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 ~~Invention~~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.

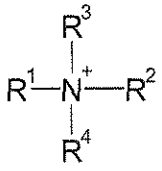
The present disclosure~~invention~~ mainly addresses the problems under Lit. A, i.e. to prevent swelling of the photoresist by using an improved developer composition.

It is an object of the ~~present invention~~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 ~~present invention~~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 ~~of the Invention~~

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

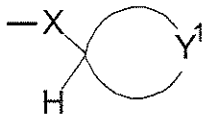


z Z (I)

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.

~~Another embodiment of the present invention is~~In a second aspect, there is provided the use of a composition ~~according to anyone of the preceding claim~~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.

~~Yet another embodiment of the present invention is~~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

(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 ~~according to anyone of claims the preceding claims~~as defined above to obtain a patterned photoresist layer; and
(iv) removing the composition from the contact with the substrate.

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~~ embodiments disclosed herein could be solved by the use or method ~~according to the invention~~as defined above.

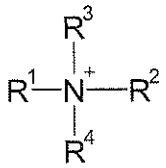
Without to be bound to any theory, it seems that the use of bulky alkyl ammonium compounds in the developer compositions could prevent swelling of the photoresist layer due to reduced diffusion.

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.