### International Application Published Under the Patent Cooperation Treaty (PCT)

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**Published**

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

### Title

ORGANIC AMINE/HYDROGEN FLUORIDE ETCHANT COMPOSITION AND METHOD

### Abstract

A process for selectively removing organic residues, damaged oxides, and native oxides from plasma-etched silicon wafers with a solution of a hydrogen fluoride adduct of an organic amine dissolved in an organic solvent.
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ORGANIC AMINE/HYDROGEN FLUORIDE ETCHANT COMPOSITION
AND METHOD

BACKGROUND OF THE INVENTION

Field of the Invention

This invention is directed to a process for removing organic residues, such as cross-linked photoresists and halogenated sidewall polymers, and damaged silicon oxides from a plasma-etched silicon wafer, and more particularly to removal of such residues and oxides with a solution comprising hydrogen fluoride adducts of organic amines dissolved in organic solvents.

Brief Description of the Prior Art

Hydrogen fluoride has been widely used in etching processes for patterning films on semiconductor wafers. However, hydrogen fluoride has very high etching rates prompting the development of alternatives to hydrogen fluoride. Kinsbron et al., U.S. Pat. No. 4,343,677, discuss film patterning and disclose an etching solution which uses buffered ammonium fluoride/hydrofluoric acid in a molar ratio of about ten to one, mixed with a suitable solvent such as ethylene glycol. Gajda, U.S. Pat. No. 4,230,523, discloses an etchant comprised of a solution of hydrogen fluoride dissolved in organic solvents such as glycerine or another polyhydric alcohol. The etchant is used for etching silicon dioxide while not attacking silicon. Gajda requires that the solution be free of unbound water and ammonium fluoride. Maeda et al., U.S. Pat. No. 3,979,241, teach an etching liquid with ammonium fluoride or an alkali fluoride dissolved in a polyhydric alcohol, such as ethylene glycol, polyethylene glycol, and glycerine. The etching solution is used for selectivity etching silicon dioxide or silicon nitride on a semiconductor wafer.
Bowden et. al., U.S. Pat. No. 5,320,709, teach a method for selectively removing organometallic residues, organosilicon residues, native silicon oxides, and damaged silicon oxides created in plasma-etching. Plasma-etched silicon wafers are emersed in a solution of anhydrous ammonium fluoride and a polyhydric alcohol which is free of added hydrogen fluoride and substantially free of water. The residues and oxides are etched, leaving the photoresist which may then be stripped using conventional photoresist strippers.

The method of Bowden et al. is limited in several aspects. Ammonium fluoride and ammonium bifluoride are soluble in a limited number of organic solvents, typically low molecular weight alcohols and glycols. In addition, in solvents in which they are soluble, the solubility may be limited. For example, in ethylene glycol, the solubility of ammonium fluoride is approximately 5 percent by weight, and it is necessary to agitate the solution for several hours to completely dissolve the ammonium fluoride. Another significant consequence of the limited solvent choices for ammonium fluoride and bifluoride is that the solvents cannot remove cross-linked photoresist residues which are formed during oxygen ashing, which is often used to remove photoresist after plasma etching. Consequently, separate wet stripping steps are required to effectively remove residues containing both inorganic and organic materials. The present invention is directed to removing materials similar to Bowden et. al. with an improved etching solution.

SUMMARY OF THE INVENTION

It is a primary object of the present invention to provide an improved method for removal from processed semiconductor wafers of oxidized organometallic residues resulting from plasma etching of metals and metal alloys, for removal of oxidized organosilicon residues from plasma-etched silicon, and for removal of organic residues such as cross-linked photoresists and halogenated sidewall polymers.
Another object of the present invention is to provide an improved method for removal of oxidized organometallic and organosilicon residues from "vias", i.e. from pathways connecting layers in a multi-layer chip pattern.

A further object of the present invention is to provide a method for selective removal of native oxides (i.e., non-furnace grown oxides) and damaged oxides created in plasma-etching or semiconductor substrates (damaged oxides are oxides in which the crystal lattice is not uniform due to impurities or damage created in plasma-etching).

Another object of the present invention is to provide a composition and method for removal of such residues and oxides in which a greater range of solvents, HF adducts and concentrations may be used, and in which the hydrogen fluoride adducts of organic amines (hereafter "HF adducts") are more readily dissolved in the solvent of choice.

A further object of the present invention is to provide compositions and a method for removal of such residues and oxides in which etch rate may be adjusted by varying the solvent, hydrogen fluoride adduct, and concentration of the adduct in the solvent.

Still another object of the present invention is to provide a composition and method for removal of such residues and oxides which allows a range of solvent and amine choices, thereby permitting maximum safety and environmental acceptability.

Still another object of the present invention is to provide a composition and method which more effectively dissolve and/or remove organometallic, organosilicon and other organic residues (such as cross-linked photoresists) created in plasma-etching of semiconductor substrates.

Briefly, the preferred embodiment of the present invention is a process for selectively removing organic residues, damaged oxides, and native oxides through emersion of plasma-etched silicon wafers in a solution of a HF adduct dissolved in an organic solvent.
IN THE DRAWING

Figs. 1(a) and 1(b) are simplified drawings of an etching process in accordance with this invention;
Fig. 1(c) is a simplified drawing of the type of residue which remains if an organometallic residue created in plasma-etching is inadequately removed;
Fig. 2 illustrates creation of metal, oxide, and organic residues when an oxygen ashing step is used; and
Fig. 3 shows etch rates of thermal silicon oxide with the mono- and tri-HF adducts of triethylamine dissolved in N-methylpyrrolidone.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

This invention provides a process for removing organometallic residues, organosilicon residues, organic polymer residues, and damaged oxides from plasma-etched silicon wafers. The invention also provides a process for removal of native oxides from silicon wafers. Bowden et al. describe how these residues and oxides are created in semiconductor processing and the problems they can create.
Fig. 1 illustrates a simplified version of the problem. With reference to Fig. 1(a), a silicon dioxide layer 12 lies on top of a silicon wafer 10. Above the silicon dioxide layer 12 is an aluminum layer 14, upon which sits patterned photoresist 16. Aluminum layer 14 is then etched in a plasma-etch process 11 which causes some back-sputtering 13 of aluminum onto the patterned photoresist 16. The photoresist becomes coated with an alumino-organic compound which will resist stripping and will also prevent clean removal of the photoresist by a photoresist stripper.

Fig. 1(b) shows the alumino-organic compound 18 on the photoresist 16 after plasma etching of the aluminum 14. With use of the composition and method disclosed herein, the alumino-organic compound 18 is removed, thereby exposing a clear photoresist layer which may also be removed by the composition and method disclosed herein.
Fig. 1(c) shows that in the absence of removal of the aluminio-organic compound, the oxidized aluminio-organic compound 18 (a "sidewall polymer") would remain as a residue. This illustration shows plasma etching of aluminum, but similar processes and residues are involved in any plasma etching, polysilicon etching, and via etching.

Recently, it has become popular to use oxygen plasma to remove photoresist after plasma etching. If effect, the oxygen plasma combusts the photoresist. This processing step is commonly referred to as "oxygen ashing". As with conventional plasma etching, oxygen ashing involves severe conditions under which back-sputtering of metals or silicon oxides, deposition of damaged silicon oxide residues, and cross-linking of photoresist occur. Fig. 2 illustrates a simplified version of this problem. With reference to Fig. 2(a), a silicon dioxide layer 12 lies on top of a silicon wafer 10. Above the silicon dioxide layer 12 is an aluminum layer 14, upon which sits patterned photoresist 16. The aluminum layer 14 is then etched in a plasma-etch process 11 which causes some back-sputtering 13 of aluminum onto the patterned photoresist 16. The photoresist 16 becomes coated with an aluminio-organic compound.

Fig. 2(b) shows the aluminio-organic compound 18 on the photoresist 16 after plasma etching of the aluminum 14. In an oxygen ashing step (Fig. 2(c)), most of the photoresist will be removed. However, oxygen ashing 15 causes additional back-sputtering 17 of silicon dioxide and cross-linking of photoresist residues which can remain in vias and other isolated areas of the wafer. Back-sputtered silicon dioxide or metal can encapsulate portions of the photoresist, further compounding the problems of removing the residues. The silicon oxide, metal, and organic residues created tend to have high surface areas and low densities.

Fig. 2(c) shows the residues that can be left after oxygen ashing.

This invention provides an improved method for removal of unwanted residues and oxides with a controlled etching
process. The etching process is controlled through use of a
solution of a hydrogen fluoride adduct of an organic amine and
an organic solvent. This solution is preferably as free of
water as possible, preferably less than 4% by weight water,
and most preferably less than 0.5% by weight water. The
hydrogen fluoride adduct of the organic amine is described by
the general formula

\[ R_1R_2R_3N \cdot 1-3 \text{HF} \]

where at least one of \( R_1, R_2 \) or \( R_3 \) is an aliphatic or aromatic
component and 1-3 HF refers to the number of molecules of HF
per molecule of amine.

Primary and secondary amines apparently form only mono-HF
adducts, believed to have the structure:

\[ \text{HO} \]

\[ \text{HO} \]

Tertiary amines will form mono, di-, and tri-hydrogen fluoride
adducts, depending upon the amount of HF added. The di-HF and
tri-HF adducts are believed to have these structures:

\[ \text{HO} \]

\[ \text{HO} \]

\[ \text{HO} \]

\[ \text{HO} \]

\[ \text{HO} \]
The adducts are non-acidic in organic solvents, indicating that the HF is bound in the adduct. As noted above, the etching solution is preferably as free of water as possible, as water will cause dissociation of the adducts and the resultant solution will be acidic and may have much higher etch rates.

The mechanism of the etching process is believed to involve dissociation of the HF adduct of the organic amine to hydrogen fluoride in small quantity:

\[ R_1R_2R_3NHR+H_2O \rightarrow R_1R_2R_3 \cdot (n-1)HF + HF \]

Among the suitable amines are triethylamine, 2-(2-aminoethoxy)ethanol, triethanolamine and tris [2-(2-methoxyethoxy)ethyl]amine. Other amines where at least one of R₁, R₂ or R₃ is an aliphatic or aromatic constituent are expected to be suitable.

The HF adducts are soluble in a much wider variety of organic solvents than ammonium fluoride. The preferred solvents are polar organic solvents (or mixtures of solvents in which a polar organic solvent is used). Among the solvents which are suitable for the present invention are N-methylpyrrolidone (NMP), N-(2-hydroxyethyl)pyrrolidone, N-cyclohexylpyrrolidone, sulfolane, dimethylsulfoxide, gamma-butyrolactone, ethyl lactate, polyhydric alcohols (such as ethylene glycol), cellosolve acetate, propylene glycol monomethyl ether acetate, 2-phenoxyethanol, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, ethyl acetate, and butyl carbitol. Of course, mixtures of these solvents may be used.

As examples of solvents that may be used, HF adducts of triethylamine are soluble in 2-(2-aminoethoxy)ethanol and NMP, and HF adducts of tris [2-(2-methoxyethoxy)ethyl]amine are soluble in butyl carbitol and NMP. This wide range of solubility allows the amine and solvent components to be selected to dissolve organic residues of differing dissolution rates (providing considerable flexibility in the residues which may be dissolved), to achieve desired etch rates, or to address safety or environmental concerns. Adducts of amines which have relatively large amounts of organic moieties (R₁, R₂, R₃)
and/or \( R_2 \) and/or \( R_3 \) appear to have best solubilities in organic solvents.

An anhydrous hydrogen fluoride component is combined with the amine to yield the HF adduct of the organic amine. The HF adducts can be created in two ways. In the first process, the amine component is dissolved in an inert solvent such as toluene, hexane, or ethers such as diethyl ether. Anhydrous hydrogen fluoride is then slowly added with cooling until the pH of an aqueous sample extract has decreased from an initial value in the range 9-12 to a final value in the range 4.5-7. The aqueous sample extract is a volume of withdrawn solution which has been added to approximately 9 times the sample volume of deionized water. Primary amines, such as 2(2-aminoethoxy) ethanol, require one mole of HF per mole of amine. Tertiary amines, such as triethanolamine, require between 1.0 and 3 moles of HF per mole of amine. The HF adducts precipitate from the solvents as liquids or solids. Solids are isolated by filtration followed by vacuum drying. Liquids are separated by gravity followed by vacuum drying.

In a second alternative, the amine is dissolved in the final formulation solvent and anhydrous HF is added slowly with cooling until one to three moles of HF per mole of amine has been absorbed. The resulting solution may then be used as is. Recently, triethylamine tris hydrogen fluoride has become available commercially.

Once the etching solution has been produced it is contacted with the plasma-etched silicon wafer for a time period sufficient to remove the residues and oxides. The use of a surfactant aids in the removal of residue oxides by increasing wetting of the semiconductor surface by the solvent system.

Fig. 3 illustrates etch rates of thermal silicon dioxide with the mono-HF and tri-HF adducts of triethylamine in \( n \)-methylpyrrolidone at different temperatures. The solutions use 0.5% to 3.0% by weight of the mono- and tri-HF adducts of triethylamine in \( n \)-methylpyrrolidone. As noted above, the
oxide and metal residues created by back-sputtering are generally high surface area and low density. Therefore, the residues will be removed faster than the thermal oxides shown in Fig. 3, and selective removal of the unwanted residues is achieved. The solutions also remove the remaining photoresist residues, as the compositions include organic solvents which are effective for removal of photoresist. Encapsulated photoresist is removed after the oxide or metal capsule is removed by the solution.

EXAMPLES

The following examples give etch rates of uniform silicon oxide layers at 21 degrees C. As noted above, etch rates for unwanted residues will be faster than etch rates for thermal oxides.

Example 1

In this example, 5% by weight of the mono-HF adduct of 2-(2-aminoethoxy)ethanol was dissolved in two different solvents to achieve specific etch rates. In ethylene glycol, an etch rate of 3.4 Å/min was achieved; in N-methylpyrrolidone, an etch rate of 3.1 Å/min was achieved.

Example 2

In this example, 5% by weight of the tri-HF adduct of triethanolamine was dissolved in two different solvents to achieve specific etch rates. In ethylene glycol, an etch rate of 0.3 Å/min was achieved; in N-methylpyrrolidone, an etch rate of 1.1 Å/min was achieved.

Example 3

In this example, 5% by weight of the tri-HF adduct of tris[2-(2-methoxyethoxy)ethyl]amine was dissolved in three different solvents to achieve specific etch rates. In ethylene glycol, an etch rate of 0.04 Å/min was achieved; in n-methylpyrrolidone, an etch rate of 0.6 Å/min was achieved; in butyl carbitol, an etch rate of 3.8 Å/min was achieved.
Example 4

In this example, 5% by weight of triethylamine tris hydrogen fluoride was dissolved in a variety of solvents. In gamma-butyrolactone, an etch rate of 5.5 Å/min was achieved; in butyl carbitol an etch rate of 6.3 Å/min was achieved; in n-methylpyrrolidone, an etch rate of 1.1 Å/min was achieved; in 2-phenoxyethanol an etch rate of 9.9 Å/min was achieved; in ethyl lactate an etch rate of 10.5 Å/min was achieved.

A typical example of wafer processing using this invention is as follows: Photoresist patterned semiconductor wafers are plasma-etched and subjected to in-situ oxygen plasma ashing. The wafers are then emersed in an etch solution at 22 degrees Centigrade for about 30 minutes. With the etching solutions of the present invention, a separate organic stripping step is not necessary. Even if plasma ashing is not used, the photoresist and the oxide, metal, and organic residues will be removed with this single etching step. The wafers are then rinsed with de-ionized water and spin-dried.

Although the present invention has been described above in terms of a specific embodiment, it is anticipated that alterations and modifications thereof will no doubt become apparent to those skilled in the art. It is therefore intended that the following claims be interpreted as covering all such alterations and modifications as fall within the true spirit and scope of the invention.

What is claimed is:
CLAIMS

1. A method for selectively removing photoresist, organic residues, damaged silicon oxides, and native silicon oxides created in processing a semiconductor substrate from said semiconductor substrate, comprising contacting said semiconductor substrate with an etching solution for a time sufficient to remove said photoresist, residues, and oxides from said semiconductor substrate, wherein
   (a) said etching solution comprises a hydrogen fluoride adduct of an organic amine dissolved in a polar organic solvent, said hydrogen fluoride adduct of the organic amine having the formula
   \[ R_1R_2R_3N \cdot 1-3 \text{HF} \]
   where at least one of \( R_1, R_2, \) or \( R_3 \) is an aliphatic or aromatic component, and
   (b) said etching solution contains less than about 4% by weight water.

2. The method of claim 1, wherein said etching solution comprises from 0.5% to 10% by weight of hydrogen fluoride adduct of the organic amine, and from 90% to 99.5% by weight polar organic solvent.

3. The method of claim 2, wherein said etching solution contains less than 0.5% by weight water.

4. The method of claim 1, wherein the polar organic solvent is selected from the group consisting of N-methylpyrrolidone (NMP), N-(2-hydroxyethyl)pyrrolidone, N-cyclohexylpyrrolidone, sulfolane, dimethylsulfoxide, gamma-butyrolactone, ethyl lactate, ethylene glycol, glycerol, propylene glycol, polyethylene glycol, polymethylene glycol, cellosolve acetate, propylene glycol monomethyl ether acetate, 2-phenoxyethanol, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, ethyl acetate, butyl carbitol, and mixtures thereof.
5. The method of claim 4, wherein said etching solution comprises from 0.5% to 10% by weight of hydrogen fluoride adduct of the organic amine, and from 90% to 99.5% by weight polar organic solvent.

6. The method of claim 5, wherein said etching solution contains less than 0.5% by weight water.

7. A method for selectively removing organic residues, damaged silicon oxides, and native silicon oxides created in plasma etch and oxygen ash processing of a semiconductor substrate from said semiconductor substrate, comprising contacting said semiconductor substrate with an etching solution for a time sufficient to remove said residues and oxides from said semiconductor substrate, wherein
   (a) said etching solution comprises a hydrogen fluoride adduct of an organic amine dissolved in a polar organic solvent, said hydrogen fluoride adduct of the organic amine having the formula
       \[ R_1R_2R_3N \cdot 1-3 \text{ HF} \]
       where at least one of \( R_1, R_2, \) or \( R_3 \) is an aliphatic or aromatic component, and
   (b) said etching solution contains less than about 4% by weight water.

8. The method of claim 7, wherein said etching solution comprises from 0.5% to 10% by weight of hydrogen fluoride adduct of the organic amine, and from 90% to 99.5% by weight polar organic solvent.

9. The method of claim 8, wherein said etching solution contains less than 0.5% by weight water.

10. The method of claim 7, wherein the polar organic solvent is selected from the group consisting of N-methylpyrrolidone (NMP), N-(2-hydroxyethyl)pyrrolidone, N-cyclohexylpyrrolidone, sulfolane, dimethylsulfoxide, gamma-butyrolactone, ethyl
lactate, ethylene glycol, glycerol, propylene glycol, polyethylene glycol, polymethylene glycol, cellosolve acetate, propylene glycol monomethyl ether acetate, 2-phenoxyethanol, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, ethyl acetate, butyl carbitol, and mixtures thereof.

11. The method of claim 10, wherein said etching solution comprises from 0.5% to 10% by weight of hydrogen fluoride adduct of the organic amine, and from 90% to 99.5% by weight polar organic solvent.

12. The method of claim 11, wherein said etching solution contains less than 0.5% by weight water.
\[ \text{Etch Rate (Å/min)} \]

- mono-HF adduct of triethylamine
- tri-HF adduct of triethylamine

\[ 45°C \]

\[ 30°C \]

\[ 20°C \]

\[ \% \text{ HF Adduct by Weight in NMP} \]

\[ 0.5\% \quad 1\% \quad 1.5\% \quad 2\% \quad 2.5\% \quad 3\% \]

**Fig. 3**

SUBSTITUTE SHEET (RULE 26)
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) : B44C 1/22; C03C 15/00; C09K 13/06, 08; G03C 5/00
US CL : 156/657, 662; 252/79.3, 79.4; 430/329, 331
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
U.S. : 156/657, 662; 252/79.3, 79.4; 430/329, 331

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched:

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used):

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>Y</td>
<td>US A, 4,230,523 (Gajda) 28 October 1980, at column 4, line 63 to column 5, line 20.</td>
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<td>Y</td>
<td>US A, 5,277,835 (Ohmi et al) 11 January 1994, at column 3, lines 32-36 and column 4, lines 3-4, 21-30 and 57-60.</td>
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<tr>
<td>Y</td>
<td>US A, 5,320,709 (Bowden et al) 14 June 1994, at column 2, lines 65-68.</td>
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