

Photoresist Compositions with Cyclic Olefin Polymers and Additive

Background of the Invention

In the microelectronics industry as well as in other industries involving construction of microscopic structures (e.g. micromachines, magnetoresistive heads, etc.), there is a continued desire to reduce the size of structural features. In the microelectronics industry, the desire is to reduce the size of microelectronic devices and/or to provide greater amount of circuitry for a given chip size.

The ability to produce smaller devices is limited by the ability of photolithographic techniques to reliably resolve smaller features and spacings. The nature of optics is such that the ability to obtain finer resolution is limited in part by the wavelength of light (or other radiation) used to create the lithographic pattern. Thus, there has been a continual trend toward use of shorter light wavelengths for photolithographic processes. Recently, the trend has been to move from so-called I-line radiation (350 nm) to 248 nm radiation.

For future reductions in size, the need to use 193 nm radiation appears likely. Unfortunately, photoresist compositions at the heart of current 248 nm photolithographic processes are typically unsuitable for use at shorter wavelengths.

While a photoresist composition must possess desirable optical characteristics to enable image resolution at a desired radiation wavelength, the photoresist composition must also possess suitable chemical and mechanical properties to enable transfer to the image from the patterned photoresist to an underlying substrate layer(s). Thus, a patternwise exposed positive photoresist must be capable of appropriate dissolution response (i.e. selective dissolution of exposed areas) to yield the desired photoresist structure. Given the extensive experience in the photolithographic arts with the use of aqueous alkaline developers, it is important to achieve appropriate dissolution behaviour in such commonly used developer solutions.

The patterned photoresist structure (after development) must be sufficiently resistant to enable transfer of the pattern to the underlying layer(s). Typically, pattern transfer is performed by some form of wet chemical etching or ion etching. The ability of the patterned photoresist layer to withstand the pattern transfer etch process (i.e., the etch resistance of the photoresist layer) is an important characteristic of the photoresist composition.

While some photoresist compositions have been designed for use with 193 nm radiation, these compositions have generally failed to deliver the true resolution benefit of shorter wavelength imaging due to a lack of performance in one or more of the abovementioned areas. Thus, there is a need for photoresist compositions that are

imageable with shorter wavelength radiation (e.g., 193 nm ultraviolet radiation) while possessing good developability and etch resistance.

Summary of the Invention

The invention provides photoresist compositions which are capable of high resolution lithographic performance, especially using 193 nm imaging radiation. The photoresist compositions of the invention possess the combination of imageability, developability and etch resistance needed to provide pattern transfer at very high resolutions which are limited only by the wavelength of imaging radiation. The photoresist compositions of the invention are generally characterised by the presence of (a) cyclic olefin polymers, and (b) a compound selected from the group consisting of a hydrophobic non-steroidal alicyclic component, a hydrophobic non-steroidal multi-alicyclic component and a saturated steroid component.

The invention also provides photolithographic methods using the photoresist compositions of the invention to create photoresist structures and methods using the photoresist structures to transfer patterns to an underlying layer(s). The photolithographic methods of the invention are preferably characterised by the use of 193 nm ultraviolet radiation patternwise exposure. The methods of the invention are preferably capable of resolving features of less than about 150 nm in size, more preferably less than about 115 nm in size (using 0.68 numerical aperture optics) without the use of a phase shift mask.

In a broad form, the invention provides a photoresist composition comprising (a) a cyclic olefin polymer, (b) a photosensitive acid generator, and (c) a compound selected from the group consisting of a hydrophobic non-steroidal alicyclic component, a hydrophobic non-steroidal multi- alicyclic component and a saturated steroid component.

In one aspect, the invention encompasses a photoresist composition comprising:

- (a) a cyclic olefin polymer comprising:
 - i) cyclic olefin units having polar functional moieties, and
 - ii) cyclic olefin units having acid labile moieties that inhibit solubility in aqueous alkaline solutions,
- (b) a photoactive component, and
- (c) a compound selected from the group consisting of a hydrophobic non-steroidal alicyclic component, a hydrophobic non-steroidal multi- alicyclic component and a saturated steroid component.

The cyclic olefin polymers of the invention preferably consist essentially of cyclic olefin monomeric units; more preferably they consist essentially of units i) and ii). Units i) preferably comprise acidic polar moieties having a $pK_a \leq 13$. The saturated steroids are preferably hydrophobic. Preferred saturated steroids are modified lithocholates. Hydrophobic non-steroidal

multialicyclic ("HNMP") components preferably comprise at least two C₇ or higher alicyclic moieties. Acid cleaving of an HNMP component preferably results in the formation of a compound having plural acidic polar functional groups and/or plural compounds each having at least one acidic polar group. A hydrophobic non-steroidal alicyclic component preferably comprises a C₁₀ or higher alicyclic moiety.

In another aspect, the invention encompasses a method of creating a patterned photoresist structure on a substrate, the method comprising:

(a) providing a substrate having a surface layer of the photoresist composition of the invention,

(b) patternwise exposing the photoresist layer to radiation whereby portions of the photoresist layer are exposed to radiation, and

(c) contacting the photoresist layer with an aqueous alkaline developer solution to remove the exposed portions of the photoresist layer to create the patterned photoresist structure.

Preferably, the radiation used in step (b) in the above method is 193 nm ultraviolet radiation.

The invention also encompasses processes for making conductive, semiconductive, magnetic or insulative structures using the patterned photoresist structures containing the compositions of the invention.

These and other aspects of the invention are discussed in further detail below.

Detailed Description of the Invention

The photoresist compositions of the invention are generally characterised by the presence of (a) a cyclic olefin polymer, and (b) a compound selected from the group consisting of a hydrophobic non-steroidal alicyclic component, a hydrophobic non-steroidal multi- alicyclic component and a saturated steroid component. The cyclic olefin polymer is characterised by the presence of at least one cyclic olefin monomeric unit. The cyclic olefin polymer preferably contains i) cyclic olefin units having polar functional moieties, and ii) cyclic olefin units having acid labile moieties that inhibit solubility in aqueous alkaline solutions. These compositions are especially capable of providing high resolution photolithographic patterns using 193 nm radiation with good developability and pattern transfer characteristics.

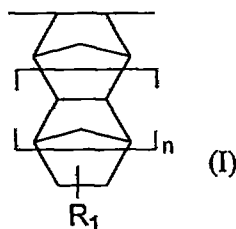
The invention further encompasses patterned photoresist structures containing the photoresist compositions of the invention, as well as processes for creating the photoresist structures and using the photoresist structures to form conductive, semiconductive and/or insulative structures.

The photoresist compositions of the invention preferably comprise:

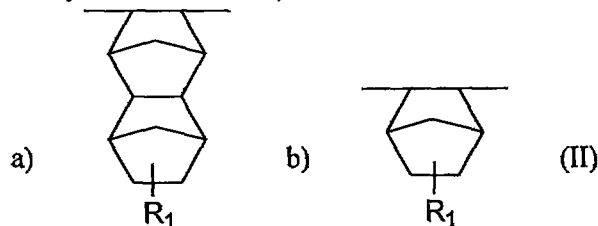
(a) a cyclic olefin polymer comprising:

- i) cyclic olefin units having polar functional moieties selected from acidic moieties that promote solubility in aqueous alkaline solutions and non-acidic polar moieties, and
- ii) cyclic olefin units having acid labile moieties that inhibit solubility in aqueous alkaline solutions,
- (b) a photoactive component, and
- (c) a compound selected from the group consisting of a hydrophobic non-steroidal alicyclic component, a hydrophobic non-steroidal multi- alicyclic component and a saturated steroid component.

Cyclic olefin units i) may be any cyclic olefin monomeric unit having an acidic polar functional group that promotes alkaline solubility or cyclic olefin monomeric unit having a non-acidic polar group. Examples of cyclic olefin monomers include the following monomers illustrated by structure (I) below where R_1 represents a polar moiety and n is zero or some positive integer:

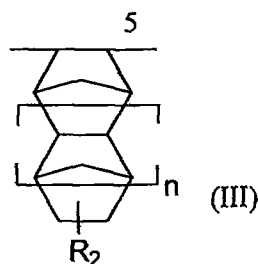


More preferably, the cyclic olefin units i) are selected from:

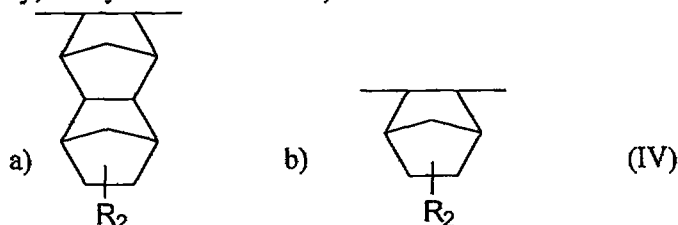


where R_1 represents either an acidic polar moiety which promotes solubility in aqueous alkaline solutions or a non-acidic polar group. Preferred acidic polar moieties have a $pK_a \leq 13$. Preferred acidic polar groups contain a selected from the group consisting of carboxyl, sulfonamidyl, fluoroalcohol, and other acidic polar groups. Preferred acidic polar moieties are carboxyl groups. Non-acidic polar moieties preferably have a $pK_a > 13$ and contain at least one heteroatom such as oxygen, nitrogen or sulfur. If desired, combinations of cyclic olefin units i) having differing polar functional groups may be used. Preferably, at least some or all of cyclic olefin units i) have acidic polar functionality.

Cyclic olefin units ii) may be any cyclic olefin monomeric unit having an acid labile moiety that inhibit solubility in aqueous alkaline solutions. Examples of cyclic olefin monomers include the following monomers illustrated by structure (III) below where R_2 represents an acid-labile protecting moiety and n is zero or some positive integer:



More preferably, the cyclic olefin units ii) are selected from:



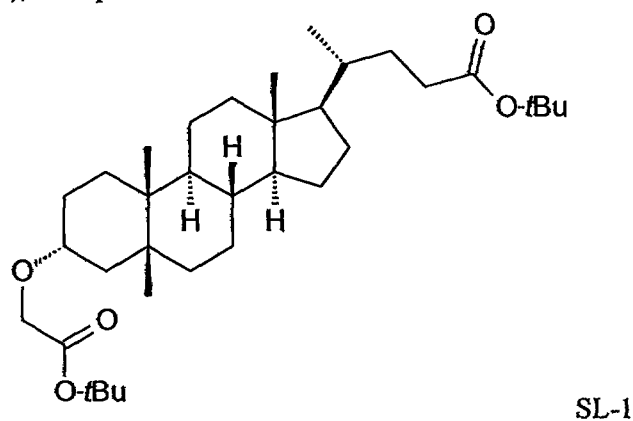
where R_2 represents an acid-labile protecting moiety. Preferred acid-labile protecting moieties are selected from the group consisting of tertiary alkyl (or cycloalkyl) carboxyl esters (e.g., *t*-butyl, methyl cyclopentyl, methyl cyclohexyl, methyl adamantyl), ester ketals, and ester acetals. Tertiary butyl carboxyl ester is a most preferred acid-labile protecting moiety. If desired, combinations of cyclic olefin units ii) having differing protecting functional groups may be used.

For photolithographic applications used in the manufacture of integrated circuit structures and other microscopic structures, the cyclic olefin polymers of invention preferably contain at least about 20 mole % of cyclic olefin units ii), more preferably about 40-90 mole %, most preferably about 60-90 mole %. The cyclic olefin polymers of the invention preferably contain about 10-80 mole % of cyclic olefin units i), more preferably about 10-60 mole %. Where cyclic olefin units i) comprise units having a carboxylic acid polar group, those units are preferably present at about 5 to 30 mole %, more preferably about 10-25 mole %, most preferably about 10-20 mole %, based on the overall cyclic olefin polymer composition. Where cyclic olefin units i) comprise units having a sulfonamidyl acidic polar group, those units are preferably present at about 15 to 50 mole %, more preferably about 20-40 mole %, based on the overall cyclic olefin polymer composition. The cyclic olefin polymers of the invention may contain other monomeric units in addition to units i) and ii). Preferably, the cyclic olefin polymers of the invention contain about 40 mole % or less of such other monomeric units, more preferably about 20 mole % or less. Most preferably, the cyclic olefin polymers of the invention consist essentially of cyclic olefin units i) and ii).

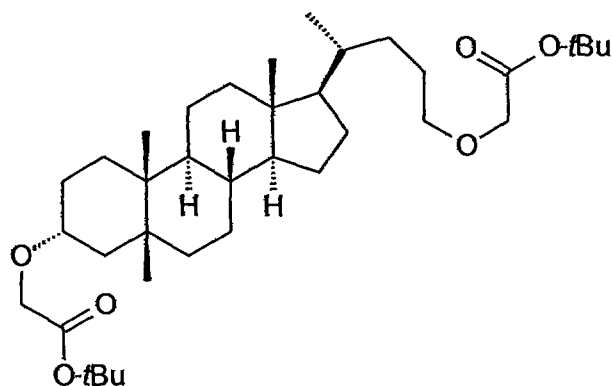
The photoresist compositions of the invention are further characterised by the presence of a component selected from a saturated steroid ("SS") component, a hydrophobic non-steroidal alicyclic ("HNA") component or a hydrophobic non-steroidal multi-alicyclic ("HNMP") component. This component generally enables and/or enhances the ability to resolve ultrafine lithographic features in response to conventional aqueous alkaline developers.

The SS component is characterised by the presence at least one saturated steroid (C_{17}) alicyclic skeletal structure. The saturated steroid component may comprise a compound having plural saturated steroid moieties (e.g., a bis-steroid or tris-steroid). Preferably, the SS component contains one or more pendant groups selected from the group consisting of acid labile moieties (e.g., a moiety that is responsive to acid generated in the photolithographic process whereby the moiety undergoes cleaving to provide a molecule which then acts to promote alkaline solubility). Preferred SS components may contain additional pendant groups, such as moieties selected from the group consisting of formyl groups, hydroxyl groups, and trifluoroacetyl groups. The pendant acid labile moiety(ies) if present, may be separated by one or more spacer groups such as shown in structures SL-1 and SL-2 below. In general, SS components that are more hydrophobic are preferred. If desired, a combination of SS components can be used.

Examples of preferred SS components include cholate esters (e.g., t-butyl lithocholate, t-butyldeoxycholate, t-butylcholate), ester-modified lithocholates (e.g., t-butyl-3-trifluoroacetyllithocholate, t-butyl-3-acetyllithocholate, t-butyl-3-pivalyllithocholate), ester-modified cholate esters (e.g., t-butyl-3,7,12-triformylcholate, t-butyl-tris-(3,7,12-trifluoroacetyl)cholate), and spaced lithocholates such as structures SL-1 and SL-2 below.



SL-1



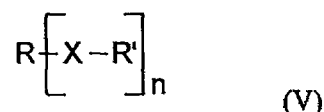
SL-2

wherein tBu is a tertiary butyl group. A most preferred SS component is t-butyl-3-trifluoroacetyllithocholate.

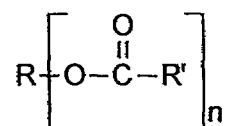
The HNMP component is characterised by the presence at least two distinct non-steroidal alicyclic structures (i.e. structures that do not contain the C₁₇ condensed cyclic structure characteristic of steroid compounds). The alicyclic ring structures each preferably contain at least 7 carbon atoms (C₇), more preferably about 10-30 carbon atoms, excluding pendant groups. The overall HNMP component preferably contains about 20-60 carbon atoms.

Broadly, the HNMP component encompasses compounds containing at least two acid labile linking groups and at least two alicyclic moieties such that an acid labile link exists between at least two alicyclic moieties.

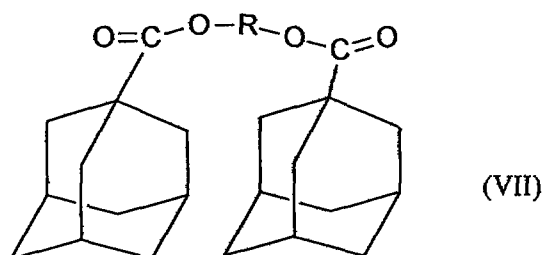
The HNMP compound contains plural acid labile linking moieties and plural alicyclic moieties. One structure of the compound may be represented by:



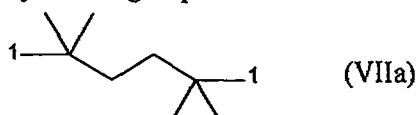
The bond between R and X is acid labile such that at least one X_c-R' derivative is formed by acid cleaving of the R-X bond where X_c is an acidic polar pendant group from R'. n is at least 2. If R contains an alicyclic moiety, then at least one R' comprises an alicyclic moiety. If R does not contain an alicyclic moiety, then at least two R' groups each comprise an alicyclic moiety. Where X is a carboxylic group, the structure becomes:



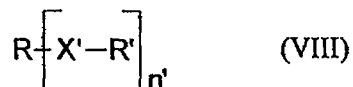
where the bond at R-O is acid labile. After cleaving, a carboxylic acid group would remain pendant on R'. Where n is 2 and R' comprises adamantane moieties, a structure might be as follows:



where R preferably is a combination of acid labile ester groups such as two t-butyl ester groups bonded together (structure VIIa below where 1 indicates the location of acid labile linking sites) or some other acid labile linkage. The result of cleaving would be plural compounds containing R' moieties with pendant carboxylic acid groups.

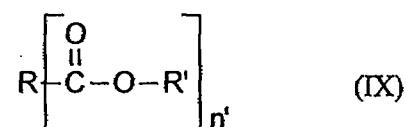


Alternatively, the HNMP compound may have a structure

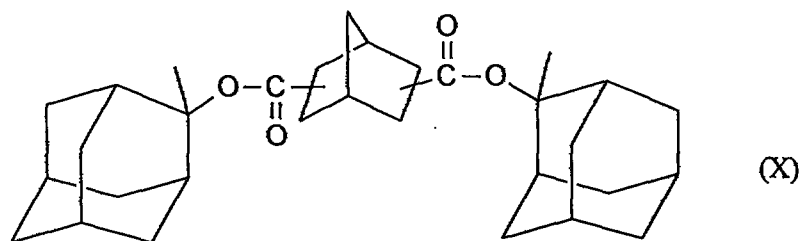


where the bond between R' and X' is acid labile such that an $R-(X_c)_n$ derivative is formed by acid cleaving of the $R'-X'$ bond where X_c is an acidic polar pendant group from R . n' is at least 2. At least one R' comprises an alicyclic moiety and at least one total of either R or the remaining R' moieties comprises an alicyclic moiety. The end result after cleaving in any case would be the creation of two smaller molecules each containing an alicyclic moiety and the creation of plural polar functional groups pendant from R .

Where X is a carboxylic group, the structure becomes:

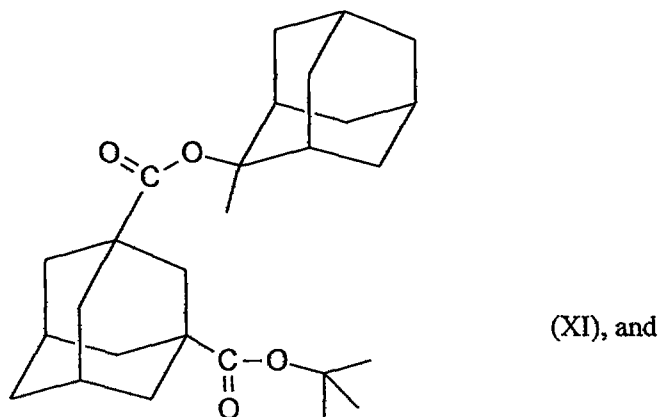


After cleaving, R would contain plural (n') carboxylic acid pendant groups. Where R is a norbornyl alicyclic, $n' = 2$ and each R' contains adamantane, an HNM additive could have the following structure:

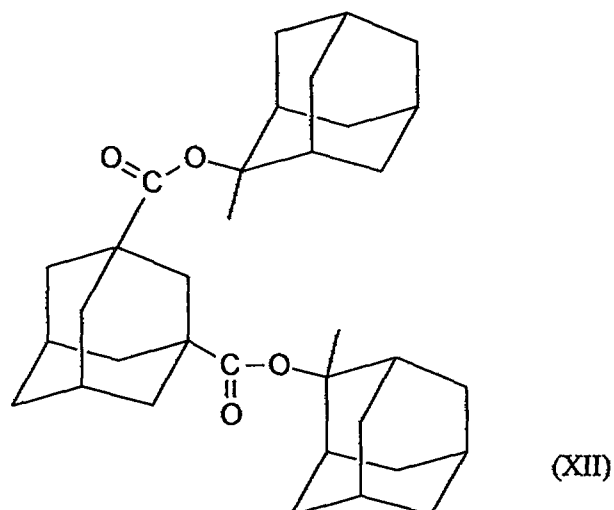


After cleaving, the norbornyl compound would have two pendant carboxylic acid groups.

Examples of other possible HNMP additive structures include:



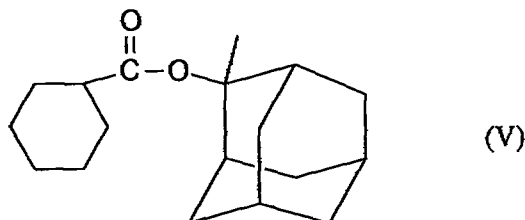
(XI), and



In the HNMP compounds used in the invention, the acid labile linking groups advantageously react with acid generated in the photolithographic process whereby the moiety undergoes cleaving to provide molecules or substantially reduced molecular weight which then act to promote alkaline solubility of radiation-exposed portions of the photoresist. Preferred acid labile linking moieties contain at least one moiety selected from the group consisting of tertiary alkyl (or cycloalkyl) carboxyl esters (e.g., t-butyl, methyl cyclopentyl, methyl cyclohexyl, methyl adamantyl), ester ketals, and ester acetals. HNMP components may also contain pendant groups which increase the bulk of the molecule and/or increase the hydrophobicity of the molecule in a way that enhances performance of the photoresist composition. If desired, a combination of HNMP components can be used.

Examples of preferred HNMP components include bis-carboxyl esters of adamantanes and higher fused ring systems. A most preferred HNMP component is bis-adamantane t-butyl carboxylate.

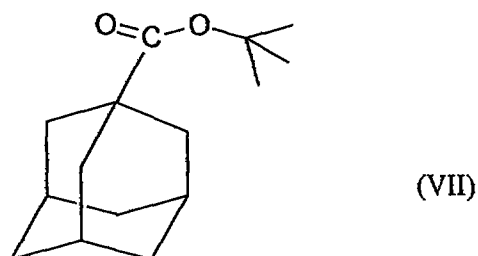
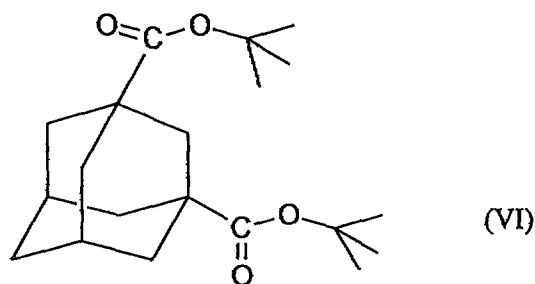
The HNA component is characterised by the presence a non-steroidal alicyclic structure (i.e. a structure that does not contain the C₁₇ condensed cyclic structure characteristic of steroid compounds). The alicyclic ring structure preferably contains at least 6 carbon atoms (C₆), more preferably at least 10 carbon atoms, most preferably about 10-30 carbon atoms. The overall HNA additive preferably contains at least about 14 carbon atoms, more preferably about 14-50 carbon atoms. If desired, the HNA additives of the invention may contain more than one alicyclic moiety. Where the composition comprises two alicyclic moieties, it is preferred that they are separated by an acid labile linking group. An example of such a multi-alicyclic compound is shown in formula (V) below:



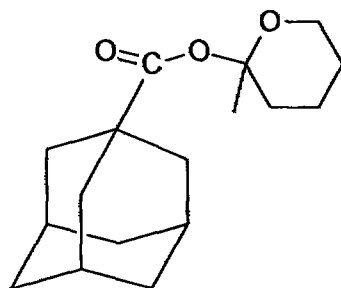
Preferably, the HNA component contains one or more pendant acid labile moieties (e.g., a moiety that is responsive to acid generated in the photolithographic process whereby the moiety undergoes cleaving to provide a molecule which then acts to promote alkaline solubility). Preferred acid labile moieties are selected from the group consisting of tertiary alkyl (or cycloalkyl) carboxyl esters (e.g., t-butyl, methyl cyclopentyl, methyl cyclohexyl, methyl adamantyl), ester ketals, and ester acetals. T-butyl carboxylate is a preferred acid labile pendant group. HNA components may also contain pendant groups which increase the bulk of the molecule and/or increase the hydrophobicity of the molecule in a way that enhances performance of the photoresist composition. The pendant acid labile moiety(ies) if present, may be separated from the alicyclic moiety by one or more spacer groups. If desired, a combination of HNA components can be used.

Examples of preferred HNA components include carboxyl esters of adamantanes and higher fused alicyclic ring systems. A most preferred HNA component is adamantane t-butyl carboxylate.

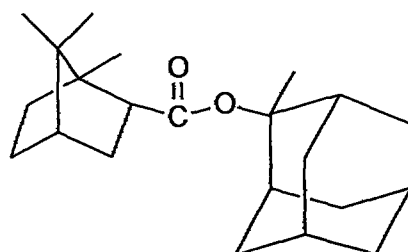
Some examples of HNA components are illustrated by the structures below:



11



(VIII), and



(IX).

In addition to the cyclic olefin polymers, the photoresist compositions of the invention contain a photosensitive acid generator (PAG). The invention is not limited to the use of any specific PAG or combination of PAG's, that is the benefits of the invention may be achieved using various photosensitive acid generators known in the art. Preferred PAG's are those which contain reduced amounts (or preferably no) aryl moieties. Where aryl-containing PAG is employed, the absorptive characteristics of the PAG at 193 nm may restrict the amount of PAG that can be included in the formulation.

Examples of suitable photosensitive acid generators include (but preferably with alkyl substituted for one or more of any indicated aryl moieties) onium salts such as triaryl sulfonium hexafluoroantimonate, diaryliodonium hexafluoroantimonate, hexafluoroarsenates, triflates, perfluoroalkane sulfonates (e.g., perfluoromethane sulfonate, perfluorobutane, perfluorohexane sulfonate, perfluorooctane, etc.), substituted aryl sulfonates such as pyrogallols (e.g. trimesylate of pyrogallol or tris(sulfonate) of pyrogallol), sulfonate esters of hydroxyimides, N-sulfonyloxynaphthalimides (N-camphorsulfonyloxynaphthalimide, N-pentafluorobenzenesulfonyloxynaphthalimide), α - α' bis-sulfonyl diazomethanes, naphthoquinone-4-diazides, alkyl disulfones and others.

The photoresist compositions of the invention will typically contain a solvent prior to their application to the desired substrate. The solvent may be any solvent conventionally used with acid-catalyzed photoresists which otherwise does not have any excessively adverse impact on the performance of the photoresist composition. Preferred solvents are propylene glycol monomethyl ether acetate, cyclohexanone, and ethyl cellosolve acetate.

The compositions of the invention may further contain minor amounts of auxiliary components such as dyes/sensitisers, base additives, etc. as are known in the art. Preferred base additives are weak bases which scavenge trace acids while not having an excessive impact on the

performance of the photoresist. Preferred base additives are (aliphatic or alicyclic) tertiary alkyl amines or t-alkyl ammonium hydroxides such as t-butyl ammonium hydroxide (TBAH).

The photoresist compositions of the invention preferably contain about 0.5-20 wt.% (more preferably about 3-15 wt.%) photosensitive acid generator based on the total weight of cyclic olefin polymer in the composition. Where a solvent is present, the overall composition preferably contains about 50-90 wt.% solvent. The composition preferably contains about 1 wt.% or less of said base additive based on the total weight of acid sensitive polymer. The photoresist compositions of the invention preferably contain at least about 5 wt.% of SS HNA or HNMP component based on the total weight of cyclic olefin polymer in the composition, more preferably about 10-25 wt.%, most preferably about 10-20 wt.%.

The invention is not limited to any specific method of synthesising the cyclic olefin polymers used in the invention. Preferably, the cyclic olefin polymers are formed by addition polymerisation. Examples of suitable techniques are disclosed in US Patents 5,468,819 and 5,705,503 assigned to B.F. Goodrich Company, the disclosures of which are incorporated herein by reference.

The cyclic olefin polymers of the invention preferably have a weight average molecular weight of about 5,000-100,000, more preferably about 10,000-50,000.

The photoresist compositions of the invention can be prepared by combining the cyclic olefin polymer, the PAG, and the SS, HNA or HNMP component and any other desired ingredients using conventional methods. The photoresist composition to be used in photolithographic processes will generally have a significant amount of solvent.

The photoresist compositions of the invention are especially useful for photolithographic processes used in the manufacture of integrated circuits on semiconductor substrates. The compositions are especially useful for photolithographic processes using 193 nm UV radiation. Where use of other radiation (e.g., mid-UV, 248 nm deep UV, x-ray, or e-beam) is desired, the compositions of the invention can be adjusted (if necessary) by the addition of an appropriate dye or sensitizer to the composition. The general use of the photoresist compositions of the invention in photolithography for semiconductors is described below.

Semiconductor photolithographic applications generally involve transfer of a pattern to a layer of material on the semiconductor substrate. The material layer of the semiconductor substrate may be a metal conductor layer, a ceramic insulator layer, a semiconductor layer or other material depending on the stage of the manufacture process and the desired material set for the end product. In many instances, an antireflective coating (ARC) is applied over the material layer before application of the photoresist layer. The ARC layer may be any conventional ARC which is compatible with acid catalysed photoresists.

Typically, the solvent-containing photoresist composition is applied to the desired semiconductor substrate using spin coating or other technique. The substrate with the photoresist coating is then preferably heated (pre-exposure baked) to remove the solvent and improve the coherence of the photoresist layer. The thickness of the applied layer is preferably as thin as possible with the provisos that the thickness is preferably substantially uniform and that the photoresist layer be sufficient to withstand subsequent processing (typically reactive ion etching) to transfer the lithographic pattern to the underlying substrate material layer. The pre-exposure bake step is preferably conducted for about 10 seconds to 15 minutes, more preferably about 15 seconds to one minute. The pre-exposure bake temperature may vary depending on the glass transition temperature of the photoresist. Preferably, the pre-exposure bake is performed at temperatures which are at least 20°C below T_g .

After solvent removal, the photoresist layer is then patternwise-exposed to the desired radiation (e.g. 193 nm ultraviolet radiation). Where scanning particle beams such as electron beam are used, patternwise exposure may be achieved by scanning the beam across the substrate and selectively applying the beam in the desired pattern. More typically, where wavelike radiation forms such as 193 nm ultraviolet radiation, the patternwise exposure is conducted through a mask which is placed over the photoresist layer. For 193 nm UV radiation, the total exposure energy is preferably about 100 millijoules/cm² or less, more preferably about 50 millijoules/cm² or less (e.g. 15-30 millijoules/cm²).

After the desired patternwise exposure, the photoresist layer is typically baked to further complete the acid-catalyzed reaction and to enhance the contrast of the exposed pattern. The post-exposure bake is preferably conducted at about 100-175°C, more preferably about 125-160°C. The post-exposure bake is preferably conducted for about 30 seconds to 5 minutes.

After post-exposure bake, the photoresist structure with the desired pattern is obtained (developed) by contacting the photoresist layer with an alkaline solution which selectively dissolves the areas of the photoresist which were exposed to radiation. Preferred alkaline solutions (developers) are aqueous solutions of tetramethyl ammonium hydroxide. Preferably, the photoresist compositions of the invention can be developed with conventional 0.26N aqueous alkaline solutions. The photoresist compositions of the invention can also be developed using 0.14N or 0.21N or other aqueous alkaline solutions. The resulting photoresist structure on the substrate is then typically dried to remove any remaining developer solvent. The photoresist compositions of the invention are generally characterised in that the product photoresist structures have high etch resistance. In some instances, it may be possible to further enhance the etch resistance of the photoresist structure by using a post-silylation technique using methods

known in the art. The compositions of the invention enable the reproduction of lithographic features.

The pattern from the photoresist structure may then be transferred to the material (e.g., ceramic, metal or semiconductor) of the underlying substrate. Typically, the transfer is achieved by reactive ion etching or some other etching technique. In the context of reactive ion etching, the etch resistance of the photoresist layer is especially important. Thus, the compositions of the invention and resulting photoresist structures can be used to create patterned material layer structures such as metal wiring lines, holes for contacts or vias, insulation sections (e.g., damascene trenches or shallow trench isolation), trenches for capacitor structures, etc. as might be used in the design of integrated circuit devices.

The processes for making these (ceramic; metal or semiconductor) features generally involve providing a material layer or section of the substrate to be patterned, applying a layer of photoresist over the material layer or section, patternwise exposing the photoresist to radiation, developing the pattern by contacting the exposed photoresist with a solvent, etching the layer(s) underlying the photoresist layer at spaces in the pattern whereby a patterned material layer or substrate section is formed, and removing any remaining photoresist from the substrate. In some instances, a hard mask may be used below the photoresist layer to facilitate transfer of the pattern to a further underlying material layer or section. Examples of such processes are disclosed in US Patents 4,855,017; 5,362,663; 5,429,710; 5,562,801; 5,618,751; 5,744,376; 5,801,094; and 5,821,469, the disclosures of which patents are incorporated herein by reference. Other examples of pattern transfer processes are described in Chapters 12 and 13 of "Semiconductor Lithography, Principles, Practices, and Materials" by Wayne Moreau, Plenum Press, (1988), the disclosure of which is incorporated herein by reference. It should be understood that the invention is not limited to any specific lithography technique or device structure.

Example 1 (comparison)

For the purpose of lithographic experiments, a photoresist formulation containing norbornene copolymers containing 85% of norbornene t-butylester (NB-t-BE) and 15% of norbornene-carboxylic acid (as pendant groups) (NB-CA) was prepared by combining the materials set forth below, expressed in part by weight.

Propylene glycol monomethyl ether acetate	37
Copolymers of NB-t-BE and NB-CA(85/15)	4
Di-t-butylphenyliodonium perfluorooctanesulfonate	0.16
Tetrabutyl ammonium hydroxide	0.008

The photoresist formulations were spin-coated (for 30 seconds) onto an antireflective material (ArX[®], Shipley Company) layer applied silicon wafers. The photoresist layer was soft

baked at 130°C for 60 seconds on a vacuum hot plate to produce film of about 0.4µm thickness. The wafers were then exposed to 193 nm radiation (0.6NA ArF, SI stepper). The exposure pattern was an array of lines and spaces of varying dimensions down to 0.1µm. The exposed wafers were post-exposure baked on a vacuum hot plate at 150°C for 90 seconds. The pattern exposed photoresist was then (puddle) developed using 0.263N tetramethyl ammonium hydroxide developer. The pattern was then examined by scanning electron microscopy (SEM). The cross-sectioned SEM pattern indicated no resolution below 200 nm L/S (lines-space pairs) due to lines falling over each other. Even lines-space pairs above 200 nm were not fully resolved because of excessive scumming/residues between the lines.

Example 2

To a 12L 4-necked round-bottomed flask equipped with an overhead stirrer, thermocouple temperature monitor and a 1L constant-pressure addition funnel with a nitrogen inlet was added 500g (1.328 mol) of lithocholic acid and 4 L of dry THF. The addition funnel was charged sequentially with 1920 mL (13.6 mol) of trifluoroacetic anhydride. The flask was cooled in ice under nitrogen and the trifluoroacetic anhydride was added in a thin stream maintaining a temperature of <10°C. The mixture was allowed to warm to room temperature with stirring overnight after which the solvent and excess trifluoroacetic anhydride was removed on a rotary evaporator. The thick, viscous intermediate was returned to the 12L flask which was refreshed with an additional 4L of THF. The addition funnel was charged with 740g (10 mol) of t-butyl alcohol (diluted with a small amount of THF to prevent solidification). The flask was again cooled in ice and the t-butyl alcohol was added in a thin stream while maintaining a temperature of less than 10°C. The mixture was allowed to reach room temperature with stirring overnight. Approximately 200g of solid NaHCO₃ was then added and stirring was continued for an additional two hours. The solvent and excess t-butyl alcohol was then removed on a rotary evaporator and the mixture taken up in 4L of ethyl ether and carefully washed with 3X800mL of saturated NaHCO₃ followed by 2X1000mL with water. The solvent was dried with stirring over MgSO₄ for 1 hour, filtered and evaporated on a rotary evaporator. The thick, viscous residue was eluted slowly with hexane through a large column containing 800g of silica gel in hexane. The combined product fractions were evaporated on a rotary evaporator and residual solvent was removed to a constant weight under vacuum at 40°C under a thin stream of nitrogen to yield 620g (88%) of the desired product as an off-white syrup. This material has been successfully crystallised from pentane at -78°C to give a low melting white wax.

Example 3

This example demonstrates the benefit of the additives of the invention. The photoresist formulation was prepared by combining the materials set forth below, expressed in part by weight.

Propylene glycol monomethyl ether acetate	38
Poly(norbornene) with t-BE and CA groups(t-BE/CA: 85/15)	4
Di-t-butylphenyliodonium perfluorooctanesulfonate	0.16
t-butyl-3-trifluoroacetylthiocholate (Example 2)	0.4
Tetrabutylammoniumhydroxide	0.008

The photoresist formulations were spin-coated onto antireflective material (ArX[®], Shipley Company) applied silicon wafers, pattern-wise exposed (193nm radiation), and developed in the same manner as in example 1. The resulting pattern was then examined by scanning electron microscopy (SEM). Line-space pairs of 140 nm and above were well resolved with clean profiles. The required exposed energy for this formulation is in the range of 25-35 mJ/cm².

Example 4

To a suspension containing 50g (0.342 mol) of 2,6-dimethyl-2,5-hexanediol in 600 ml of methylene chloride, 76.14g (0.762 mol) of triethylamine was added at room temperature. The resultant suspension was stirred at room temperature until it turned into clear solution. 149.5g (0.7524 mol) of adamantane-1-carbonyl chloride was added to the above solution at 0°C. After the addition was complete, the reaction mixture was stirred at room temperature for 12 hours, and subsequently under refluxing conditions for 2 hours. The reaction mixture was filtered to remove the triethylamine hydrochloride formed during the reaction. The filtrate was washed with water (x500 ml) several times, dried over anhydrous sodium sulfate, and then concentrated under reduced pressure. Purification of the residue through a column chromatography (silica gel; hexane/methylene chloride: 9:1) resulted in 128g (~80%) of white solid which was identified as 2,5-bis(adamantane-1-carboxyloxy)-2,5-dimethylhexane by NMR spectroscopy.

Example 5

This example demonstrates the benefit of the additives of the invention. The photoresist formulation was prepared by combining the materials set forth below, expressed in part by weight.

Propylene glycol monomethyl ether acetate	38
Poly(norbornene) with t-BE and CA groups(t-BE/CA: 85/15)	4
Di-t-butylphenyliodonium perfluorooctanesulfonate	0.16
2,5-Bis(adamantane-1-carboxyloxy)-2,5-dimethylhexane (Example 4)	0.4
Tetrabutylammoniumhydroxide	0.008

The photoresist formulations were spin-coated onto antireflective material (ArX[®], Shipley Company) on silicon wafers, pattern-wise exposed (193nm radiation), and developed in the same manner as in example 1. The resulting pattern was then examined by scanning electron microscopy (SEM). Line-space pairs of 130 nm and above were well resolved with clean profiles. The exposure energy required for this formulation is in the range of 20-30 mJ/cm².

Example 6

To a suspension containing 25.34g (0.342 mol) of t-butylalcohol in 600 ml of methylene chloride, 38.07g (0.3815 mol) of triethylamine was added at room temperature. The resultant suspension was stirred at room temperature until it turned into clear solution. 74.75g (0.3762 mol) of adamantane-1-carbonyl chloride was added to the above solution at 0°C. After the addition was complete, the reaction mixture was stirred at room temperature for 12 hours, and subsequently under refluxing conditions for 2 hours. The reaction mixture was filtered to remove the triethylamine hydrochloride formed during the reaction. The filtrate was washed with water (x500 ml) several times, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. Purification of the residue through a column chromatography (silica gel; hexane/methylene chloride: 9:1) resulted in 48.4g (~60%) of white solid which was identified as adamantane-1-carboxylic acid t-butylester by NMR spectroscopy.

Example 7

This example demonstrates the benefit of the additives of the invention. The photoresist formulation was prepared by combining the materials set forth below, expressed in part by weight.

Propylene glycol monomethyl ether acetate	38
Poly(norbornene) with t-BE and CA groups(t-BE/CA: 85/15)	4
Di-t-butylphenyliodonium perfluorooctanesulfonate	0.16
Adamantane-1-carboxylic acid t-butyl ester (Example 6)	0.4
Tetrabutyl ammonium hydroxide	0.008

The photoresist formulations were spin-coated onto antireflective material (ArX[®], Shipley Company) on silicon wafers, pattern-wise exposed (193 nm radiation), and developed in the same manner as in example 1. The resulting pattern was then examined by scanning electron microscopy (SEM). Line-space pairs of 140 nm and above were well resolved with clean profiles. The exposure energy required for this formulation is in the range of 20-30 mJ/cm².



The claims defining the invention are as follows:

1. A photoresist composition comprising (a) a cyclic olefin polymer, (b) a photosensitive acid generator, and (c) a compound selected from the group consisting of a hydrophobic non-steroidal alicyclic component, a hydrophobic non-steroidal multi-alicyclic component and a saturated steroid component.
2. The photoresist composition of claim 1 wherein said cyclic olefin polymer comprises:
 - (A) cyclic olefin units having acidic polar functional moieties, and
 - (B) cyclic olefin units having acid labile moieties that inhibit solubility in aqueous alkaline solutions.
3. The composition of claim 1 or 2 wherein said cyclic olefin polymer contains about 5-40 mole % of cyclic olefin units i).
4. The composition of any one of claims 1 to 3 wherein said cyclic olefin polymer consists essentially of cyclic olefin units i) and cyclic olefin units ii).
5. The composition of claim 2 wherein said polar functional moieties are selected from the group consisting of acidic polar functional moieties having a pKa of about 13 or less and non-acidic polar functional moieties having a pKa greater than 13 or combinations thereof.
6. The composition of any one of the preceding claims wherein said cyclic olefin units i) contain an acidic polar functional moiety comprising an acidic polar group selected from the group consisting of carboxyl, sulfonamidyl, fluoroalcohol, and other acidic polar groups.
7. The composition of any one of the preceding claims wherein said cyclic olefin units ii) contain an acid-labile protecting group containing a moiety selected from the group consisting of tertiary alkyl carboxyl esters, tertiary cycloalkyl carboxyl, ester ketals and ester acetals.
8. The composition of claim 1 wherein said hydrophobic compound contains at least 10 carbon atoms and has an alicyclic moiety.
9. The composition of any one of the preceding claims wherein said hydrophobic non-steroidal alicyclic component comprises at least one non-steroidal C₆ or higher alicyclic moiety, said non-steroidal multi-alicyclic component comprises at least two non-steroidal C₇ or higher alicyclic moiety and said saturated steroid compound comprises at least one saturated C₁₇ steroidal alicyclic skeleton having at least one pendant acid labile protecting group.
10. The composition of claim 9 wherein said hydrophobic nonsteroidal alicyclic component comprises at least one nonsteroidal C₁₀-C₃₀ alicyclic moiety.
11. The composition of claim 1 wherein said saturated steroid component further comprises at least one additional pendant moiety selected from the group consisting of hydroxyl, formyl, acetyl, and fluoroacetyl groups.



12. The composition of claim 1 wherein said saturated steroid component comprises a steroid compound selected from the group consisting of cholate esters, ester-modified cholate esters and spaced lithocholates.

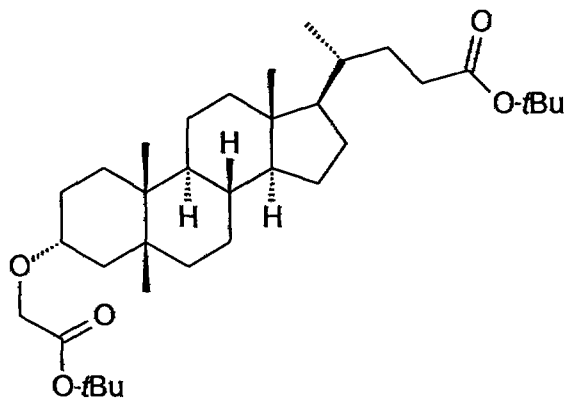
13. The composition of claim 9 wherein said hydrophobic non-steroidal multi-alicyclic component comprises two acid labile linking moieties.

14. The composition of claim 13 wherein said two acid labile linking moieties are two tertiary alkyl carboxylic esters bonded to each other.

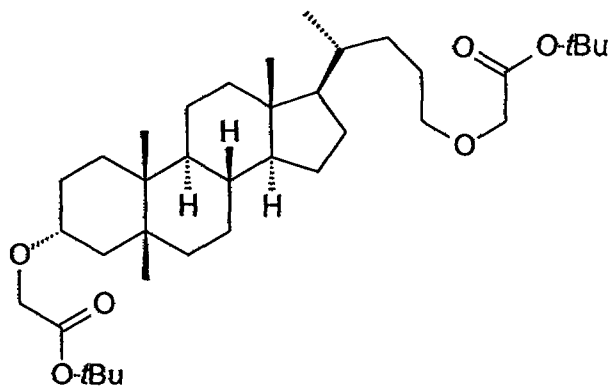
15. The composition of claim 1 comprising about 5-25 wt. % of said non-steroidal alicyclic component based on the weight of said cyclic olefin polymer.

16. The composition of claim 1 wherein said cyclic olefin polymer contains about 10-80 mole % of cyclic olefin units i) and about 20-90 mole % of cyclic olefin units ii). preferably about 10-20 mole % of cyclic olefin units i) and about 40-90 mole % of cyclic olefin units ii).

17. The composition of claim 12 wherein said saturated steroid component is selected from the group consisting of t-butyl lithocholate, t-butyldeoxycholate, t-butylcholate, t-butyl-3-trifluoroacetylithocholate, t-butyl-3-acetylithocholate, t-butyl-3-pivalyllithocholate, t-butyl-3,7,12-triformylcholate, t-butyl-tris-(3,7,12-trifluoroacetyl)cholate, and spaced lithocjolate structures:



SL-1



SL-2

wherein tBu is a tertiary butyl group.



18. A patterned photoresist structure on a substrate said photoresist comprising a composition according to any one of the preceding claims.

19. A method of forming a patterned photoresist structure on a substrate, said method comprising:

(A) applying a photoresist composition according to any one of claims 1 to 17 to said substrate to form a photoresist layer on said substrate,

(B) patternwise exposing said substrate to radiation whereby acid is generated by said photosensitive acid generator in exposed regions of said photoresist layer by said radiation, and

(C) contacting said substrate with an aqueous alkaline developer solution, whereby said exposed regions of said photoresist layer are selectively dissolved by said developer solution to reveal said patterned photoresist structure on said substrate.

20. The method of claim 19 wherein said radiation used in step (B) is 193 nm ultraviolet radiation.

21. The method of claim 19 wherein said substrate is baked between steps (B) and (C).

22. A method of forming a patterned material structure on a substrate, said material being selected from the group consisting of semiconductors, ceramics and metals, said method comprising:

(A) providing a substrate with a layer of said material,

(B) applying a photoresist composition according to any one of claims 1 to 17 to said substrate to form a photoresist layer over said material layer,

(C) patternwise exposing said substrate to radiation whereby acid is generated by said photosensitive acid generator in exposed regions of said photoresist layer by said radiation,

(D) contacting said substrate with an aqueous alkaline developer solution, whereby said exposed regions of said photoresist layer are selectively dissolved by said developer solution to reveal said patterned photoresist structure on said substrate, and

(E) transferring photoresist structure pattern to said material layer, by etching into said material layer through spaces in said photoresist structure pattern.

23. The method of claim 22 wherein said etching comprises reactive ion etching.

24. The method of claim 22 wherein at least one intermediate layer is provided between said material layer and said photoresist layer, and step (E) comprises etching through said intermediate layer.