



05 MAY 2006

## ORIGIN OF THE INVENTION

## BACKGROUND OF THE INVENTION



## 2. Description of the Prior Art:

As integrated circuit manufacturing has become more complex and the dimensions of circuit elements fabricated on silicon or other semiconductor wafers have become smaller, continued improvement in techniques used to remove residues formed from such materials has been required. Oxygen plasma oxidation is often used for removal of photoresist or other polymeric materials after their use during the fabrication process has been completed. Such high energy processes typically result in the formation of organometallic and other residues on sidewalls of the structures being formed in the fabrication process.

A variety of metal and other layers are commonly employed in integrated circuit fabrication, including aluminum, aluminum/silicon/copper, titanium, titanium nitride, titanium/tungsten, tungsten, silicon oxide, polysilicon crystal, and the like. The use of such different layers results in the formation of different organometallic residues in the high energy processes. In addition to being effective for removing such residues, cleaning compositions should also not attack the different metallurgies or insulators used in integrated circuit fabrication.

A variety of residue removal compositions and processes suitable for integrated circuit fabrication have been developed and marketed by EKC Technology, Inc., the assignee of the present application. Some of these compositions and processes are also useful for stripping photoresist, polyamide or other polymeric layers from substrates in integrated circuit fabrication, and EKC has also developed a variety of compositions and processes for stripping such polymeric layers from substrates in integrated circuit fabrication. Such compositions and processes are disclosed in the following commonly assigned issued patents: U.S. Patent 5,482,566, issued January 9, 1996 to Lee; U.S. Patent 5,399,464, issued March 21, 1995 to Lee; U.S. Patent 5,381,807, issued January 17, 1995 to Lee; U.S. Patent 5,334,332, issued August 2, 1994 to Lee; U.S. Patent 5,279,771, issued January 18, 1994 to Lee; U.S. Patent 4,824,763, issued April 25, 1989 to Lee and U.S. Patent 4,395,348, issued July 26, 1983 to Lee.

These compositions have achieved substantial success in integrated circuit fabrication applications. However, further development of integrated circuits and

their fabrication processes have created a need for improvement in residue removal compositions and processes.

As a result of a continuous effort to decrease critical dimension size in the integrated circuit industry, such as in the fabrication of sub-micron size devices, etching residue removal and substrate compatibility with chemicals employed in wet processing is becoming more and more critical for obtaining acceptable yield in very large scale integration (VLSI) and ultra large scale integration (ULSI) processes. The composition of such etching residue is generally made up of the etched substrates, underlying substrate, photoresist and etching gases. The substrate compatibility of the wafers with wet chemicals is highly dependent on the processing of the polysilicon, multilevel interconnection dielectric layers and metallization in thin film deposition, etching and post-etch treatment of the wafers, which are often quite different from one fabrication process to another. Some of the above compositions have produced corrosion on certain metal or insulator substrates, such as those including a titanium metal layer. Titanium has become more widely used in semiconductor manufacturing processes. It is employed both as a barrier layer to prevent electromigration of certain atoms and as an antireflective layer on top of other metals.

## **SUMMARY OF THE INVENTION**

Accordingly, it is an object of this invention to provide an improved composition for residue removal and process using such a composition suitable for meeting current semiconductor fabrication requirements.

It is another object of the invention to provide such a composition and process which is suitable for removing residues from wafers and other substrates including one or more titanium metal layers without substantial attack on such titanium layers.

The attainment of these and related objects may be achieved through use of the residue removal composition and process herein disclosed. A residue removal composition in accordance with this invention comprises ethylenediaminetetraacetic acid or a mono- di- tri- or tetraammonium salt thereof and water or a polar organic solvent. A process for removing a residue from a substrate in accordance

with this invention comprises contacting the substrate with a composition that contains ethylenediaminetetraacetic acid or a mono- di- tri- or tetraammonium salt thereof for a time and at a temperature sufficient to remove the residue from the substrate. When the ethylenediaminetetraacetic acid is used in its acid form, it can  
5 either be employed alone as the principal active ingredient or in combination with ammonia to form ammonium salt in situ.

In practice, we have found that use of an ethylenediaminetetraacetic acid or a mono- di- tri- or tetraammonium salt thereof gives a residue removing composition that attacks titanium, for example, at least about 3 times less' than  
10 prior compositions. At the same time, the ethylenediaminetetraacetic acid or a mono- di-tri- or tetraammonium salt thereof containing composition gives at least equivalent performance as a residue removing composition to prior art cleaning compositions.

The attainment of the foregoing and related objects, advantages and  
15 features of the invention should be more readily apparent to those skilled in the art, after review of the following more detailed description of the invention, taken together with the drawings, in which:

#### BRIEF DESCRIPTION OF THE DRAWINGS

20 Figures 1A-8C are scanning electron microscope (SEM) photographs showing comparative results achieved using the composition and process of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

25 The ethylenediaminetetraacetic acid (EDTA) or a mono- di- tri- or tetraammonium salt thereof suitable for use in the invention preferably have relatively high decomposition temperatures. Preferred higher decomposition temperature specific examples of such EDTA salts include diammonium EDTA and tetraammonium EDTA.

30 The composition desirably contains at least about 1 to 50 % by weight of at least one ethylenediaminetetraacetic acid or a mono- di- tri- or tetraammonium salt thereof; optionally, from about 25 % to about 75 % by weight of one or more

amines or alkanolamines; optionally, from about 25% to about 75% percent by weight of an organic polar solvent; optionally, from about 0.15% to about 10% by weight of an organic or inorganic ammonium salt; optionally, from about 5% to about 25% by weight of an additional chelating agent, such as catechol or gallic acid; and from about 25% to about 75% by weight of water (e.g., as part of the EDTA or its ammonium salt). When ethylenediaminetetraacetic acid is employed in the acid form, the composition may optionally contain from about 1% to about 10% percent by weight of ammonia.

Ethylenediaminetetraacetic acid (EDTA) is one of the most widely used chelating agents in the world. Its ammonium salts, soluble in water and most of the organic solvents, should be stronger chelants than EDTA due to extra ammonium chelating sites. These organic ammonium salts are good starting chemicals for ammonium based integrated circuit cleaning formulations.

Suitable amines for the composition include ethylene diamine, diethylene triamine, 2-methyleneaminopropylenediamine, and the like.

Examples of suitable alkanolamines for the composition include monoethanolamine, diethanolamine, triethanolamine, tertiarybutyldiethanolamine, isopropanolamine, diisopropanolamine (2-amino-1-propanol, 1-amino-2-propanol), triisopropanolamine, 3-amino-1-propanol, isobutanolamine, 2-(2-aminoethoxy)ethanol (diglycolamine), 2-amino-2-ethoxy-propanol, methylethanol amine, N,N-diethylene hydroxylamine, and the like.

Suitable examples of polar solvents for the composition, in addition to water, include dimethyl sulfoxide, ethylene glycol, ethylene glycol alkyl ether, diethylene glycol alkyl ether, triethylene glycol alkyl ether, propylene glycol, propylene glycol alkyl ether, N-substituted pyrrolidone, sulfolane, dimethyl acetamide, and the like. Additional polar solvents as known in the art can also be used in the composition of the present invention.

Suitable examples of ammonium salts for the composition include organic ammonium salts in addition to EDTA ammonium salts, such as ammonium tartrate, ammonium citrate, ammonium formate; ammonium glucomate; inorganic ammonium salts, such as ammonium fluoride, ammonium nitrate, ammonium

thiosulfate, ammonium persulfate, ammonium bicarbonate, ammonium phosphate, and the like.

The residue cleaning compositions of the present composition are effective in removing organometallic and metal oxide residue from a variety of integrated circuit silicon wafer substrates, including metal layers, such as aluminum or titanium, oxide layers, such as silicon oxides, nitride layers, such as silicon nitride, and the like. The cleaning compositions of the present invention are also effective in removing organometallic and metal oxide residue generated on the substrate of etching equipment utilized in the fabrication of integrated circuits. Examples of commercially available etching equipment include that available from Lam Research, Tegal, Electrotech, Applied Materials, Tokyo Electron, Hitachi and the like.

The method of cleaning a substrate using the cleaning compositions of the present invention involves contacting a substrate having organometallic and metal oxide residue thereon with a stripping and cleaning composition of the present invention for a time and at a temperature sufficient to remove the residue. The substrate is generally immersed in the stripping and cleaning composition. The time and temperature are determined based on the particular material being removed from a substrate. Generally, the temperature is in the range of from about ambient or room temperature to about 120° C. and the contact time is from about 2 to 60 minutes.

The substrate may then be rinsed in a polar solvent, such as isopropyl alcohol, followed by a deionized water rinse. The substrate is then mechanically dried, such as with a spin drier, or nitrogen blow dried.

The following represent non-limiting examples and describe the invention further.

Examples of cleaning compositions according to the present invention suitable for removing resist or other organic residues from a substrate are set forth in Table I below.

Table 1

|    | Cleaning<br>Composition | EDTA or<br>Salt Wt. % | Other Component<br>Wt. %                                   | AlkanolAmine<br>Wt. %    | Solvent<br>Wt. %         |
|----|-------------------------|-----------------------|------------------------------------------------------------|--------------------------|--------------------------|
| 5  | A                       | 17.5 % TAE            | 5 % Catechol                                               | 60 % DGA                 | 17.5 % Water             |
|    | B                       | 5 % DAE               | 5 % Citric Acid                                            | 12.5 % HDA;<br>5 % MEA   | 72.5 % Water             |
|    | C                       | 5 % DAE               |                                                            | 17.5 % HDA;<br>60 % DGA; | 17.5 % Water             |
| 10 | D                       | 5 % EDTA              |                                                            | 15 % HDA;<br>10 % DHA    | 15 % Water,<br>55 % DMSO |
|    | E                       | 5 % DAE               |                                                            | 15 % HDA;<br>10 % DHA    | 15 % Water,<br>55 % DMSO |
|    | F                       | 5 % DAE               |                                                            | 20 % HDA;                | 20 % Water,<br>55 % DMSO |
| 15 | G                       | 5 % TAE               |                                                            | 20 % HDA;                | 20 % Water;<br>55 % DMAC |
|    | H                       | 13 % EDTA             | 5 % Catechol<br>3 % NH <sub>3</sub><br>(28-30 % Aq. Sol'n) | 60 % DGA                 | 19 % Water               |

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## Abbreviations:

EDTA = ethylenediaminetetraacetic acid

DAE = diammonium EDTA

TAE = tetraammonium EDTA

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DGA = diglycolamine

HDA = hydroxylamine

MEA = monoethanolamine

DMSO = dimethylsulfoxide

DMAC = dimethylacetamide

5 DHA = N,N-diethylene hydroxylamine

The following experimental procedure was used with the above compositions. The chemicals were used as received. The solutions were prepared by stirring the mixture at room temperature until a clear solution was obtained. Heating was required in some cases to accelerate the solvation of solid  
10 components.

Ashed-via, unashed wafers and metal wafers with a TiN/Al-Cu/Ti/TiN/Ti or TiN/Al-Cu-Si/Ti stack were processed in these prepared cleaning solutions for 30 minutes at 45°C, 55°C and 65°C, depending on the nature of the formulations. The wafers were broken into pieces before and after processing in these different  
15 cleaning solutions and subsequently viewed under a FE Hitachi 4500 Scanning Electron Microscope for post ash residue removal in vias and substrate compatibility on metal stacks.

#### EXAMPLE 1

20 A via opening with a size of 1.2 micron in a silicon oxide dielectric layer was etched through a photoresist patterned opening using a standard silicon oxide plasma etching process. The photoresist was removed by oxygen plasma ashing. Figure 1A is a micrograph of a scanning electron microscope (SEM) image for a representative substrate of the type used in this example, showing that heavy  
25 organometallic etch residue remained on the substrate surface, particularly around the via opening. The substrate was then processed in composition A for 30 minutes at 55° C. Figure 1B, the resulting SEM photograph, shows that composition A removed all the organometallic residue.

#### 30 EXAMPLE 2

This example shows that composition A does not attack a titanium metallurgy. A sandwich metal thin film substrate of TiN/Al-Cu/Ti/TiN/Ti

metallurgy was patterned and etched in a plasma metal etcher. Figure 2A shows that there is organometallic residue left on the metal line surface after photoresist removal by oxygen plasma ashing. The wafer was exposed to composition A at 55° C. for 30 minutes, with substantially complete removal of the organometallic residue and no attack on the titanium metallurgy, as shown in Figure 2B.

### EXAMPLE 3

The procedures of Examples 1 and 2 were repeated with composition B but at a cleaning temperature of 45 °C. Figures 3A and 3B show the results obtained. Approximately a 90% cleaning of the ashed via wafer was obtained, as determined by visual observation of Figure 3A. There was either no metal corrosion or perhaps just the start of attack on the underlying aluminum metallurgy. Figure 3B shows complete cleaning of a TiN/Al-Cu/Ti/TiN/Ti stack wafer, with no metal corrosion, or just starting to attack the aluminum layer in the stack metallurgy.

### EXAMPLE 4

The procedures of Example 3 were repeated with composition C, also at a cleaning temperature of 45°C. Figures 4A and 4B show the results obtained. Complete cleaning of the ashed via wafer was obtained, as determined by visual observation of Figure 4A. There was complete control of metal corrosion. Figure 4B shows complete cleaning of the TiN/Al-Cu/Ti/TiN/Ti stack wafer, as shown by the clean appearance of the top TiN layer with no metal corrosion.

### EXAMPLE 5

The procedures of Example 3 were repeated with composition D but at a cleaning temperature of 65°C. Figures 5A, 5B and 5C show the results obtained. A 90% cleaning of the ashed via wafer was obtained, as determined by visual observation of Figure 5A. There was no metal corrosion. Figure 5B shows almost complete cleaning of residue an unashed via wafer, with some residue only on the bottom of the via. Figure 5C shows complete cleaning of the TiN/Al-Cu/Ti/TiN/Ti stack wafer, with no metal corrosion.

### EXAMPLE 6

The procedures of Example 5 were repeated with composition E. Figures 6A, 6B and 6C show the results obtained. Surface and sidewall cleaning of the ashed via wafer, with residue only on the bottom of the via was obtained, as determined by visual observation of Figure 6A. There was no metal corrosion.

5 Figure 6B shows complete cleaning of residue on the surface and sidewall of the via of the no-ash wafer, with some residue only on the bottom of the via, with no metal corrosion. Figure 6C shows complete cleaning of the TiN/Al-Cu-Si/Ti stack wafer.

#### 10 EXAMPLE 7

The procedures of Example 5 were repeated with composition F. Figures 7A, 7B and 7C show the results obtained. The sidewall and bottom of the via of the ashed via wafer were not quite cleaned, as determined by visual observation of Figure 7A. There was no metal corrosion. Figure 7B shows complete cleaning of  
15 25 residue on the no-ash wafer, with only a possible small aluminum undercut. Figure 7C shows complete cleaning of the TiN/Al-Cu/Ti/TiN/Ti stack wafer, with no metal corrosion.

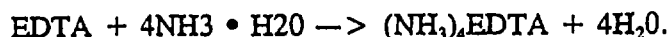
#### EXAMPLE 8

20 The procedures of Example 5 were repeated with composition G. Figures 8A, 8B and 8C show the results obtained. Surface and sidewall cleaning of the ashed via wafer, with residue only on the bottom of the via, was obtained, as determined by visual observation of Figure 8A. There was no metal corrosion. Figure 8B shows complete cleaning of residue on the surface and sidewall of the  
25 via of the no-ash wafer, with residue only on the bottom of the via, with no metal corrosion. Figure 8C shows complete cleaning of the TiN/Al-Cu/Ti/TiN/Ti stack wafer, with either no metal corrosion or just a start of titanium corrosion.

#### EXAMPLE 9

30 The procedure of Example 1 was repeated with composition H on three different wafer types. When composition H was mixed, a substantial amount of

10 heat was generated, indicating the in situ formation of tetraammonium EDTA according to the equation:



5 Figures 9A, 9B and 9C show the results obtained. The ashed via wafer was only about 80% cleaned, as determined by visual observation of Figure 9A. Some bulk polymer strips were observed. The TiN/Al-Cu/Ti/TiN/Ti stack wafer was completely cleaned and showed no corrosion of either the aluminum or the titanium layers, as shown in Figure 9B. The Ti/Al-Cu-Si/TiN stack was also completely cleaned with no aluminum or Ti corrosion, as shown in Figure 9C.

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It should now be readily apparent to those skilled in the art that a novel composition and process capable of achieving the stated objects of the invention has been provided. The improved ethylenediaminetetraacetic acid or a mono- di- tri- or tetraammonium salt thereof based composition and process using such a  
15 composition of this invention is suitable for meeting current semiconductor fabrication requirements. The composition and process is suitable for removing photoresist residues and other residues from wafers and other substrates including one or more titanium metal layers without substantial attack on such titanium layers.

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It should further be apparent to those skilled in the art that various changes in form and details of the invention as shown and described may be made. It is intended that such changes be included within the spirit and scope of the claims appended hereto.

### CLAIMS

1. A composition for removing an organic, organometallic or metal oxide residue from a substrate including titanium comprising from about 1% to 50% by weight of ethylenediaminetetraacetic acid or a mono-, di-, tri- or tetraammonium salt thereof, water, and from about 25% to about 75% by weight of a polar organic solvent.
2. The composition of claim 1 wherein the water is present in an amount of from about 25% to about 75% by weight.
3. The composition of any of claims 1-2 wherein the organic polar solvent is selected from the group consisting of dimethyl sulfoxide, ethylene glycol, ethylene glycol alkyl ether, diethylene glycol alkyl ether, triethylene glycol alkyl ether, propylene glycol, propylene glycol alkyl ether, N-substituted pyrrolidone, sulfolane, and dimethyl acetamide.
4. The composition of any of claims 1-3 further comprising from about 25% to about 75% of amine or alkanolamine.
5. The composition of claim 4 wherein the at least one amine or alkanolamine is selected from the group consisting of ethylene diamine, diethylene triamine, 2-methyleneaminopropylenediamine, monoethanolamine, diethanolamine, triethanolamine, tertiarybutyldiethanolamine, isopropanolamine, diisopropanolamine, triisopropanolamine, 3-amino-1-propanol, isobutanolamine, 2-(2-aminoethoxy)ethanol, 2-amino-2-ethoxy-propanol, methylethanol amine, and N,N-dimethyl hydroxylamine.
6. The composition of any of claims 1-5 further comprising from about 0.15% to about 10% by weight of an organic or inorganic ammonium salt.
7. The composition of claim 6 wherein the organic or inorganic ammonium salt is selected from the group consisting of ammonium tartrate, ammonium citrate, ammonium formate, ammonium glucomate, ammonium fluoride, ammonium nitrate, ammonium thiosulphate, ammonium persulfate, ammonium bicarbonate, and ammonium phosphate.

8. The composition of any of claims 1-7 further comprising from about 5% to about 25% by weight of an additional chelating agent.
9. The composition of claim 8 wherein the additional chelating agent is catechol or gallic acid.
10. The composition of claim any of claims 1-9 further comprising ammonia.
11. A composition for removing an organic, organometallic or metal oxide residue from a substrate comprising from about 13% to about 50% by weight of ethylenediaminetetraacetic acid or a mono-, di-, tri- or tetraammonium salt thereof, from about 25% to about 75% by weight of a polar organic solvent, and water.
12. The composition of claim 11 wherein the water is present in an amount of from about 25% to about 75% by weight.
13. The composition of claim 11 wherein the water is present in an amount of from about 15% to about 75% by weight.
14. The composition of any of claims 11-13 further comprising from about 25% to about 75% by weight of at least one amine or alkanolamine.
15. The composition of any of claims 11-14 wherein the ethylenediaminetetraacetic acid consists essentially of di-, tri- or tetraammonium salt thereof present in an amount from about 17.5% and about 50% by weight.
16. A composition for removing an organic, organometallic or metal oxide residue from a substrate including titanium consisting essentially of about 1% to 50% by weight of ethylenediaminetetraacetic acid or a mono-, di-, tri- or tetraammonium salt thereof, water, and from about 25% to about 75% by weight of a polar organic solvent.
17. The composition of claim 16 wherein the water is present in an amount of from about 25% to about 75% by weight.

18. The composition of any one of claims 16-17 wherein the organic polar solvent is selected from the group consisting of dimethyl sulfoxide, ethylene glycol, ethylene glycol alkyl ether, diethylene glycol alkyl ether, triethylene glycol alkyl ether, propylene glycol, propylene glycol alkyl ether, N-substituted pyrrolidone, sulfolane, and dimethyl acetamide.
19. A composition for removing an organic, organometallic or metal oxide residue from a substrate consisting essentially of from about 13% to about 50% by weight of ethylenediaminetetraacetic acid or a mono-, di-, tri- or tetraammonium salt thereof, from about 25% to about 75% by weight of a polar organic solvent, and water.
20. The composition of claim 19 wherein the water is present in an amount of from about 25% to about 75% by weight.
21. The composition of claim 19 wherein the water is present in an amount of from about 15% to about 75% by weight.
22. The composition of any one of claims 19-21 wherein the ethylenediaminetetraacetic acid consists essentially of di-, tri- or tetraammonium salt thereof present in an amount from about 17.5% and about 50% by weight.
23. A composition for removing an organic, organometallic or metal oxide residue from a substrate including titanium consisting essentially of about 1 to 50% by weight of ethylenediaminetetraacetic acid or a mono-, di-, tri- or tetraammonium salt thereof, from about 25% to about 75% by weight of a polar organic solvent, from about 25% to about 75% by weight of at least one amine or alkanolamine, and water.
24. A method for removing an organic, organometallic or metal oxide residue from a substrate including titanium, the method comprising the steps of contacting the substrate with the composition of any one of claims 1 to 23.
25. A method for removing an organic, organometallic or metal oxide residue from a substrate, the method comprising the steps of contacting the substrate with the composition of any one of claims 11-23.