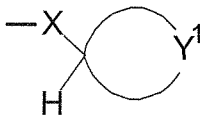
wherein

(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

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

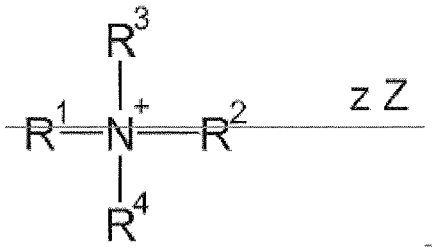
wherein Y^1 is C_4 to C_{20} alkanediyl, Y^2 is a one-, two- or tricyclic C_5 to C_{20} carbocyclic or heterocyclic aromatic system, and R^3 and R^4 are selected from R^1 or a C_1 to C_{10} alkyl, C_1 to C_{10} hydroxyalkyl, C_1 to C_{30} aminoalkyl, or C_1 to C_{20} alkoxyalkyl, and X is a chemical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



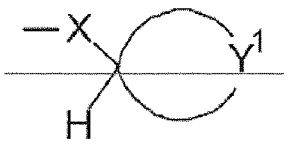
(I)

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_{40} alkyl, C_1 to C_{40} 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

(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_{40} alkyl, C_1 to C_{40} 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, 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_4 to C_{40} alkyl, C_4 to C_{40} hydroxyalkyl, or C_4 to C_{20} alkoxyalkyl, and X is a chemical bond or a C_1 to C_4 divalent organic radical, or~~

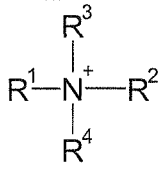
~~(d) a combination thereof, and~~

~~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, t~~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 an aspect, there is provided the use of a composition 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, wherein the composition is an aqueous composition for developing photoresists applied to semiconductor substrates, said composition comprising a quaternary ammonium compound of formula I



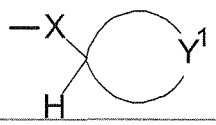
$z\,Z$ (I)

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 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, or C_1 to C_{20} alkoxyalkyl, 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, 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 third aspect, t~~There is provided 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 a composition as defined above to obtain a patterned photoresist layer;
and
(iv) removing the composition from the contact with the substrate.

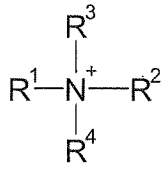
In another aspect, there is provided a method for manufacturing integrated circuit devices, optical devices, micromachines and mechanical precision devices comprising the steps of

(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 for developing photoresists applied to semiconductor substrates, said composition comprising a quaternary ammonium compound of formula I



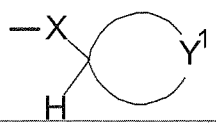
z Z (I)

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 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, 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, 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,to obtain a patterned photoresist layer; and

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

Advantages

In view of the prior art, it was surprising and could not be expected by the skilled artisan that the objects of the embodiments disclosed herein could be solved by the use or method as defined above.

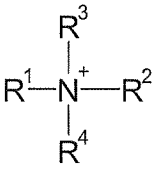
Without to be bound to any theory, it seems that the use of bulky alkyl ammonium compounds in the developer compositions could prevent swelling of the photoresist layer due to reduced diffusion.

Furthermore the use of a surface active bulky ammonium compound it may be possible to lower the surface tension of the developer composition and thereby further reducing pattern collapse.

The photoresist surface after developing is more hydrophobic due to the more hydrophobic alkyl substituents compared to the developers according to the prior art. Without to be bound to any theory it is believed that both, reduced swelling of the photoresist as well as the more hydrophobic surface of the photoresist is beneficial for pattern collapse reduction.

Detailed Description of the Invention

The composition according to the invention is used for stripping and dissolving a photoresist pattern that is formed on a substrate. An essential component in the developer composition is one or more quaternary ammonium represented by the following general formula (Ia):

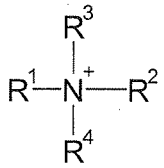


(Ia)

The quaternary ammonium compounds according to the invention are referred to as bulky ammonium compounds in the following.

Claims

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



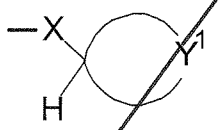
z Z (I)

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



(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.

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 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.

5. 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.

6. 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.

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

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

9. 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.

10. 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.

11. 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.

12. The method according to claim 11, wherein the substrate is a semiconductor substrate.

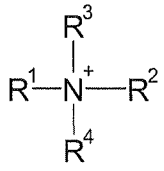
13. The method according to anyone of claims 11 or 12, wherein the patterned material layers are having a feature dimensions of 50 nm or less and aspect ratios of more than 2.

14. The method according to anyone of claims 11 to 13, wherein the photoresist is an immersion photoresist, an EUV photoresist or eBeam photoresist.

15. The method according to anyone of the claims 11 to 14, 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).

Claims

1. Use of a composition 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, wherein the composition is an aqueous composition for developing photoresists applied to semiconductor substrates, said composition comprising a quaternary ammonium compound of formula I



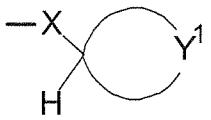
z Z (I)

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 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, or C_1 to C_{20} alkoxyalkyl, 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, 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 use 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 use 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 use according to any one 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.

5. The use according to any one 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.

6. The use according to any one 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.

7. The use according to any one of the preceding claims, further comprising a surfactant.

8. The use according to any one of the preceding claims, wherein Z is OH^-.

9. The use according to any one of the preceding claims, the composition having a pH of 8 or more, preferably a pH of from 9 to 14.

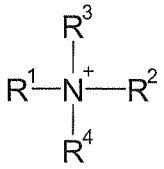
10. A method for manufacturing integrated circuit devices, optical devices, micromachines and mechanical precision devices comprising the steps of

(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 for developing photoresists applied to semiconductor substrates, said composition comprising a quaternary ammonium compound of formula I



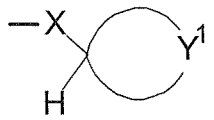
z Z (I)

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 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, 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, 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,to obtain a patterned photoresist layer; and

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

11. The method according to claim 10, 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.

12. The method according to claim 10, 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.

13. The method according to any one of claims 10 to 12, wherein at least two of R^{10}, R^{11} and R^{12} together form a mono, bi or tri cyclic ring system.

14. The method according to any one of claims 10 to 13, 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.

15. The method according to any one of claims 10 to 14, 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.

16. The method according to any one of claims 10 to 15, further comprising a surfactant.

17. The method according to any one of claims 10 to 16, wherein Z is OH^-.

18. The method according to any one of claims 10 to 17, the composition having a pH of 8 or more, preferably a pH of from 9 to 14.

19. The method according to any one of claims 10 to 18, wherein the substrate is a semiconductor substrate.

20. The method according to anyone of claims 10 to 19, wherein the patterned material layers are having a feature dimensions of 50 nm or less and aspect ratios of more than 2.

21. The method according to anyone of claims 10 to 20, wherein the photoresist is an immersion photoresist, an EUV photoresist or eBeam photoresist.

22. The method according to anyone of the claims 10 to 21, 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).