1.5g, 5.8 mmol), GBLMA (0.986g, 5.8 mmol), HadMA (0.685g, 2.9 mmol), were dissolved in 8.2 ml of Dioxane. AIBN (0.071g, 0.43 mmol) was added to the solution. Nitrogen was bubbled thru the mixture for 10 min. The mixture was then heated at 80°C for 3.5 hours. The reaction was cooled and added to 30 ml of ether, after which a white solid formed. The solvents were filtered away from the solid. The polymer (**40**) was obtained as a white solid 2.6g (80%). GPC MW 11,500.

LITHOGRAPHIC EVALUATION

[00101] **Formulation and Coating:** Polymer (0.626g), bis(4-tert-butylphenyl)iodonium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate(PAG) (0.113g) and 1.125g of a 1% ethyl lactate solution tetrabutylammonium hydroxide (TBAH) were all dissolved in 23.14 g of PMA, followed by filtration through a 0.22 μ m Pall CR13 PTFE syringe filter to make a 3 wt% photoresist solution. 1.5 to 4 mL of this photoresist solution was applied to a virgin 4" silicon wafer or 300mm silicon wafer coated with HMDS. The wafer was spun at 2000 RPM for 45 seconds to form an

amorphous, uniform thin film with a thickness of 60 nm. The coated wafer was optically inspected for defects and recoated, if necessary.

[00102] **Facilities.** EUV (extreme ultraviolet) exposures were performed at Lawrence Berkeley National Laboratory (LBNL), Advanced Light Source (ALS) on the SEMATECH Berkeley Microexposure Tool (BMET) or EUV exposures were performed at SUNY Polytechnic Institute on the SEMATECH Albany Microexposure Tool (AMET). 193-nm exposures were performed at SUNY Polytechnic Institute using the ASML TWINSCAN XT:1700i.

[00103] **Exposure Procedures.** Coated wafer were inserted into exposure tools and irradiated with extreme ultraviolet (EUV, $\lambda=13.5$ nm) light or 193-nm light and tested for: 1. Photosensitivity and 2. Imaging. EUV exposures at the LBNL ALS and EUV AMET consisted of the following: 1. DCT (Dose Calibration Tool) exposures consisted of 50 pinhole exposures of increasing dose to demonstrate photoresist EUV sensitivity and to generate a contrast curve to help evaluate the photoresist's performance. 2. 193-nm exposures at the Albany 1700i consist of a contrast curve exposure consisting of 100 stops with 1 cm square exposures of increasing dose to demonstrate photoresist 193-nm sensitivity and to generate a contrast curve to help evaluate the photoresist's performance. The wafer coated with resist was inserted into the exposure tool (DCT at LBNL, AMET) and evaluated with a wide dose range contrast curve exposure. After exposure, the wafer was removed from the tool and developed in 0.26N TMAH for 45 seconds. The development step removed any exposed resist material from the wafer (positive tone development). The dose (mJ/cm^2) required to achieve E_0 was determined optically and recorded. The E_0 dose determined from the contrast curve was multiplied by 2.5 for the control resist (P-COOt-Bu) and 3.5 for the DD-CAMP resists as a rough estimate of the centering dose. 3. Focus Exposure Matrix (FEM) exposures on BMET consisted of a dose and focus array of mask patterning using the LBNL Dark Field Mask to evaluate the resist imaging performance. The array size can vary, but an 11x7 array (11 dose variations, 7 focus variations) was typical. Although many illumination types are possible, most exposures were performed using annular illumination. After exposure, the wafer was removed from the tool and developed in 0.26N TMAH for 45 seconds. The developed chips were analyzed for patterning with a scanning electron microscope

(SEM). Although each site used a different SEM (Hitachi S4800 SEM at LBNL), the protocol for obtaining images was identical. Accelerating voltage was set to 2 keV and the working distance was typically 3-4 mm. The in-lens detector was used to maximize signal: noise. Micrographs were obtained at 150 – 200 kx magnification, if possible.

[00104] **Lithographic Evaluation – Line Edge Roughness (LER).** Line edge roughness determined by importing TIFF files of the SEM images into SuMMIT software. SuMMIT is an interactive off-line analysis package for critical dimension (CD) and line-edge/width roughness (LER/LWR) processing of SEM images. SuMMIT has integrated stochastic resist modeling capabilities. Load an aerial image into SuMMIT, define the resist parameters, and SuMMIT will compute the resulting stochastic resist image and automatically compute the LER. Information on SuMMIT software for LER analysis can be found at the Company website <http://www.lithometrix.com/index.html>.

Results

[00105] Various procedural modifications should be considered when optimizing the DD-CAMP resists. For instance, the post-exposure bake (PEB) times of DD-CAMP resists are able to be optimized to give the best LER. An example of this is illustrated in FIG. 2. The LER of the Control (t-BuO) changes linearly with PEB time, while the LER of the two DD-CAMP examples (OAc and OCOOEt) possess an optimum PEB time. "(P)" designates the polymer, and the value of (P) was the same for all compounds shown in FIG. 2. Without being held to any one theory, it is believed that this phenomena is a result of the need to balance the relative rates of the first and second deprotection steps to get the highest exponent value.

[00106] Representative compounds falling within the genus disclosed herein were tested in EUV imaging experiments. FIG. 3 illustrates a graph resulting from the plot of focus vs. line edge roughness (LER). In general, better focus leads to more desirable LER. A single-deprotection CAMP was used as a control, while the DD-CAMP compound (OAc) was tested at varying temperatures, doses and times. The control was tested at 110°C for 180 seconds (designated "Ctrl/110/180"), while OAc was tested at a number of different temperatures and times (110°C for 180 seconds,

110°C for 210 seconds, 110°C for 240 seconds, and 100°C for 270 seconds). "(P)" designates the polymer, and the value of (P) was the same for both compounds shown in FIG. 3. As can be seen by the graph, all test compound parameters resulted in lower LER values than the control. FIG. 4 shows the scanning electron microscope results for each curve of the graph.

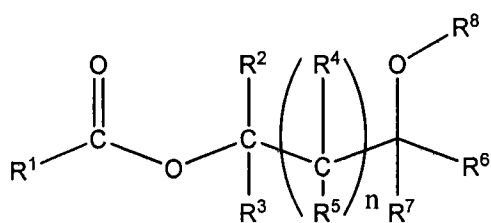
[00107] FIG. 5 illustrates a graph resulting from the plot of focus vs. line edge roughness (LER) for some embodiments of the invention. "(P)" designates the polymer, and the value of (P) was the same for all compounds shown in FIG. 5. The post exposure bake for this experiment was 110°C for 210 seconds.

[00108] While several aspects of the present invention have been described and depicted herein, alternative aspects may be effected by those skilled in the art to accomplish the same objectives. Accordingly, it is intended by the appended claims to cover all such alternative aspects as fall within the true spirit and scope of the invention.

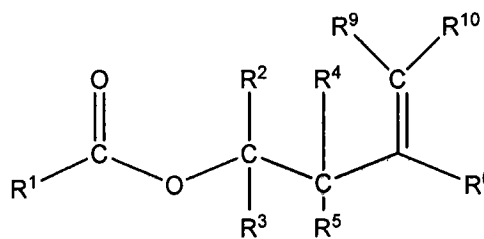
CLAIMS

We claim:

1. A compound of formula I or II:



I



II;

wherein

R¹ is a (C₂₋₃) alkene;

R² is (C₁₋₂₀)hydrocarbon optionally substituted with halogen;

R³, R⁴, R⁵, and R⁷ are selected independently in each instance from the group consisting of hydrogen and (C₁₋₂₀)hydrocarbon, wherein said (C₁₋₂₀)hydrocarbon may in each instance be substituted independently with halogen, and wherein a -CH₂- in the (C₁₋₂₀)hydrocarbon may be replaced by -Si(CH₃)₂-, -N(C=O)-, -O-, or -S-;

R⁶ is selected from the group consisting of hydrogen; -OR⁶⁰; and (C₁₋₂₀)hydrocarbon optionally substituted with halogen;

R⁶⁰ is (C₁₋₂₀)hydrocarbon;

R⁸ is selected from the group consisting of hydrogen; (C₁₋₂₀)hydrocarbon optionally substituted with one or more substituents selected from halogen, dioxane, and dioxolane; -C(=O)R⁸⁰; -C(=O)C(=O)-O-R⁸⁰; -C(=O)OR⁸⁰; and -C(=O)NHR⁸⁰;

R⁸⁰ is (C₁₋₂₀)hydrocarbon optionally substituted with halogen;

R⁹ and R¹⁰ are selected independently in each instance from the group consisting of hydrogen, (C₁₋₆)alkyl, and phenyl;

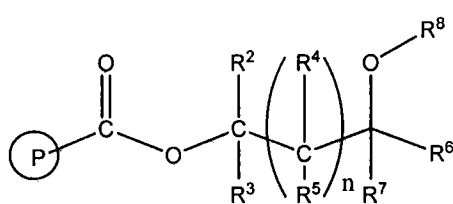
n is selected from 0, 1, or 2;

or, alternatively, a plurality of R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R⁶⁰, and R⁸⁰, together with the atoms to which they are attached, may form a monocyclic ring or a polycyclic ring system; and wherein a -CH₂- in the monocyclic ring or polycyclic ring system may be replaced by -Si(CH₃)₂-, -N(C=O)-, -O-, or -S-;

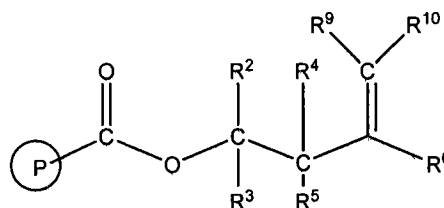
wherein:

when n is 0, at least one of R^6 and R^7 must be an aliphatic (C_{2-20})hydrocarbon;
and
when n is 2, the two R^5 substituents, together with the carbons to which they are attached, form a cyclopropyl ring.

2. A polymer of formula Ip or IIp:



Ip



IIp;

wherein

P is a polymer chain;

R^2 is (C_{1-20})hydrocarbon optionally substituted with halogen;

R^3 , R^4 , R^5 , and R^7 are selected independently in each instance from the group consisting of hydrogen and (C_{1-20})hydrocarbon, wherein said (C_{1-20})hydrocarbon may in each instance be substituted independently with halogen, and wherein a $-CH_2-$ in the (C_{1-20})hydrocarbon may be replaced by $-Si(CH_3)_2-$, $-N(C=O)-$, $-O-$, or $-S-$;

R^6 is selected from the group consisting of hydrogen; $-OR^{60}$; and (C_{1-20})hydrocarbon optionally substituted with halogen;

R^{60} is (C_{1-20})hydrocarbon;

R^8 is selected from the group consisting of hydrogen; (C_{1-20})hydrocarbon optionally substituted with one or more substituents selected from halogen, dioxane, and dioxolane; $-C(=O)R^{80}$; $-C(=O)C(=O)-O-R^{80}$; $-C(=O)OR^{80}$; and $-C(=O)NHR^{80}$;

R^{80} is (C_{1-20})hydrocarbon optionally substituted with halogen;

R^9 and R^{10} are selected independently in each instance from the group consisting of hydrogen, (C_{1-6})alkyl, and phenyl;

n is selected from 0, 1, or 2;

or, alternatively, a plurality of R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{60} , and R^{80} , together with the atoms to which they are attached, may form a monocyclic ring or a polycyclic ring system; and wherein a $-CH_2-$ in the monocyclic ring or polycyclic ring system may be replaced by $-Si(CH_3)_2-$, $-N(C=O)-$, $-O-$, or $-S-$;

wherein:

when n is 0, at least one of R⁶ and R⁷ must be an aliphatic (C₂₋₂₀)hydrocarbon;

and

when n is 2, the two R⁵ substituents, together with the carbons to which they are attached, form a cyclopropyl ring.

3. A compound according to claim 1, wherein the compound is of formula I.
4. A compound according to claim 1, wherein the compound is of formula II.
5. A polymer according to claim 2, wherein the compound is of formula Ip.
6. A polymer according to claim 2 wherein the compound is of formula IIp.
7. A compound according to claim 1, wherein R¹ is -C(=C)H or -C(=C)CH₃.
8. A compound or polymer according to claim 1 or claim 2, wherein R² is (C₁₋₁₀)hydrocarbon optionally substituted with fluorine and R³ is selected from hydrogen and methyl.
9. A compound or polymer according to any one of claim 1, claim 2, or claim 5, wherein R⁴ is hydrogen and R⁵ is hydrogen or methyl.
10. A compound or polymer according to claim 1 or claim 2, wherein R⁶ is hydrogen or (C₁₋₁₀)hydrocarbon and R⁷ is hydrogen, methyl, or phenyl.
11. A compound or polymer according to claim 1 or claim 2, wherein R⁵ and R⁷, together with the carbons to which they are attached, form a 3- to 6-membered monocyclic ring or a 7- to 10-membered bicyclic ring system, wherein a -CH₂- in the monocyclic ring or bicyclic ring system may be replaced by -Si(CH₃)₂-, -O-, -NC(=O)-, or -S-.
12. A compound or polymer according to claim 1 or claim 2, wherein R² and R⁶, or R² and R⁷, together with the carbons to which they are attached, form a 3- to 6-membered monocyclic carbocycle or a 7- to 10-membered bicyclic carbocycle; or
wherein R² and R⁶, together with the atoms to which they are attached, form a 5- or 6-membered oxygen-containing heterocycle.

13. A compound or polymer according to claim 1 or claim 2, wherein R² and R⁵, together with the carbons to which they are attached, form a monocyclic or bicyclic carbocycle.
14. A compound or polymer according to claim 1 or claim 2, wherein R² and R³, R⁴ and R⁵, or R⁶ and R⁷, together with the carbons to which they are attached, form a 3- to 6-membered monocyclic carbocycle or a 7- to 10-membered polycyclic carbocycle.
15. A compound or polymer according to claim 14, wherein R² and R³, together with the carbons to which they are attached, form a 3- to 6-membered monocyclic carbocycle, or R⁶ and R⁷, together with the carbons to which they are attached, form a 7- to 10-membered polycyclic carbocycle.
16. A compound or polymer according to claim 1 or claim 2, wherein R⁸ is – C(=O)OR⁸⁰.
17. A compound or polymer according to claim 16, wherein R⁸⁰ is (C₁₋₄)alkyl, phenyl, –CH₂-adamantyl, or adamantyl, wherein said phenyl and (C₁₋₄)alkyl may optionally be substituted with fluorine.
18. A compound or polymer according to claim 1 or claim 2, wherein R⁸ is – C(=O)R⁸⁰, and R⁸⁰ is selected from phenyl and (C₁₋₄)alkyl, wherein said phenyl and (C₁₋₄)alkyl may optionally be substituted with fluorine.
19. A compound or polymer according to claim 1 or claim 2, wherein R⁸ and R⁶⁰ form a dioxane or dioxolane optionally substituted with one or two methyl groups.
20. A compound or polymer according to claim 19, wherein R⁵ and R⁷ or R² and R⁷ form a ring and R⁸ and R⁶⁰ form a dioxane or dioxolane optionally substituted with one or two methyl groups.
21. A compound or polymer according to claim 1 or claim 2, wherein R⁸ is selected from the group consisting of hydrogen, (C₁₋₆)alkyl, and phenyl.
22. A compound or polymer according to claim 4 or claim 6, wherein R⁹ and R¹⁰ are each hydrogen.

23. A compound or polymer according to claim 4 or claim 6, wherein R⁶ and R⁹, together with the carbons to which they are attached, form an unsaturated 3- to 6-membered monocyclic carbocycle or an unsaturated 7- to 10-membered bicyclic carbocycle.
24. A compound or polymer according to claim 4 or claim 6, wherein R⁶ is hydrogen or methyl.
25. A compound or polymer according to claim 1 or claim 2, wherein R⁸⁰ is adamantyl.
26. A compound or polymer according to claim 1 or claim 2, wherein R² is methyl or phenyl.
27. A compound or polymer according to claim 1 or claim 2, wherein n is 0.
28. A compound or polymer according to claim 27, wherein R² and R⁷ form a 3- to 6-membered monocyclic carbocycle or a 7- to 10-membered bicyclic carbocycle.
29. A compound or polymer according to claim 28, wherein R² and R⁷ form a 5- or 6-membered monocyclic carbocycle.
30. A compound or polymer according to claim 27, wherein at least one of R² and R³ is (C₁₋₆)alkyl, and at least one of R⁶ and R⁷ is (C₁₋₆)alkyl.
31. A compound or polymer according to claim 30, wherein at least one of R² and R³ is methyl, and at least one of R⁶ and R⁷ is (C₁₋₃)alkyl.
32. A compound or polymer according to one of claims 28 to 31, wherein R⁸ and R⁶⁰ form a dioxane or dioxolane optionally substituted with one or two methyl groups.
33. A compound or polymer according to claim 1 or claim 2, wherein n is 1.
34. A compound or polymer according to claim 1 or claim 2, wherein n is 2.
35. A compound or polymer according to claim 1 or claim 2, wherein the halogen is fluorine.

36. A polymer according to claim 2, wherein P is a polyacrylate.
37. A polymer according to claim 2, wherein P is a polymethacrylate.
38. A polymer according to claim 2, wherein P is a copolymer of two or more monomers chosen from styrenes, acrylates and methacrylates.
39. A composition for photolithography comprising a polymer according to any one of claims 2-38.
40. A photoresist composition comprising a polymer according to any one of claims 2-38.
41. A photoresist substrate which is coated with a photoresist composition according to claim 40.
42. A method for preparing a substrate for photolithography, comprising coating said substrate with a composition according to claim 40.
43. A method for conducting photolithography on a substrate, comprising (a) providing a substrate, (b) coating said substrate with a composition according to claim 40, and (c) irradiating the coated substrate through a photomask.
44. A method according to claim 43, wherein said irradiation is conducted using electromagnetic radiation of wavelength 248 nm, 193 nm, 13.5 nm, or radiation from electron or ion beams.

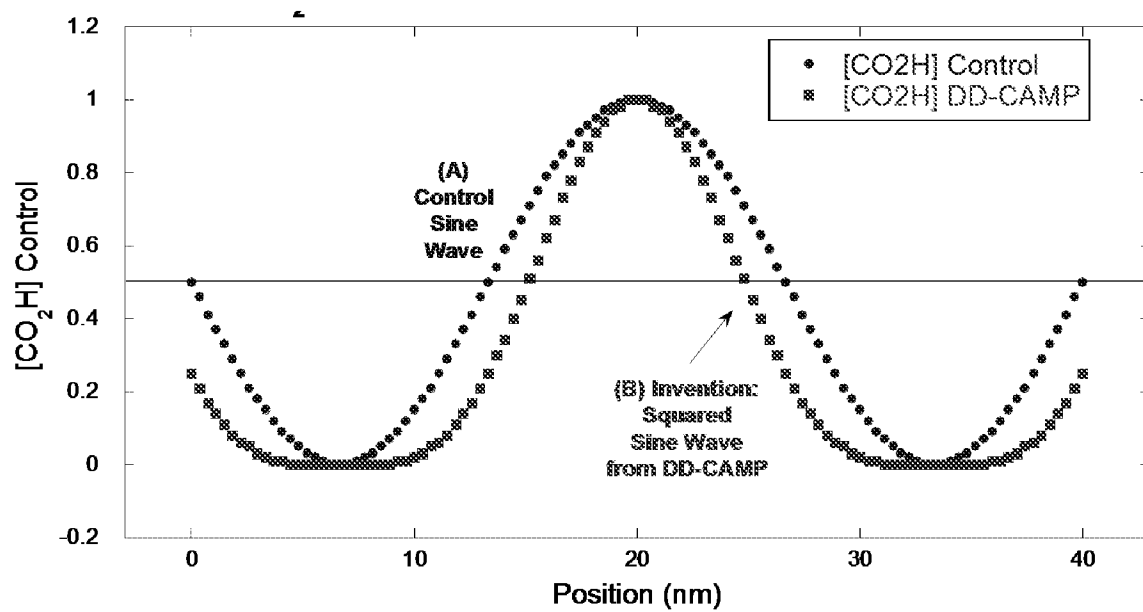


FIG. 1

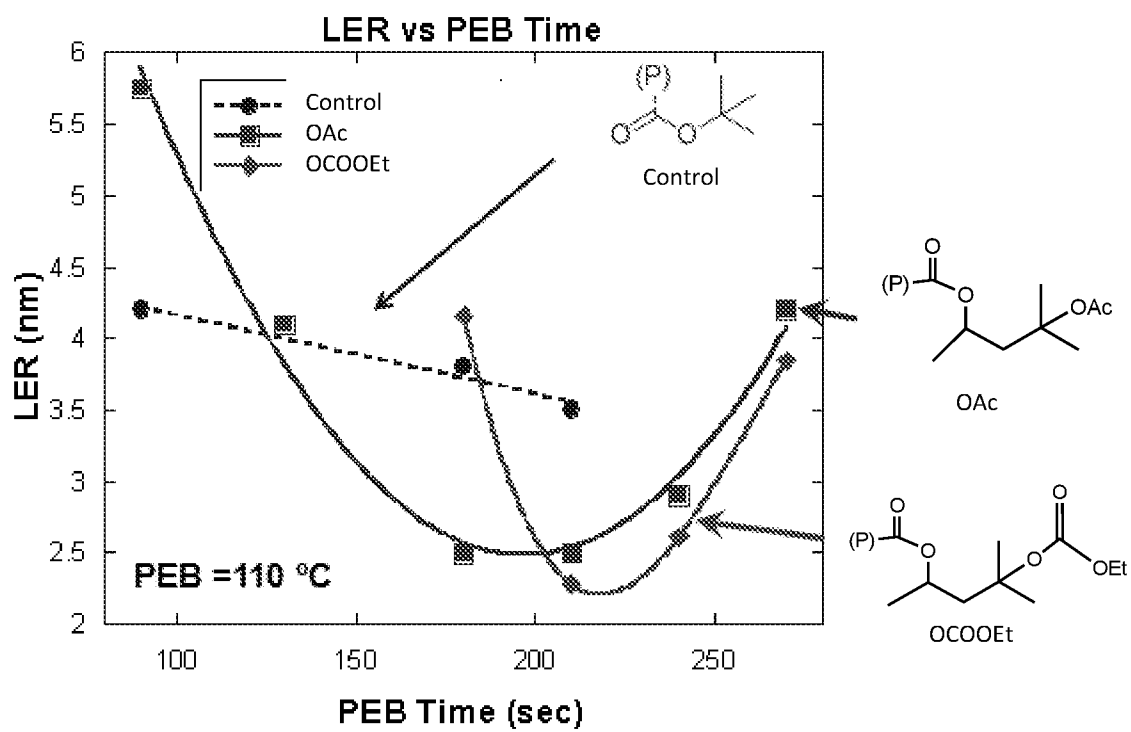


FIG. 2

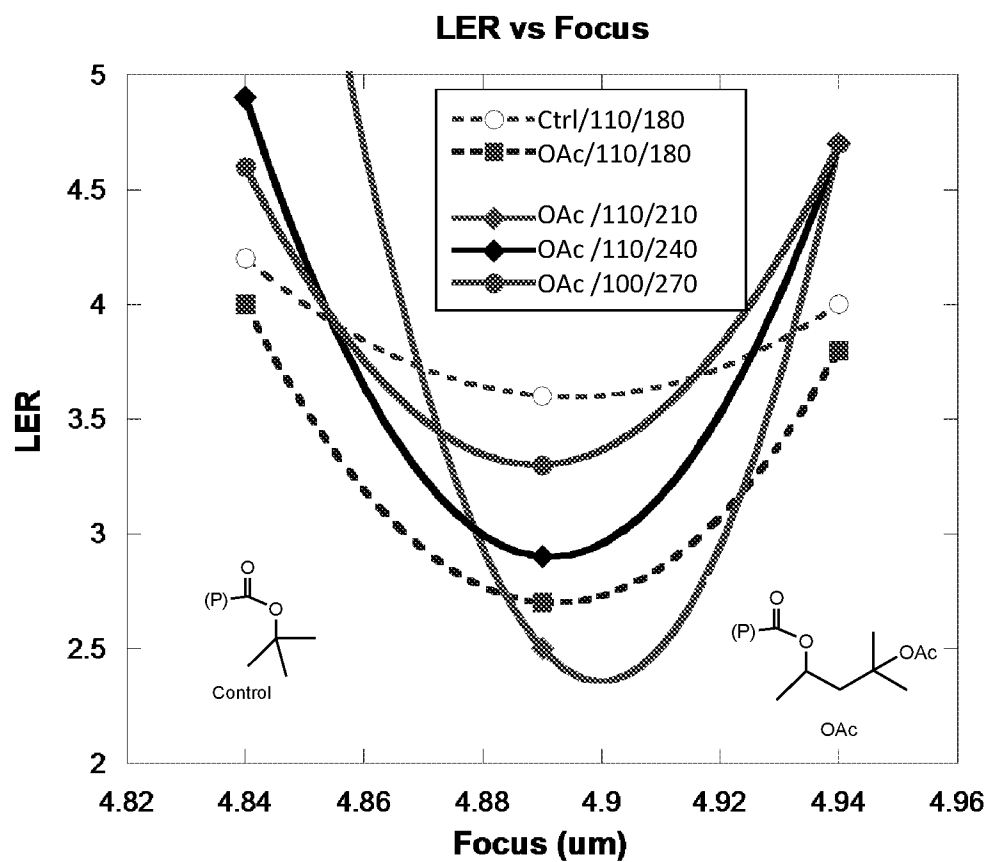


FIG. 3

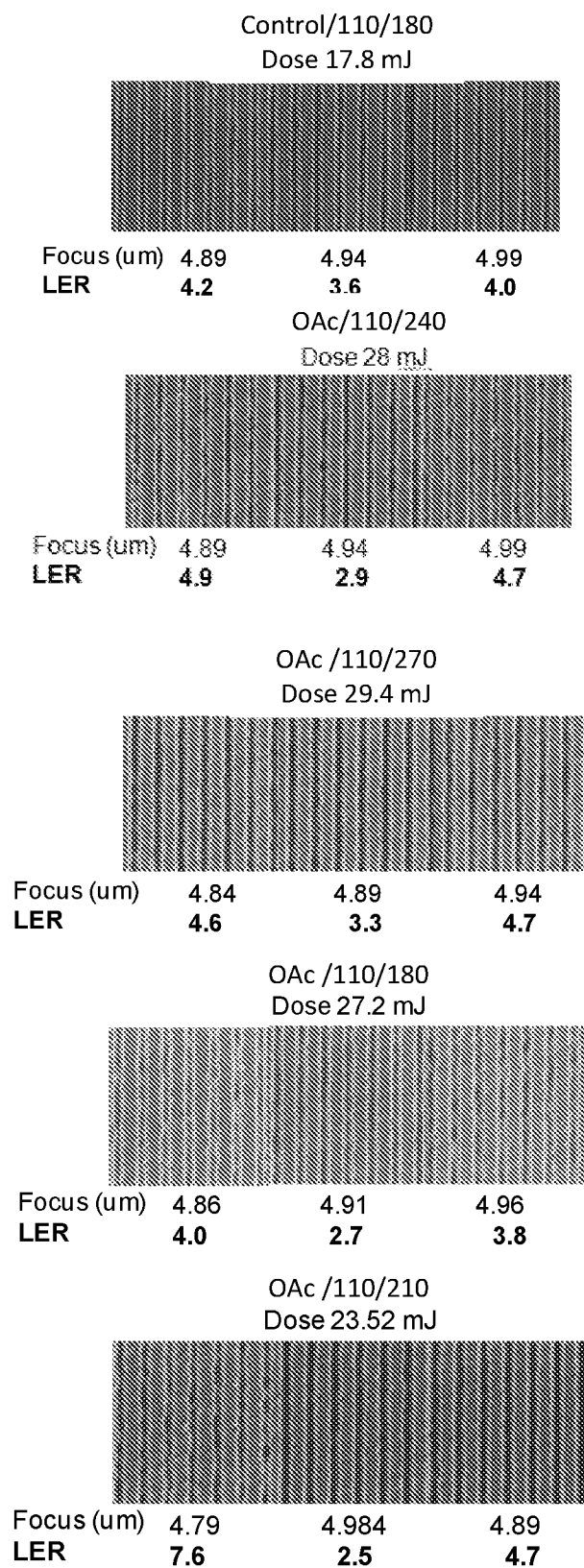


FIG. 4

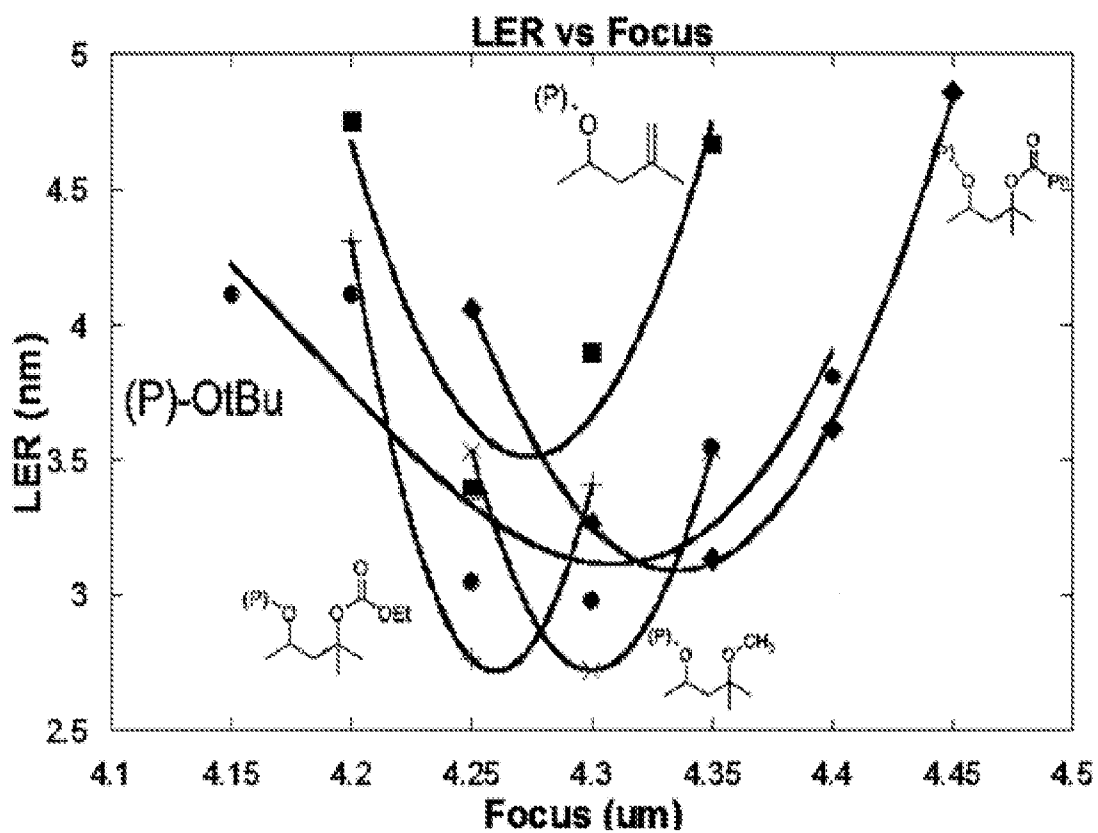


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/025171**A. CLASSIFICATION OF SUBJECT MATTER****C07C 69/025(2006.01)i, C08F 20/18(2006.01)i, C08F 12/08(2006.01)i, G03F 7/004(2006.01)i, G03F 7/039(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C 69/025; C08F 20/18; C08F 12/08; G03F 7/004; G03F 7/039

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: acrylate, 1-methyl-2-hydroxyethyl, hydroxycyclohexyl, cyclohexenyl, polymer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	UNEP PUBLICATIONS, HYDROXYPROPYL ACRYLATE CAS N° : 25584-83-2, SIDS Initial Assessment Report For SIAM 20, 2005, pp. 1-8 See the whole document.	1-3,5,7,36
A		4,6,37,38
X	JIN-BAEK KIM et al., Synthesis of copolymers containing 3-hydroxycyclohexyl methacrylate and their application as ArF excimer laser resists, Polymer, Volume 40, Issue 1, January 1998, pp. 273-276 See the whole document.	1-3,5,7,38
A		4,6,36,37
X	US 3536687 A1 (JOHN DAVID NORDSTROM) 27 October 1970 See abstract, columns 1-6, and claims 1-4.	1,2,4,6,7,37
A		3,5,36,38



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

21 July 2016 (21.07.2016)

Date of mailing of the international search report

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Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US2016/025171**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 8-35 and 41-44
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 8 to 35 do not comply with PCT Rule 6.1(a) since they have more than one subject matter, respectively.
Claims 41 to 44 do not comply with PCT Article 6 because they are referring to a multiple dependent claim which does not comply with PCT Rule 6.4(a).
3. ☒ Claims Nos.: 32, 39 and 40
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/025171Patent document
cited in search reportPublication
datePatent family
member(s)Publication
date

US 3536687 A1

27/10/1970

None