An additional problem of the conventional photolithographic process is the presence of watermark defects. Watermarks may form on the photoresist as the deionized water or rinse liquid cannot be spun off from the hydrophobic surface of the photoresist. The photoresist may be hydrophobic particularly in areas of isolated, or non-dense, patterning. The watermarks have a harmful effect on yield and IC device performance.

However, besides the rinsing/cleaning step described above, also the swelling of the photoresist in the photoresist developing step may increase the risk of pattern collapse and should therefore be avoided.

EP 1 553 454 A2 discloses the use of cetylmethylammonium, stearylmethylammonium, cetyltrimethylammonium, stearyltrimethylammonium, distearyldimethylammonium, stearyldimethylbenzylammoium, dodecylmethylammonium, dodecyltrimethylammonium, benzylmethylammonium, benzyltrimethylammonium, and benzalkonium chloride as cationic surfactants in rinsing compositions for patterns having line-space dimensions of 90 nm.

US 6670107 B2 discloses a method for the reduction of defects in an electronic device comprising of cationic and non-ionic surfactants in concentration less than or equal to the critical micelle concentration. US 2010/0248164 A1 discloses a rinse solution for preventing pattern collapse consisting of an anionic surfactant, an amine and water.

Patent application US 2000/53172 A1 discloses that the acetylenic diol-type of surfactant solutions prevent pattern collapse by making the surface of a photoresist hydrophilic thus improving the wettability of the rinse or solution.

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~~invention~~ mainly addresses the problems under Lit. A and B, i.e. to prevent swelling of the photoresist and to prevent pattern collapse by using a defect reduction rinse after the development of the photoresist.

It is therefore an object of the ~~present invention~~embodiments disclosed herein to provide a method for manufacturing integrated circuits for nodes of 50 nm and lower, in particular for nodes of 32 nm and lower and, especially, for nodes of 22 nm and lower, which method no longer exhibits the disadvantages of prior art manufacturing methods.

In particular, the compounds according to the present disclosure~~invention~~ shall allow for the immersion photolithography of photoresist layers,

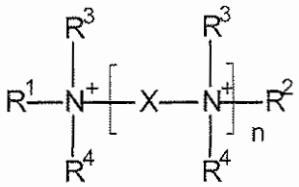
the developing of the photoresist layers exposed to actinic radiation through a mask,
the chemical rinse of patterned material layers
comprising patterns with a high aspect ratio and line-space dimensions of 50 nm and less, in particular, of 32 nm and less, especially, of 22 nm and less, without causing pattern collapse, an increase of LER, LWR and watermark defects.

The components according to the present disclosure~~invention~~ should allow for a significant reduction of LER and LWR by smoothing the roughness of the surfaces of the developed photoresist patterns. It should also allow for the efficient prevention and/or the removal of watermark defects on patterned material layers, in particular, but not limited to photoresist patterns. Furthermore it should allow for the efficient removal of particles in order to achieve a significant defect reduction on patterned material layers.

The components according to the present disclosure~~invention~~ should also allow for a significant reduction of photoresist swelling.

Summary ~~of the Invention~~

~~A first embodiment of the present invention is~~In a first aspect, there is provided the use of gemini additives of the general formula I in compositions for treating semiconductor substrates:



zZ (I)

wherein:

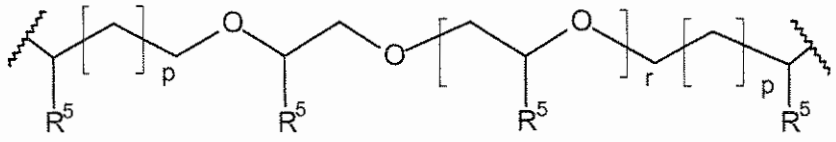
X is a divalent group, for each repeating unit 1 to n independently selected from

(a) 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) a 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) a C_6 to C_{20} organic group of formula $-X^1\text{-}A\text{-}X^2-$, 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_{12} 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) a polyoxyalkylene diradical of formula II:



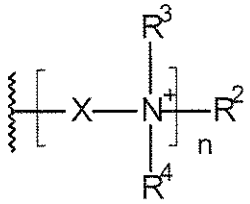
(II)

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.

~~According to another embodiment of the present invention~~ In a second aspect, 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.

Advantages ~~of the Invention~~

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~~invention~~.

It was surprising that the use of Gemini additives according to the ~~invention~~ 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 ~~invention~~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~~invention~~ 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 ~~invention~~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 ~~invention~~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