US 2004/0106532 A1 discloses the use of a composition for stripping and dissolving a photoresist pattern having a film thickness of 10-150 micrometers, comprising C_1 to C_6 alkyl quaternary ammonium compounds. Tetrabutylammonium hydroxide and methyltributylammonium hydroxide are used in the composition along with water-soluble organic solvents like dimethyl sulfoxide and water.

EP 2088468 A1 discloses a method of preparing lithographic printing plate and lithographic printing plate precursor. By means of a binder polymer containing a carboxylic acid group, a sulfonic acid group and a phosphoric acid group in the form of an ammonium salt bulky groups like adamantyl or dicyclohexyl may be introduced into the photoresist. However, the developer used therein does not contain any ammonium compounds comprising such bulky groups.

Objects of the embodiments disclosed herein

In summary, pattern collapse may generally be caused by:

A. Swelling of the photoresist in the developing phase,
B. Capillary action of the rinsing/cleaning composition during the liquid spin-off at the end of the rinse,
C. Poor adhesion of the patterned structures to the underlayer,
D. Material incompatibility leading to swelling and weakening of the structures.

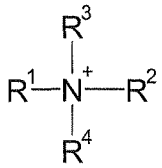
The present disclosure mainly addresses the problems under Lit. A, i.e. to prevent swelling of the photoresist by using an improved developer composition.

It is an object of the embodiments disclosed herein to provide a composition for use in developing a photoresist pattern on an electronic component substrate such as a semiconductor wafer to avoid pattern collapse of the developed photoresist.

It is another object of the embodiments disclosed herein to provide a method for developing a photoresist pattern on an electronic component substrate such as a semiconductor wafer to avoid pattern collapse of the developed photoresist.

Summary

~~In a first aspect, t~~There is provided an aqueous composition for developing photoresists applied to semiconductor substrates, said aqueous composition comprising a quaternary ammonium compound of formula I

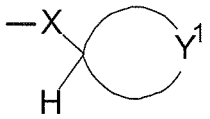


z Z (I)

wherein

(a) R^1 is selected from a C_4 to C_{30} organic radical of formula $-X-CR^{10}R^{11}R^{12}$, wherein R^{10}, R^{11} and R^{12} are independently selected from a C_1 to C_{20} alkyl and two or three of R^{10}, R^{11} and R^{12} may together form a ring system, and
R^2, R^3 and R^4 are independently selected from R^1 or a C_1 to C_{10} alkyl, C_1 to C_{10} hydroxyalkyl, C_1 to C_{30} aminoalkyl or C_1 to C_{20} alkoxyalkyl, and X is a chemical bond or a C_1 to C_4 divalent organic radical, or

(b) R^1 and R^2 are independently selected from an organic radical of formula IIa or IIb



(IIa)

or

$$-X-Y^2 \qquad \text{(IIb)}$$

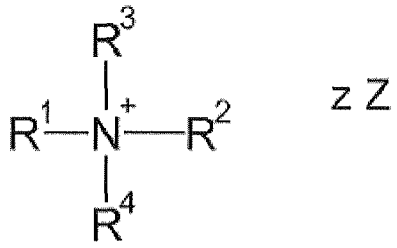
wherein Y^1 is C_4 to C_{20} alkanediyl, Y^2 is a one-, two- or tricyclic C_5 to C_{20} carbocyclic or heterocyclic aromatic system, and R^3 and R^4 are selected from R^1 or a C_1 to C_{10} alkyl, C_1 to C_{10} hydroxyalkyl, C_1 to C_{30} aminoalkyl, or C_1 to C_{20} alkoxyalkyl, and X is a chemical bond or a C_1 to C_4 divalent organic radical, and X is a chemical bond or a C_1 to C_4 divalent organic radical, or

(c) at least two of R^1, R^2, R^3, and R^4 together form a saturated mono, bi or tricyclic C_5 to C_{30} organic ring system and the remaining R^3 and R^4, if any, together form a monocyclic C_5 to C_{30} organic ring system or are selected from a C_1 to C_{10} alkyl, C_1 to C_{10} hydroxyalkyl, C_1 to C_{30} aminoalkyl, or C_1 to C_{20} alkoxyalkyl, and X is a chemical bond or a C_1 to C_4 divalent organic radical, or

(d) a combination thereof, and

wherein Z is a counter-ion and z is an integer, which is chosen so that the overall bulky quaternary ammonium compound is electrically uncharged.

In a first aspect, there is provided an aqueous composition for developing photoresists applied to semiconductor substrates, said composition comprising a quaternary ammonium compound of formula I



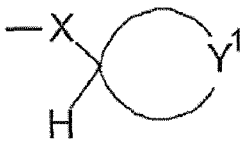
(I)

in a solvent,

wherein

(a) R^1 is selected from a C_4 to C_{30} organic radical of formula $-X-CR^{10}R^{11}R^{12}$, wherein R^{10}, R^{11} and R^{12} are independently selected from a C_1 to C_{20} alkyl and two or three of R^{10}, R^{11} and R^{12} may together form a ring system, and
R^2, R^3 and R^4 are selected from R^1 or a C_1 to C_{10} alkyl, C_1 to C_{10} hydroxyalkyl C_1 to C_{30} aminoalkyl or C_1 to C_{20} alkoxyalkyl, and X is a chemical bond or a C_1 to C_4 divalent organic radical, or

(b) R^1 and R^2 are independently selected from an organic radical of formula IIa or IIb



(IIa)

or

-X-Y^2 (IIb)

wherein Y^1 is C_4 to C_{20} alkanediyl, Y^2 is a one-, two- or tricyclic C_5 to C_{20} carbocyclic or heterocyclic aromatic system, and R^3 and R^4 are selected from R^1 or a C_1 to C_{10} alkyl, C_1 to C_{10} hydroxyalkyl, C_1 to C_{30} aminoalkyl, or C_1 to C_{20} alkoxyalkyl, and X is a chemical bond or a C_1 to C_4 divalent organic radical, and X is a chemical bond or a C_1 to C_4 divalent organic radical, or

(c) at least two of R^1, R^2, R^3, and R^4 together form a saturated mono, bi or tricyclic C_5 to C_{30} organic ring system and the remaining R^3 and R^4, if any, together form a monocyclic C_5

to C_{30} organic ring system or are selected from a C_1 to C_{10} alkyl, C_1 to C_{10} hydroxyalkyl, or C_1 to C_{20} alkoxyalkyl, and X is a chemical bond or a C_1 to C_4 divalent organic radical, or

(d) a combination thereof, and

wherein Z is a counter-ion and z is an integer, which is chosen so that the overall bulky quaternary ammonium compound is electrically uncharged,

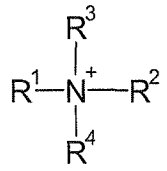
wherein the solvent consists essentially of water.

In a second aspect, there is provided the use of a composition as defined above for developing photoresist layers applied to semiconductor substrates to obtain a patterned photoresist layer having line-space dimensions of 50 nm or less and an aspect ratio of 2 or more.

In a third aspect, there is provided a method for manufacturing integrated circuit devices, optical devices, micromachines and mechanical precision devices comprising the steps of

Claims

1. An aqueous composition for developing photoresists applied to semiconductor substrates, said composition comprising a quaternary ammonium compound of formula I



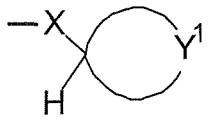
z Z (I)

in a solvent,

wherein

(a) R^1 is selected from a C_4 to C_{30} organic radical of formula $-X-CR^{10}R^{11}R^{12}$, wherein R^{10}, R^{11} and R^{12} are independently selected from a C_1 to C_{20} alkyl and two or three of R^{10}, R^{11} and R^{12} may together form a ring system, and R^2, R^3 and R^4 are selected from R^1 or a C_1 to C_{10} alkyl, C_1 to C_{10} hydroxyalkyl C_1 to C_{30} aminoalkyl or C_1 to C_{20} alkoxyalkyl, and X is a chemical bond or a C_1 to C_4 divalent organic radical, or

(b) R^1 and R^2 are independently selected from an organic radical of formula IIa or IIb



(IIa)

or

$-X-Y^2$ (IIb)

wherein Y^1 is C_4 to C_{20} alkanediyl, Y^2 is a one-, two- or tricyclic C_5 to C_{20} carbocyclic or heterocyclic aromatic system, and R^3 and R^4 are selected from R^1 or a C_1 to C_{10} alkyl, C_1 to C_{10} hydroxyalkyl, C_1 to C_{30} aminoalkyl, or C_1 to C_{20} alkoxyalkyl, and X is a chemical bond or a C_1 to C_4 divalent organic radical, and X is a chemical bond or a C_1 to C_4 divalent organic radical, or

(c) at least two of R^1, R^2, R^3, and R^4 together form a saturated mono, bi or tricyclic C_5 to C_{30} organic ring system and the remaining R^3 and R^4, if any, together form a monocyclic C_5 to C_{30} organic ring system or are selected from a C_1 to C_{10} alkyl, C_1 to C_{10} hydroxyalkyl, ~~C_4 to C_{30} aminoalkyl,~~ or C_1 to C_{20} alkoxyalkyl, and X is a chemical bond or a C_1 to C_4 divalent organic radical, or

(d) a combination thereof, and

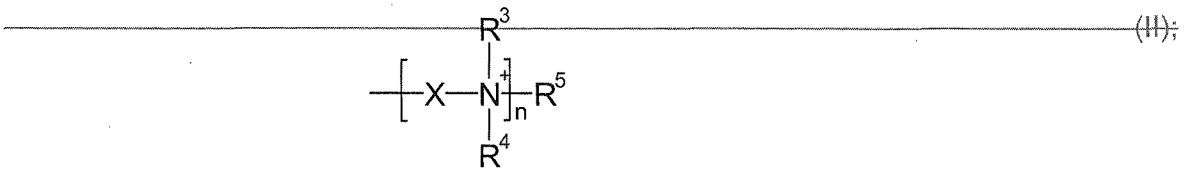
wherein Z is a counter-ion and z is an integer, which is chosen so that the overall bulky quaternary ammonium compound is electrically uncharged,

wherein the solvent consists essentially of water.

2. The aqueous composition according to claim 1, wherein R^{10}, R^{11} and R^{12} of R^1 are independently selected from C_1 to C_8 alkyl and R^2, R^3 and R^4 are independently selected from C_1 to C_4 alkyl.

3. The aqueous composition according to claim 1, wherein
R^1, R^2 are independently selected from cyclohexyl, cyclooctyl or cyclodecyl, which may be unsubstituted or substituted by C_1 to C_4 alkyl, and
R^3, R^4 are independently selected from C_1 to C_4 alkyl.

~~4. The aqueous composition according to claim 1, wherein the C_4 to C_{30} aminoalkyl is selected from~~



~~(II);~~

~~wherein:~~

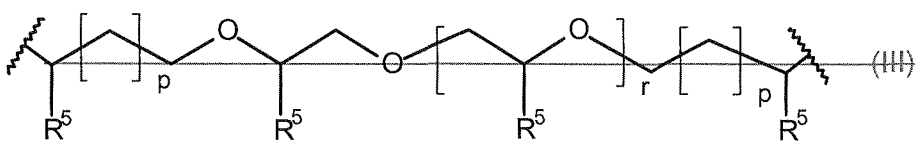
~~X is a divalent group, for each repeating unit 1 to n independently selected from~~

~~(a) linear or branched C_4 to C_{20} alkanediyl, which may optionally be substituted and which may optionally be interrupted by up to 5 heteroatoms selected from O and N,~~

~~(b) C_5 to C_{20} cycloalkanediyl, which may optionally be substituted and which may optionally be interrupted by up to 5 heteroatoms selected from O and N,~~

~~(c) C_6 to C_{20} organic group of formula X^1-A-X^2-, wherein X^1 and X^2 are independently selected from a C_1 to C_7 linear or branched alkanediyl and A is selected from a C_5 to C_{42} aromatic moiety or a C_5 to C_{30} cycloalkanediyl, which H atoms may optionally be substituted and which C atoms may optionally be interrupted by up to 5 heteroatoms selected from O and N,~~

~~(d) polyoxyalkylene diradical of formula III:~~



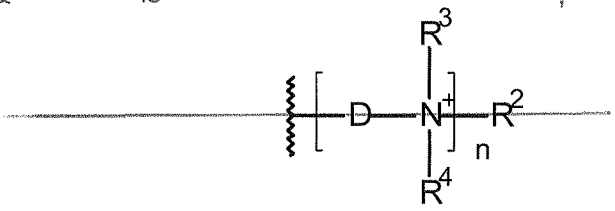
~~(III)~~

~~wherein p is 0 or 1, r is an integer from 1 to 100, and R^5 is selected from H and a linear or branched C_1 to C_{20} alkyl group;~~

~~R^3 and R^4 are monovalent groups independently selected from a linear or branched C_5 to C_{30} alkyl group, a C_5 to C_{30} cycloalkyl, a C_4 to C_{20} hydroxyalkyl, and a C_2 to C_4 oxyalkylene homo or copolymers , all of which may optionally be substituted, and wherein pair-wise R^3, R^4 and adjacent R^4, R^4 and R^3, R^3 may optionally together form a bivalent group X, and may also be a continuation Q of the molecule by branching, and, if n is equal to or greater than 2, R^3, R^4 or R^3 and R^4 may also be hydrogen atoms;~~

~~n is an integer from 1 to 5, or, in case at least one of X, R^3 and R^4 comprises a C_2 to C_4 polyoxyalkylene group, n may be an integer from 1 to 10000, and provided that, if at least one Q is present, n includes all repeating units of branches Q;~~

~~Q is~~



~~;~~

~~n is an integer from 1 to 5~~

~~D is a divalent group, for each repeating unit 1 to n independently selected from~~

~~(a) linear or branched C_4 to C_{20} alkanediyl,~~

~~(b) C_5 to C_{20} cycloalkanediyl,~~

~~(c) C_5 to C_{20} aryl,~~

~~(d) C_6 to C_{20} arylalkanediyl of formula $-Z^1-A-Z^2-$, wherein Z^1 and Z^2 are independently selected from a C_4 to C_7 alkanediyl and A is a C_5 to C_{12} aromatic moiety,~~

~~all of which may optionally be substituted and which may optionally be interrupted by one or more heteroatoms selected from O, S, and N;~~

~~R^5 is a monovalent groups independently selected from linear or branched, C_4 to C_{20} alkyl, C_5 to C_{20} cycloalkyl, C_5 to C_{20} aryl, C_6 to C_{20} alkylaryl, and C_6 to C_{20} arylalkyl, which may optionally be substituted.~~

46. The aqueous composition according to anyone of the preceding claims, wherein at least two of R^{10}, R^{11} and R^{12} together form a mono, bi or tri cyclic ring system.

57. The aqueous composition according to anyone of the preceding claims, wherein R^1 is selected from bicyclo[2.2.1]heptane, Tricyclo[3.3.1.$1^{3,7}$]decane and R^2, R^3 and R^4 are independently selected from linear C_1 to C_4 alkyl.

68. The aqueous composition according to anyone of the preceding claims, wherein R^1 and R^2 are selected from C_5 to C_{10} cycloalkyl and R^3 and R^4 are independently selected from linear C_1 to C_4 alkyl.

79. The aqueous composition according to anyone of the preceding claims, further comprising a surfactant.

810. The aqueous composition according to anyone of the preceding claims, wherein Z is OH^-.

911. The aqueous composition according to anyone of the preceding claims, the composition having a pH of 8 or more, preferably a pH of from 9 to 14.

~~12. The aqueous composition according to anyone of the preceding claims, wherein the solvent consist essentially of water.~~

103. Use of a composition according to anyone of the preceding claim for developing photoresist layers applied to semiconductor substrates to obtain a patterned photoresist layer having line-space dimensions of 50 nm or less and an aspect ratio of 2 or more.

114. A method for manufacturing integrated circuit devices, optical devices, micromachines and mechanical precision devices comprising the steps of

(i) providing a substrate

(ii) providing the substrate with a photoresist layer;

(iii) exposing the photoresist layer to actinic radiation through a mask with or without an immersion liquid;

(iii) contacting the substrate at least once with an aqueous composition according to anyone of claims the preceding claims to obtain a patterned photoresist layer; and

(iv) removing the composition from the contact with the substrate.

125. The method according to claim 114, wherein the substrate is a semiconductor substrate.

136. The method according to anyone of claims 114 or 125, wherein the patterned material layers are having a feature dimensions of 50 nm or less and aspect ratios of more than 2.

147. The method according to anyone of claims 114 to 136, wherein the photoresist is an immersion photoresist, an EUV photoresist or eBeam photoresist.

158. The method according to anyone of the claims 114 to 147, the integrated circuit devices comprise integrated circuits having a large-scale integration (LSI), very-large-scale integration (VLSI) or the ultra-large-scale integration (ULSI).