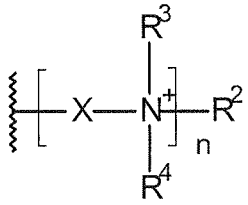
wherein p is 0 or 1, r is an integer from 1 to 100; R^5 is selected from H and a linear or branched C_1 to C_{20} alkyl group;

R^1 and R^2 are monovalent groups independently selected from H, linear or branched C_1 to C_{20} alkyl, C_5 to C_{20} cycloalkyl, C_5 to C_{20} aryl, C_6 to C_{20} alkylaryl, C_6 to C_{20} arylalkyl, C_1 to C_{20} hydroxyalkyl, or C_2 to C_4 oxyalkylene homo or copolymers, all of which may optionally be further substituted;

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_1 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 as defined above, 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;

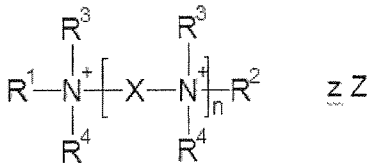
n is an integer from 1 to 5, or, in case at least one of X, R^3 and R^4 comprising a C_2 to C_4 polyoxyalkylene group, n may be an integer from 1 to 10000, and provided that, if at least one Q is present, n includes all repeating units of branches Q;

Q is  ;

z is an integer, which is chosen so that the overall surfactant is electrically uncharged;

Z is a counter-ion.

In an~~-first~~ aspect, there is provided the use of a gemini additive of the general formula I in aqueous compositions for cleaning semiconductor substrates after the development of the photoresist:

 z Z (I);

wherein

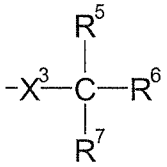
X is a divalent group, for each repeating unit 1 to n independently selected from

(a) linear or branched C_1 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,

R^1 and R^2 are monovalent groups independently selected from H, linear or branched C_1 to C_{20} alkyl, C_5 to C_{20} cycloalkyl, C_5 to C_{20} aryl, C_6 to C_{20} alkylaryl, C_6 to C_{20} arylalkyl,or C_1 to C_{20} hydroxyalkyl~~, or C_2 to C_4 oxyalkylene~~ homo or copolymers, all of which may optionally be further substituted;

~~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_1 to C_{20} hydroxyalkyl, and a C_2 to C_4 oxyalkylene homo or copolymers , all of which may optionally be substituted,~~ R^3 and R^4 are selected from formula VI



(VI),

wherein

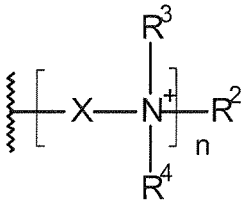
X^3 is selected from a chemical bond and a linear or branched, preferably linear, C_1 to C_4 alkanediyl, most preferably methanediyl.

R^5 is selected from OH, H and a linear or branched C_1-C_5 alkyl, preferably methyl or OH,

R^6 is selected from H and a linear or branched C_1 to C_{20} alkyl, a C_1 to C_{20} cycloalkyl, a C_1 to C_{20} aryl , C_1 to C_{20} alkylaryl and C_1 to C_{20} arylalkyl.

R^7 is selected from H and linear or branched C_1 to C_{10} alkyl, preferably methyl or tert butyl, 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  ;

z is an integer, which is chosen so that the overall surfactant is electrically uncharged;

Z is a counter-ion.

There is provided a method for manufacturing integrated circuit devices, optical devices, micromachines and mechanical precision devices has been found, the said method comprising the steps of

(a) providing a substrate,
(b) providing the substrate with a photoresist layer,
(c) exposing the photoresist layer to actinic radiation through a mask with or without an immersion liquid,
(d) contacting the substrate at least once with a developing composition for developing the photoresist to obtain a pattern having line-space dimensions of 32 nm or less and an aspect ratio of 2 or more,
(e) contacting the substrate at least once with an aqueous cleaning composition,

wherein at least one of the developing composition of step (d) and the cleaning composition of step (e) comprises a gemini additive.

In another ~~second~~ aspect, there is provided a method for manufacturing integrated circuit devices, the method comprising the steps of

(a) providing a semiconductor substrate,

(b) providing the substrate with a photoresist layer,

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

(d) contacting the substrate at least once with a developing composition for developing the photoresist to obtain a pattern having line-space dimensions of 32 nm and less and an aspect ratio >2,

(e) contacting the substrate at least once with an aqueous cleaning composition,

wherein the cleaning composition of step (e) comprises a gemini additive of formula (I), wherein

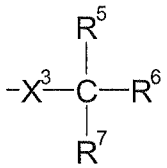
X is a divalent group, for each repeating unit 1 to n independently selected from

(a) linear or branched C_1 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;

R^1 and R^2 are monovalent groups independently selected from H, linear or branched C_1 to C_{20} alkyl, C_5 to C_{20} cycloalkyl, C_5 to C_{20} aryl, C_6 to C_{20} alkylaryl, C_6 to C_{20} arylalkyl, or C_1 to C_{20} hydroxyalkyl~~, or C_2 to C_4 oxyalkylene~~ homo or copolymers, all of which may optionally be further substituted;

~~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_1 to C_{20} hydroxyalkyl, and a C_2 to C_4 oxyalkylene homo or copolymers , all of which may optionally be substituted,~~R^3 and R^4 are selected from formula VI



(VI),

wherein

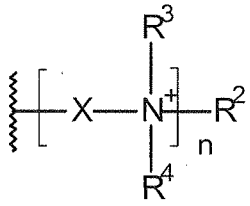
X^3 is selected from a chemical bond and a linear or branched, preferably linear, C_1 to C_4 alkanediyl, most preferably methanediyl.

R^5 is selected from OH, H and a linear or branched C_1-C_5 alkyl, preferably methyl or OH,

R^6 is selected from H and a linear or branched C_1 to C_{20} alkyl, a C_1 to C_{20} cycloalkyl, a C_1 to C_{20} aryl , C_1 to C_{20} alkylaryl and C_1 to C_{20} arylalkyl.

R^7 is selected from H and linear or branched C_1 to C_{10} alkyl, preferably methyl or tert butyl, 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 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 ;

z is an integer, which is chosen so that the overall surfactant is electrically uncharged;

Z is a counter-ion.

Advantages

In view of the prior art, it was surprising and could not be expected by the skilled artisan that the objects of the invention could be solved by the use or method according to the disclosure.

It was surprising that the use of Gemini additives according to the disclosure allowed for the immersion photolithography of photoresist layers, the developing of photoresist layers exposed to actinic radiation through a mask, the cleaning of patterned material layers, or combinations thereof.

The surfactants according to the disclosure are particularly useful for pattern developing or cleaning developed photoresist layers comprising patterns having line-space dimensions of 50 nm or less, particularly of 32 nm or less and, most particularly 22 nm or less.
Furthermore, the gemini additives according to the disclosure are particularly useful for aspect ratios greater or equal 2 in the case of photoresist structures, and, in particular, greater or equal 10 in the case of non-photoresist structures, without causing pattern collapse, line edge roughness (LER), line width roughness (LWR) and watermark defects in the photoresist case and anti pattern collapse, defect reduction and cleaning in the high aspect ratio case.

It has to be noted that the compositions comprising the gemini additives according to the present disclosure are generally useful for avoiding anti pattern collapse of photoresist structures as well as of non-photoresist patterns with high aspect ratios (HARS, typical aspect ratios are greater or equal 10).

Quite to the contrary, the method of the disclosure allowed for a significant reduction of LER and LWR by smoothing the roughness of the surfaces of the developed photoresist patterns, for the efficient prevention and/or the removal of watermark defects not only on photoresist patterns, but also on other patterned material layers, and the efficient removal of particles whereby a significant defect reduction not only on photoresist patterns but also on other patterned material layers could be achieved.

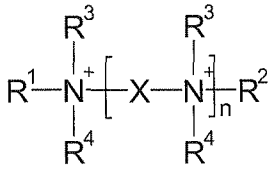
Without to be bound to any theory, it seems that the use of the gemini additives in the developer compositions could prevent swelling of the photoresist layer due to reduced diffusion. This also reduces the risk of pattern collapse of the photoresist during the subsequent steps. The use of the gemini additives in the developer solutions enables tuning surface tension and the interaction of the developer solution with the photo resist.

Detailed Description of the Invention

The gemini-surfactants of the general formula I

Claims

1. Use of a gemini additive of the general formula I in aqueous compositions for cleaning semiconductor substrates after the development of the photoresist:



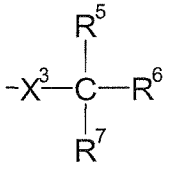
z Z (I);

wherein

X is a divalent group, for each repeating unit 1 to n independently selected from
(a) linear or branched C_1 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,

R^1 and R^2 are monovalent groups independently selected from H, linear or branched C_1 to C_{20} alkyl, C_5 to C_{20} cycloalkyl, C_5 to C_{20} aryl, C_6 to C_{20} alkylaryl, C_6 to C_{20} arylalkyl, or C_1 to C_{20} hydroxyalkyl~~, or C_2 to C_4 oxyalkylene~~ homo or copolymers, all of which may optionally be further substituted;

~~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_1 to C_{20} hydroxyalkyl, and a C_2 to C_4 oxyalkylene homo or copolymers , all of which may optionally be substituted,~~ R^3 and R^4 are selected from formula VI



(VI),

wherein

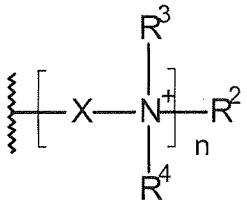
X^3 is selected from a chemical bond and a linear or branched, preferably linear, C_1 to C_4 alkanediyl, most preferably methanediyl.

R^5 is selected from OH, H and a linear or branched C_1-C_5 alkyl, preferably methyl or OH,

R^6 is selected from H and a linear or branched C_1 to C_{20} alkyl, a C_1 to C_{20} cycloalkyl, a C_1 to C_{20} aryl , C_1 to C_{20} alkylaryl and C_1 to C_{20} arylalkyl.

R^7 is selected from H and linear or branched C_1 to C_{10} alkyl, preferably methyl or tert butyl, 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 

;

z is an integer, which is chosen so that the overall surfactant is electrically uncharged;

Z is a counter-ion.

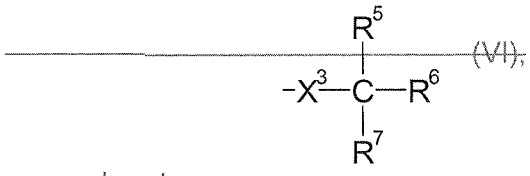
2. The use according to claim 1, wherein X is selected from unsubstituted linear or branched C_3-C_{12} alkanediyl.

3. The use according to claim 1, wherein X is selected from butane-1,4-diyl, hexane-1,6-diyl, or octane-1,8-diyl.

4. The use according to anyone of the preceding claims, wherein R^1 and R^2 are independently selected from C_1-C_{12} alkyl.

5. The use according to anyone of the preceding claims, wherein R^1 is selected from H and R^2 are independently selected from H, linear or branched C_1 to C_{20} alkyl, C_5 to C_{20} cycloalkyl, C_5 to C_{20} aryl, C_6 to C_{20} alkylaryl, C_6 to C_{20} arylalkyl, or C_1 to C_{20} hydroxyalkyl, ~~or C_2 to C_4 oxyalkylene~~ homo or copolymers, all of which may optionally be further substituted.

~~6. The use according to anyone of the preceding claims, wherein R^3 and R^4 are selected from formula VI~~



~~(VI),~~

~~wherein~~

~~X^3 is selected from a chemical bond and a linear or branched, preferably linear, C_1 to C_4 alkanediyl, most preferably methanediyl.~~

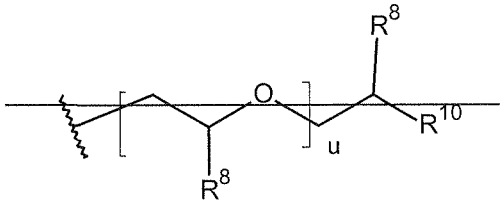
~~R^5 is selected from OH, H and a linear or branched C_1-C_5 alkyl, preferably methyl or OH,~~

~~R^6 is selected from H and a linear or branched C_1 to C_{20} alkyl, a C_1 to C_{20} cycloalkyl, a C_1 to C_{20} aryl , C_1 to C_{20} alkylaryl and C_1 to C_{20} arylalkyl.~~

~~R^7 is selected from H and linear or branched C_1 to C_{10} alkyl, preferably methyl or tert. butyl.~~

~~7. The use according to anyone of claims 1 to 6, wherein R^3 and R^4 are selected from formula V~~

~~(V)~~



~~wherein~~

~~u is an integer of from 0 to 100;~~

~~R^8 is, for each repeating unit u independently, selected from H and a C_1 to C_2 alkyl group, and~~

~~R^{10} is selected from hydroxy (-OH), carboxy (-CO-OH or its salts), amine (-NH_2), amide (-CO-NH2), sulphonamide (-SO_2-NH_2), sulphonate (-SO_2OH or its salts), sulphate (-OSO_2OH or its salts), phosphonate (-$PO(OH)_2$ or its salts) and phosphate (-O-$PO(OH)_2$, or its salts).~~

~~8~~6. The use according to anyone of the preceding claims, wherein the semiconductor substrate comprises structures comprising apertures of 30 nm or below.

~~9~~7. The use according to anyone of the preceding claims for cleaning of semiconductor substrates.

~~10~~8. A method for manufacturing integrated circuit devices, the method comprising the steps of

(a) providing a semiconductor substrate,

(b) providing the substrate with a photoresist layer,

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

(d) contacting the substrate at least once with a developing composition for developing the photoresist to obtain a pattern having line-space dimensions of 32 nm and less and an aspect ratio >2,

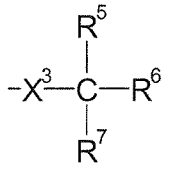
(e) contacting the substrate at least once with an aqueous cleaning composition,

wherein the cleaning composition of step (e) comprises ~~a~~ the gemini additive of formula (I), wherein

X is a divalent group, for each repeating unit 1 to n independently selected from
(a) linear or branched C_1 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;

R^1 and R^2 are monovalent groups independently selected from H, linear or branched C_1 to C_{20} alkyl, C_5 to C_{20} cycloalkyl, C_5 to C_{20} aryl, C_6 to C_{20} alkylaryl, C_6 to C_{20} arylalkyl, or C_1 to C_{20} hydroxyalkyl~~, or C_2 to C_4 oxyalkylene~~ homo or copolymers, all of which may optionally be further substituted;

~~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_1 to C_{20} hydroxyalkyl, and a C_2 to C_4 oxyalkylene homo or copolymers , all of which may optionally be substituted,~~ R^3 and R^4 are selected from formula VI



(VI),

wherein

X^3 is selected from a chemical bond and a linear or branched, preferably linear, C_1 to C_4 alkanediyl, most preferably methanediyl.

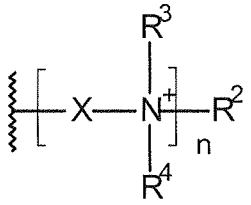
R^5 is selected from OH, H and a linear or branched C_1-C_5 alkyl, preferably methyl or OH,

R^6 is selected from H and a linear or branched C_1 to C_{20} alkyl, a C_1 to C_{20} cycloalkyl, a C_1 to C_{20} aryl , C_1 to C_{20} alkylaryl and C_1 to C_{20} arylalkyl.

R^7 is selected from H and linear or branched C_1 to C_{10} alkyl, preferably methyl or tert butyl,

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 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  ;

z is an integer, which is chosen so that the overall surfactant is electrically uncharged;

Z is a counter-ion.

.

~~11~~9. The method according to claim ~~10~~8, wherein the patterned material layers are having line-space dimensions of 32 nm and less and aspect ratios of greater 10 for non-photoresist structures and aspect ratios of greater 2 for photoresist structures.

~~12~~10. The method according to anyone of the claims ~~8~~10 to ~~9~~11, wherein the patterned material layers are selected from the group consisting of patterned developed photoresist layers, patterned barrier material layers, patterned multi-stack material layers and pattern dielectric material layers.

~~13~~11. The method according to anyone of the claims ~~8~~10 to ~~10~~12, wherein the composition contains, based on a complete weight of the solution, 0.0005 to 1% by weight of the gemini additive.

~~14~~12. The method according to anyone of the claims ~~8~~10 to ~~13~~11, wherein the cleaning solution has a pH of 6 to 8.

~~15. The method according to anyone of the claims 10 to 14, wherein the substrate is provided by a photolithographic process comprising the steps of~~
~~(i) providing the substrate with an immersion photoresist , EUV photoresist or eBeam photoresist layer;~~
~~(ii) exposing the photoresist layer to actinic radiation through a mask with or without an immersion liquid;~~
~~(iii) developing the exposed photoresist layer with a developer solution to obtain a pattern having line-space dimensions of 32 nm and less and an aspect ratio >2;~~
~~(iv) applying a chemical rinse solution to the developed patterned photoresist layer; and~~
~~(v) spin drying the semiconductor substrate after the application of the chemical rinse solution;~~

~~wherein at least one of the following: the immersion liquid and the chemical rinse solution, is an aqueous solution comprising a gemini additive.~~

~~16~~13. The method according to anyone of the claims ~~8~~10 to ~~15~~12, characterized in that it is used for preventing pattern collapse, for reducing line edge roughness, for preventing and removing watermark defects and for reducing defects by removing particles.

~~17~~14. The method according to anyone of the claims ~~8~~10 to ~~16~~13, characterized in that 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).