

## **CHEMICAL ETCHING SOLUTION AND METHOD FOR SELECTIVELY ETCHING TITANIUM**

### **TECHNICAL FIELD OF THE INVENTION**

5 The invention relates to a stable chemical etching solution for etching titanium-based materials, in particular titanium-based barrier layers formed on microelectronic devices, while being substantially selective with other materials potentially exposed thereto, such as copper, aluminum/copper, tin or its alloys, and/or dielectric materials.

The invention also relates to a method for etching titanium-based materials using said  
10 solution.

### **STATE OF THE ART**

In the manufacturing of new generation electrical contacts, for example copper pillars, a barrier layer is deposited before copper deposition to reduce diffusion in dielectric materials  
15 and improve adhesion performance.

Such a barrier layer can be deposited either by the CVD (Chemical Vapor Deposition) or PVD (Physical Vapor Deposition) methods, and generally has a thickness less than or equal to 100 nm.

The metals of choice for such barrier layers are titanium, titanium nitride or titanium  
20 tungsten.

In the manufacture of copper pillars, the titanium-based barrier layer is deposited on a dielectric or polyimide surface already having contact holes with the underlying copper metal layers and possibly aluminum pads, then a copper primer layer is deposited by PVD.

A thick layer of photoresist is applied and developed to form holes through which  
25 electrochemical copper can grow, and eventually a thin layer of tin or tin/silver alloy is deposited over the copper.

After removal of the photoresist and the remaining thin layer of copper primer deposited by PVD, the titanium-based barrier must be selectively removed from other exposed metals to form isolated conductive pillars.

30 Copper removal is usually carried out in mixtures of dilute sulfuric acid or phosphoric acid and hydrogen peroxide. Some aluminum pads may be partially exposed due, for example, to a misalignment of the lithography.

It is then desirable to have a barrier layer removal solution that is selective with copper, aluminum/copper, tin or tin alloys, as well as with dielectric materials and polyimide.

The removal of the titanium-based barrier layer is generally carried out with a heated concentrated hydrogen peroxide solution (comprising 5 to 30% by weight of hydrogen peroxide), such as for example with the S.C.1 cleaning solution. (Standard Clean 1 for a solution of ammonia mixed with hydrogen peroxide) or a similar mixture or with very  
5 diluted hydrogen fluoride solutions at room temperature used specifically for dissolving pure titanium.

The usual solutions for removing barrier layers of titanium-based material suffer from several weaknesses.

For example, hydrogen peroxide can hardly be recirculated due to its susceptibility to  
10 decomposition and the rapid change in etching speed occurring when contaminated with metals. In addition, when titanium nitride or titanium is used as a barrier layer, pure hydrogen peroxide can hardly remove the titanium oxide usually present on the surface and at the interface with the dielectric. The S.C.1 solution corresponding to a mixture of hydrogen peroxide and ammonium hydroxide can improve the etching speed on titanium oxide but  
15 becomes very difficult to be controlled with regard to the selectivity with aluminum. Indeed, the mixture of ammonium hydroxide and hydrogen peroxide at the point of use would require extremely specific equipment to allow the mixture to remain at a pH below 8 in order to ensure its selectivity with aluminum and control of copper oxidation.

Dilute solutions of hydrogen fluoride, on the other hand, can easily dissolve titanium oxide  
20 but do not dissolve titanium nitride or titanium tungsten. In addition, diluted solutions of hydrogen fluoride are not compatible with aluminum, tin or its alloys, and silicon oxide-based dielectrics.

In addition, it is quite difficult to control etch profiles with hydrogen fluoride-based etching agents, due to the very high etching speeds even at very low hydrogen fluoride  
25 concentrations because dissolution does not stop as soon as the rinsing step begins.

Complexing agents such as EDTA (ethylenediamine tetraacetic acid) and CDTA (trans-1,2-diamino cyclohexane, N,N,N,N tetraacetic acid) can be added to the mixture of hydrogen peroxide with an inorganic base to increase stability and allow recirculation but this can cause problems in waste treatment plants because these molecules, which are very effective  
30 in capturing metals, are difficult to eliminate.

Patent application EP3436621 thus describes a chemical etching solution for titanium-based materials comprising hydrogen peroxide, potassium hydroxide and a complexing agent which is preferentially CDTA because the chemical etching solutions obtained are then the more stable.

## DISCLOSURE OF THE INVENTION

From an industrial point of view, it is desirable to have a chemical etching solution that has the following advantages:

- 5       - it is stable for a sufficient duration to be usable industrially,
- it can quickly dissolve Titanium-based barriers selectively to exposed materials (for example copper, copper aluminum, tin or tin alloys, dielectric materials and polyimide) with easy control of the etching profile,
- it can be recirculated in the presence of metals and
- 10       - and it meets environmental criteria in terms of toxicity.

Surprisingly, it was found that a chemical etching solution comprising hydrogen peroxide, a complexing agent derived from phosphonic acid of the diethylenetriamine-pentamethylenephosphonic acid (DTPMP) or aminotrimethylenephosphonic acid (ATMP) type, and tribasic potassium phosphate ( $K_3PO_4$ ) has optimized properties in terms of stability

15       over time, particularly in the presence of metal-type contaminants, and allows to etch titanium-based barriers selectively to other exposed materials such as copper, aluminum/copper, tin and its alloys, or else dielectric materials and polyimide, while maintaining good control of the etching profiles. Furthermore, such a solution is satisfactory in terms of environmental criteria.

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### *Summary of the invention*

The object of the invention is a chemical etching solution for a titanium-based material comprising:

- from 26% by weight to 39% by weight of hydrogen peroxide,
- 25       - from 1% by weight to 6% by weight of tribasic potassium phosphate ( $K_3PO_4$ ),
- from 0.015% by weight to 0.2% by weight of a compound selected from diethylenetriamine-pentamethylenephosphonic acid (DTPMP), aminotrimethylenephosphonic acid (ATMP) and mixtures thereof
- water,

30       the percentages by weight being expressed relative to the weight of the chemical etching solution,

said solution having a pH of 6.5 to 8.6.

The invention also relates to a method for chemically etching a layer of a titanium-based material on a microelectronic device, said method comprising contacting said layer with the chemical etching solution as described above for a duration sufficient to eliminate said layer, said titanium-based material consisting of titanium, titanium nitride, titanium-tungsten or mixtures thereof, preferably titanium.

Advantageously, the chemical etching solution, after etching the microelectronic device, is reused to etch one or more other microelectronic devices.

Advantageously, the chemical etching solution is heated and contacted with the microelectronic device at a temperature of 20°C to 60°C, preferably 35°C to 50°C.

The invention also relates to a method for preparing a chemical etching solution as described above comprising the mixture:

- of a composition comprising:
  - o tribasic potassium phosphate ( $K_3PO_4$ ),
  - o the compound selected from diethylenetriamine-pentamethylenephosphonic acid (DTPMP), aminotrimethylenephosphonic acid (ATMP) and mixtures thereof
  - o water,
- and of an aqueous solution of hydrogen peroxide at a mass concentration of hydrogen peroxide of 30% by weight to 40% by weight relative to the weight of the aqueous solution.

to reach a pH of 6.5 to 8.6.

Advantageously, the chemical etching solution is prepared using a point-of-use mixing technique consisting of mixing just before distributing the aqueous solution of hydrogen peroxide and the composition comprising the potassium phosphate salt, the compound selected from diethylenetriamine-pentamethylenephosphonic acid (DTPMP), aminotrimethylenephosphonic acid (ATMP) and mixtures thereof and water.

Other aspects of the invention are as described below and in the claims.

### ***Definitions***

In this text, the expression “the balance being water” means that the percentage by weight of water corresponds to 100% minus the sum of the percentages by weight of the other chemical substances present in the composition.

In this text, the term “microelectronic device” means semiconductor substrates, flat screens,  
5 phase change memory devices, solar panels and other products, including solar cell devices, photovoltaic systems and microelectromechanical systems (MEMS), manufactured for use in microelectronics, integrated circuit applications, energy harvesting or computer chips.

It should be understood that the terms “microelectronic device”, “microelectronic substrate” and “microelectronic device material” are in no way intended to be limiting and include any  
10 substrate or structure that will eventually become a microelectronic device or microelectronic assembly.

The term “Titanium-based material” means a material consisting of Titanium, Titanium Nitride or Titanium Tungsten or a mixture thereof. It is understood that the surface of the material may have a layer of titanium oxide due to the oxidation of titanium. Thus a layer of  
15 titanium-based material can have a superficial layer of titanium oxide, at the surface and at the interface with the dielectric.

In the present text, the term “Titanium-based barrier layer” means any thin film with a thickness ranging from 5 nm to 500 nm, composed of Titanium, Titanium Nitride, Titanium Tungsten or a mixture thereof.

20 As used herein, the term “approximately” is intended to be  $\pm 5\%$  of the stated value.

As used herein, the term “room temperature” means a temperature ranging from 20°C to 25°C.

As defined herein, the term “complexing agent” comprises compounds which are understood by a person skilled in the art to be complexing agents, chelating agents, sequestering agents  
25 and combinations thereof. Complexing agents chemically combine or physically associate with the metal atom and/or metal ion to be removed. Complexing agents are used to capture contaminants, in particular metallic contaminants, in the chemical etching solution, which has the effect of improving the stability of the chemical etching solution and therefore limiting the attack or corrosion of the potentially exposed materials other than titanium-  
30 based materials. The terms “complexing agents” and “anti-corrosion agents” are equivalent here.

The terms “aqueous hydrogen peroxide solution” and “oxygenated water” are equivalent here.

“Percentages” of a compound, as indicated herein, are percentages by weight or mass of said

compound relative to the weight of the composition comprising said compound.

“The etching solution consists of” means that the etching solution does not comprise any components other than those mentioned.

5 “The etching solution consists essentially of” means that the etching solution contains other components than the obligatory components in the etching solution, provided that the essential features of the etching solution, such as its stability, the etching speed of titanium-based materials and the selectivity of the etching with respect to exposed materials are not affected by the presence of these components.

10 “The etching solution is stable or has satisfactory stability” means an etching solution whose stability is evaluated in the stability test described in the examples (point 1.3) and for which the variation in pH ( $\Delta[\text{pH}]$ ) in absolute value ranges from 0 to 10% and the variation in the hydrogen peroxide content ( $\Delta[\text{H}_2\text{O}_2]$ ) in absolute value ranges from 0 to 35%.

## FIGURES

15 [Fig. 1] illustrates the evolution of the thickness of the remaining titanium layer (expressed as a percentage of the initial thickness) according to the etching test described in paragraph 1.1. of the examples as a function of the immersion time for the different etching solutions of example 1 at 25°C ( •solution 1/▲ solution 2/◆solution 3).

20 [Fig. 2] illustrates the evolution of the thickness of the remaining titanium layer (expressed as a percentage of the initial thickness) according to the etching test described in paragraph 1.1. of the examples as a function of immersion time and temperature for the etching solution of Example 6.

25 [Fig. 3] illustrates the evolution of the etching speed in nm/min of the titanium layer according to the etching test described in paragraph 1.1. of the examples as a function of temperature for the etching solution of Example 6.

[Fig. 4] illustrates the effectiveness of cleaning the titanium layer of copper pillars according to example 6 by etching solutions aged at 50°C for different durations:

- top left (1): chemical etching solution aged for 5 min at 50°C
- top right (2): chemical etching solution aged for 1h30 at 50°C
- 30 - bottom left (3): chemical etching solution aged for 3 hours at 50°C
- bottom right (4): chemical etching solution aged for 6 hours at 50°C.

[Fig. 5] shows the foot of a copper pillar etched according to example 6 using the unaged chemical etching solution 1 (photo on the left - A) and this same etching solution aged for 2

hours at 50°C (right photo - B).

## DETAILED DESCRIPTION OF THE INVENTION

5 The main difficulty in developing an effective chemical etching solution for a titanium-based barrier layer lies in the need to etch the titanium oxide surface or interface at an acceptable speed while remaining selective with respect to exposed metals, such as copper, aluminum/copper or tin.

The inventors know that titanium and tungsten materials can be dissolved in hydrogen peroxide at an appreciable speed.

10 The inventors also know that increasing the pH by adding ammonia or any base can improve not only the etching speed on bulk materials, but also the dissolution rate of titanium oxide, thanks to increasing the concentration of  $\text{HO}_2^-$  which is considered the active species in etching titanium-based materials.

15 However, given the current limitations of most industrial equipment, it is difficult to maintain a point-of-use mixture with a stable pH. As a result, the corrosion of exposed metals and decomposition of hydrogen peroxide are difficult to control.

Furthermore, complexing agents such as CDTA allow to stabilize etching solutions but their use poses environmental problems.

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The inventors have developed a chemical etching solution meeting the needs expressed.

The inventors have thus surprisingly discovered that the use of a complexing agent derived from phosphonic acid of the diethylenetriamine-pentamethylenephosphonic acid (DTPMP) or aminotrimethylenephosphonic acid (ATMP) type and a potassium phosphate salt allows  
25 to optimize the properties of hydrogen peroxide-based etching solutions.

Without wishing to be bound by any theory, potassium phosphate could allow the generation of  $\text{HOO}^-$  ions for the attack on titanium while allowing to stabilize the pH by exerting a  
30 buffer effect in the chemical etching solution.

A first object of the invention thus relates to a solution for chemical etching of a titanium-based material comprising:

- from 26% by weight to 39% by weight of hydrogen peroxide,

- from 1% by weight to 6% by weight of tribasic potassium phosphate ( $K_3PO_4$ ),
- from 0.015% by weight to 0.2% by weight of a compound selected from diethylenetriamine-pentamethylenephosphonic acid (DTPMP), aminotrimethylenephosphonic acid (ATMP) and mixtures thereof

5 - water,

the percentages by weight being expressed relative to the weight of the chemical etching solution,

said solution having a pH of 6.5 to 8.6.

10 By the chemical etching solution comprising a potassium phosphate salt as described above, it should be understood that the chemical etching solution can be prepared from said potassium phosphate salt.

Phosphate salt can also be generated once in solution by mixing phosphoric acid and potassium hydroxide.

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Tribasic potassium phosphate is used according to the present invention because its aqueous solubility is higher than that of tribasic sodium phosphate, which allows to obtain more concentrated salt solutions. This is particularly advantageous when the chemical etching solution is prepared by mixing an aqueous concentrate comprising the phosphate salt and a

20 concentrated hydrogen peroxide solution.

Moreover, surprisingly, the etching solutions obtained from tribasic potassium phosphate have better chemical selectivity with respect to exposed materials such as copper, aluminum or else polyimide than the etching solutions obtained from ammonium phosphate salts.

25 The percentage by weight of tribasic potassium phosphate in the chemical etching solution is 1% to 6%, preferably 1 to 4%, more preferably 1 to 2%.

When the weight percentage of tribasic potassium phosphate in the chemical etching solution is less than 1%, the stability of the chemical etching solution is reduced.

30

When the weight percentage of tribasic potassium phosphate in the chemical etching solution is greater than 6%, the pH of the resulting solution may be too high, which may lead to excessive attack of exposed materials such as aluminum or at an etching speed that is too fast, making the etching operation difficult to control.

The chemical etching solution according to the invention further comprises hydrogen peroxide.

5 The source of hydrogen peroxide may be commercially available hydrogen peroxide of any initial concentration equal to or greater than 30% by weight with or without phosphate/phosphonate/stanate stabilizers, but may also be prepared by diluting with pure water a more concentrated solution of hydrogen peroxide.

10 The percentage by weight of hydrogen peroxide in the chemical etching solution is chosen so as to optimize the etching of the titanium and the stability of the chemical etching solution. It is 26 to 39%, preferably 26% to 35%, even more preferably 27 to 30%.

The weight percentage of hydrogen peroxide entering the chemical etching solution of the present invention is expressed as pure hydrogen peroxide relative to the total weight of the chemical etching solution.

15 The chemical etching solution according to the invention also comprises a complexing agent allowing to improve the stability of the chemical etching solution and which is selected from diethylenetriamine-pentamethylenephosphonic acid (DTPMP), aminotrimethylenephosphonic acid (ATMP) and mixtures thereof.

20 The complexing agents conventionally used in etching solutions are for example EDTA (ethylenediamine tetraacetic acid) and CDTA (trans-diamino-1,2 cyclohexane, N,N,N,N tetraacetic acid). Such complexing agents are difficult to remove during the treatment of wastewater in wastewater treatment plants, which can pose environmental problems.

25 The use of less toxic complexing agents such as diethylenetriamine-pentamethylenephosphonic acid (DTPMP), aminotrimethylenephosphonic acid (ATMP) and mixtures thereof in the chemical etching solution allows to overcome this difficulty.

30 The percentage by weight of complexing agent in the chemical etching solution is 0.015% to 0.2%, preferably 0.015% to 0.1%, more preferably 0.015% to 0.04%.

When the mass percentage of DTPMP, ATPMP or their mixture in the chemical etching solution is less than 0.015%, the stabilizing effect of the complexing agent with respect to the chemical etching solution is reduced.

When the mass percentage of DTPMP, ATPMP or their mixture in the chemical etching solution is greater than 0.2%, there is no increase in the stabilizing effect of the complexing agent with respect to the chemical etching solution.

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Advantageously, the complexing agent is diethylenetriamine-pentamethylenephosphonic acid (DTPMP) used alone.

The pH of the chemical etching solution according to the invention is 6.5 to 8.6, preferably 10 7 to 8, more preferably 7.3 to 7.8.

When the pH of the chemical etching solution is above 8.5, it is difficult to control the temperature of the cleaning solution to avoid self-accelerated decomposition in the event of accidental contamination for example.

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Advantageously, the chemical etching solution according to the invention consists or essentially consists of:

- hydrogen peroxide,
- tribasic potassium phosphate ( $K_3PO_4$ ),
- 20 - diethylenetriamine-pentamethylenephosphonic acid (DTPMP),  
aminotrimethylenephosphonic acid (ATMP) or mixtures thereof,
- and water.

Advantageously, the chemical etching solution according to the invention consists or essentially consists of:

- 25 - hydrogen peroxide,
- tribasic potassium phosphate ( $K_3PO_4$ ),
- diethylenetriamine-pentamethylenephosphonic acid (DTPMP),
- and water.

The chemical composition according to the invention may comprise other components 30 provided that the essential features of the etching solution, such as its stability, the etching speed of titanium-based materials and the selectivity of the etching with respect to exposed materials are not affected by the presence of these components.

Advantageously, the chemical etching solution according to the invention does not comprise any other complexing agent or other anti-corrosion agent than diethylenetriamine-pentamethylenephosphonic acid (DTPMP), aminotrimethylenephosphonic acid (ATMP) and mixture thereof.

5 Advantageously, the chemical etching solution according to the invention does not comprise an organic acid capable of complexing metals such as citric acid.  
Being able to selectively remove titanium compared to other exposed metals without using any other corrosion inhibitor allows to reduce the costs of manufacturing etching solutions, therefore reducing the costs of the etching methods of microelectronic devices using such  
10 solutions.

An etching method is proposed.

A second object of the invention relates to a method for chemically etching a layer of a titanium-based material on a microelectronic device, said method comprising contacting said  
15 layer with the chemical etching solution as described above for a duration sufficient to eliminate said layer, said titanium-based material consisting of titanium, titanium nitride, titanium-tungsten or mixtures thereof, preferably titanium.

According to one embodiment, the chemical etching solution is heated and contacted with  
20 the microelectronic device at a temperature of 20°C to 60°C, preferably 35°C to 50°C.

According to the etching method of the invention, the chemical etching solution is contacted with the layer of titanium-based material for a duration of approximately 45 seconds to approximately 10 minutes, preferably from approximately 1 minute to approximately 5  
25 minutes.

Such contact times are illustrative, and can be adapted depending on the temperature of the chemical etching solution and its composition.

Advantageously, the etching method allows to effectively eliminate the layer of titanium-based material from the surface of a microelectronic device without substantially eliminating  
30 other materials present on the microelectronic device such as copper, copper aluminum, tin or tin alloys or else dielectric materials or polyimide.

Due to its stability over time, the chemical etching solution is reusable and can be stored in a tank before further use.

Thus, advantageously, the chemical etching solution, after etching the microelectronic device, can be reused to etch one or more other microelectronic devices.

A third object of the invention relates to a method for preparing a chemical etching solution as described above comprising the mixture:

- of a composition comprising:
  - o tribasic potassium phosphate ( $K_3PO_4$ ),
  - o the compound selected from diethylenetriamine-pentamethylenephosphonic acid (DTPMP), aminotrimethylenephosphonic acid (ATMP) and mixtures thereof
  - o water,
- and of an aqueous solution of hydrogen peroxide at a mass concentration of hydrogen peroxide of 30% by weight to 40% by weight relative to the weight of the aqueous solution. to reach a pH of 6.5 to 8.6.

The method for preparing the chemical etching solution thus comprises the addition of an aqueous concentrate of the potassium phosphate salt and the complexing agent to a concentrated solution of hydrogen peroxide.

When the aqueous hydrogen peroxide solution comprises more than 40% hydrogen peroxide, controlling the temperature of the cleaning solution becomes too difficult to avoid self-accelerated decomposition in the event of accidental contamination for example.

The percentage of tribasic potassium phosphate in the concentrate is limited by the aqueous solubility of the salt. Advantageously, the concentrate according to the invention comprises a maximum of 46% by weight of tribasic potassium phosphate.

When the mass percentage of tribasic potassium phosphate in the concentrate is low the amount of water added to the hydrogen peroxide to reach the target pH reduces the effectiveness of the final solution. Advantageously, the concentrate according to the invention comprises at least 5% by weight of tribasic potassium phosphate.

Adjusting the pH of the solution as described above to a value of 6.5 to 8.6 allows titanium-based materials to be etched efficiently while avoiding corrosion of potentially exposed metals other than titanium, such as copper or aluminum for example.

The chemical etching solution as described above may be a ready-to-use solution or may be prepared before use by implementing the preparation method detailed above.

- Advantageously, the chemical etching solution is prepared using a point-of-use mixing technique consisting of mixing just before distributing the aqueous solution of hydrogen peroxide and the composition comprising tribasic potassium phosphate, the compound selected from diethylenetriamine-pentamethylenephosphonic acid (DTPMP), aminotrimethylenephosphonic acid (ATMP) and mixtures thereof and water.
- Manufacturing the composition at point of use means that the aqueous solution of hydrogen peroxide and the composition comprising tribasic potassium phosphate, the compound selected from diethylenetriamine-pentamethylenephosphonic acid (DTPMP), aminotrimethylenephosphonic acid (ATMP) and mixtures thereof and water, are mixed just before contacting the composition obtained with the substrate to be cleaned.
- According to one embodiment, the aqueous solution of hydrogen peroxide and the composition comprising tribasic potassium phosphate, the compound selected from diethylenetriamine-pentamethylenephosphonic acid (DTPMP), aminotrimethylenephosphonic acid (ATMP) and mixtures thereof and water, are mixed and heated in a tank.
- Other point-of-use mixing techniques (for example, on-line mixing of constituents just before distribution) may be used.
- Then, the substrate is immersed in the chemical etching solution inside the tank.
- Other techniques for contacting the substrate and the chemical etching solution can be used without departing from the scope of the invention, such as for example sprinkling the substrate with the composition.
- Preferably, the chemical etching solution is used at a temperature of 35°C to 50°C, in order to reduce cleaning time. A lower temperature is however possible, the cleaning time then being extended.

- The features and advantages of the solution are further illustrated by the examples discussed below.

## **EXAMPLES**

### **1.Tests carried out**

### 1.1 Titanium etching test

A volume of 50 ml of chemical etching solution is previously activated by two 6 cm<sup>2</sup> silicon coupons with a 500 nm thick layer of titanium.

The etching test consists of immersing a full plate coupon comprising a 100 nm layer of Titanium deposited by PVD on silicon oxide in the activated chemical etching solution.

The solution is then heated to the temperature of use, with moderate stirring (200 rpm, rpm meaning “revolution per minute”). The remaining thickness of the titanium, measured at regular intervals, is evaluated by measuring the electrical resistance using a four-point probe.

From the remaining thickness of titanium, it is also possible to calculate an etching speed expressed for example in nm/min. The evolution of the remaining thickness is not necessarily linear over time so that it can be difficult to determine an etching speed. The etching speed can be reduced at the start and end of etching. This can be attributed to the presence of a thin oxide layer at the interface with air and at the interface with the silicon oxide layer. The etching speed value as defined below corresponds to the thickness of titanium removed for a given time.

Coupons comprising structures comprising copper pillars were also used (see example 6). The resin was removed with a TechniStrip®P1331 solution at 60°C for 5 minutes, then removal of the copper primer layer was carried out with a TechniEtch Cu Select solution at 20°C for 1 minute 30 without stirring. The same method as described previously was used to remove the titanium barrier during the time required to clean the coupon. Then the coupons were observed under a scanning electron microscope in order to determine whether or not the presence of titanium residues and whether or not the exposed layers were over-etched.

### 1.2 Chemical selectivity test

The chemical selectivity test with respect to metallic elements consists of evaluating the speed of attack of layers of said metallic elements in the presence of the chemical etching solution.

Thus, silicon wafer coupons of 500 nm of aluminum (AlCu) deposited by PVD on silicon oxide, or of 40 nm of copper deposited by PVD on silicon oxide are used.

A volume of 50 ml of chemical etching solution is heated to 50°C and previously activated by two 6 cm<sup>2</sup> silicon coupons with a 500 nm thick layer of titanium.

The copper and aluminum coupons are immersed for one hour while stirring at 200 rpm. The remaining thickness of the film on the coupons is evaluated over time by measuring the electrical resistance using a four-point probe.

5 A speed of attack can also be calculated.

The higher the attack speed value, the less selective the chemical etching solution is with the metallic element.

### 1.3 Stability test of etching solutions

10 The stability test of etching solutions comprises the following steps:

- heating the chemical etching solution with initial concentration of hydrogen peroxide ( $C_{H_2O_2\text{initial}}$ ) with stirring at 65°C
- measuring the pH of the solution (initial pH)
- activating 50 ml of the solution with 2 6 cm<sup>2</sup> silicon coupons with a 500 nm thick layer of titanium
- 15 • aging for 6 hours at 65°C with stirring
- titrating the remaining hydrogen peroxide ( $C_{H_2O_2\text{final}}$ ) by titration with potassium permanganate
- measuring the pH (final pH)

20 The variation in pH ( $\Delta[\text{pH}] = (\text{pH}_{\text{final}} - \text{pH}_{\text{initial}})/\text{pH}_{\text{initial}} * 100$ ) and the variation in the hydrogen peroxide content ( $\Delta[\text{H}_2\text{O}_2] = ((C_{H_2O_2\text{final}} - C_{H_2O_2\text{initial}})/C_{H_2O_2\text{initial}} * 100)$  allow to characterize the stability of the chemical etching solution.

### 1.4 Test of loading etching solutions with metal elements - influence of metal

25 contaminants on the etching speed

The chemical etching solution is heated to 50°C and is loaded with metallic contaminant by immersing the equivalent of 10 wafers of 300 mm diameter with or without pattern per liter for a time sufficient to remove the 100 nm layer of titanium present at the surface of the coupons.

30 When the coupons have a pattern, the exposed parts may be copper or polyimide.

The solution then undergoes aging at 50°C and the etching speed of the titanium in the aged solution is measured.

In all the examples, the percentages of the constituents of the compositions are mass percentages expressed relative to the mass of said compositions, the remaining mass percentage corresponding to water.

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## **2. Examples**

### **Example 1:**

The following chemical etching solutions are used:

- 5        - Solution S.C.1. (Standard Clean 1) obtained by mixing one volume of a hydrogen peroxide solution, one volume of an aqueous ammonia solution at 30% by weight and 20 volumes of water. The pH of the solution is 10.8. This solution is denoted solution 1.
- 10       - Aqueous solution of 30% by weight of hydrogen peroxide (denoted solution 2). The pH of solution 2 is 3.7.
- 15       - Solution according to the invention obtained by mixing 94% by mass of an aqueous solution containing 30% by mass of hydrogen peroxide and 6% by mass of an aqueous solution comprising 25% by mass of tribasic potassium phosphate ( $K_3PO_4$ ) and 0.4% by mass of diethylenetriamine-pentamethylenephosphonic acid (DTPMP). The pH of the chemical etching solution is 7.6. This solution is denoted solution 3.

- titanium etching test

Figure 1 shows the change in thickness of the titanium layer, as a function of the immersion time in the different solutions at 25°C.

- 20       The data in Figure 1 show that the chemical etching solution according to the invention is more effective for etching titanium than the solutions of the prior art.

- selectivity of etching solutions with respect to copper and aluminum/copper

- 25       The selectivity with respect to copper and aluminum/copper of the 3 etching solutions above as well as an aqueous solution (denoted solution 4) based on hydrogen peroxide, potassium hydroxide and CDTA (trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid) as described in patent application EP 3436621 was evaluated.

Solution 4 has the following composition: 28.2%  $H_2O_2$ /0.35% KOH/0.012% CDTA, the percentages being percentages by weight relative to the weight of the solution.

- 30       The attack speed for copper (Cu) and aluminum/copper (AlCu) is shown in Table 1. For copper, the value shown is the average value measured during the first 2 minutes of the test. For aluminum copper, the value indicated corresponds to the average value measured during the first 10 minutes of the test (except for solution 1 for which the value indicated

corresponds to the value measured during the first minute of the test).

[Table 1]

| Speed of attack nm/min<br>@50°C | Cu  | AlCu  |
|---------------------------------|-----|-------|
| Solution 1                      | 3.9 | 400.0 |
| Solution 2                      | 2.6 | 0.1   |
| Solution 3                      | 0.9 | 0.9   |
| Solution 4                      | 0.9 | 1.5   |

The low speed of attack of Cu and Aluminum copper with solution 3 according to the invention shows that this solution is compatible with these metallic elements.

The results obtained with solution 3 according to the invention are comparable to those obtained with solution 4 of the prior art.

#### Example 2: effect of the nature of the counter-ion of the tribasic phosphate salt

The following 3 chemical etching solutions are tested:

- solution 1 of composition: 28.2% hydrogen peroxide; 1.5% tribasic potassium phosphate; 0.024% diethylenetriamine-pentamethylenephosphonic acid (DTPMP)
- Solution 2 of composition: 28.2% hydrogen peroxide; 1.1% tribasic sodium phosphate; 0.024% diethylenetriamine-pentamethylenephosphonic acid (DTPMP)
- Solution 3 of composition: 28.2% hydrogen peroxide; 1.1% tribasic ammonium phosphate; 0.024% diethylenetriamine-pentamethylenephosphonic acid (DTPMP)

The percentages are mass percentages expressed relative to the mass of the chemical etching solution, the remaining percentage being water.

The 3 solutions are equimolar in tribasic phosphate salt.

- solubility of phosphate salts depending on the nature of the counter-ion of the phosphate salt:

The solubility in water at 25°C of tribasic potassium phosphate is 900 g/l.

The solubility in water at 25°C of tribasic sodium phosphate is 110 g/l.

The solubility in water at 25°C of tribasic ammonium phosphate is 580 g/l.

Potassium salt is preferred to sodium salt because of its greater aqueous solubility.

From an industrial point of view, the chemical etching solution is prepared from a concentrate in water of the phosphate salt. High aqueous solubility is thus preferred.

- speed of etching of titanium depending on the nature of the counter-ion of the phosphate salt:

The etching speed was evaluated at 50°C with stirring in the different solutions prepared.

It is respectively equal to 82 nm/min, 81 nm/min and 85 nm/min for the potassium salt, the sodium salt and the ammonium salt.

The titanium etching speed is therefore independent of the nature of the counter-ion of the phosphate salt.

- evaluation of the stability of etching solutions 1 and 3

The hydrogen peroxide content is reduced by 31% whether the counter-ion of the phosphate salt is the potassium ion or the ammonium ion.

- evaluation of the selectivity of etching solutions 1 and 3 with respect to copper and aluminum

The speed of attack of copper and aluminum is shown in Table 2.

For copper, the value indicated corresponds to the average value measured during the first 2 minutes of the test. For aluminum copper, the value indicated corresponds to the average value measured during the first 10 minutes of the test.

[Table 2]

| Speed of attack nm/min<br>@50°C | Cu  | AlCu |
|---------------------------------|-----|------|
| Solution 1                      | 0.9 | 0.9  |
| Solution 3                      | 3.0 | 3.3  |

The speeds of attack of copper and aluminum are lower (respectively 3.3 times and 2.4 times) when the counter-ion of the phosphate salt is a potassium ion (case of solution 1) rather than an ammonium ion (case of solution 3).

- copper loading test of etching solutions 1 and 3

The chemical etching solution 1 is heated to 50°C and is loaded with copper by immersing the equivalent of 10 patterned copper wafers with a diameter of 300 mm per liter, or 44 coupons of 3 cm<sup>2</sup> in 20 mL, for a sufficient time to remove the 100 nm layer of titanium present on the surface of the coupons.

The titanium etching speed is evaluated at  $t_0$  (after loading with copper), then after aging at 50°C of the chemical etching solution loaded with copper.

The results are shown in Table 3.

The chemical etching solution 3 shows a loading capacity of only 3 wafers/liter before running away and degrading (strong gas release) after 0.58 hours.

[Table 3]

| Ti etching speed in nm/min after different aging times of the chemical etching solution at 50°C | Solution 1 | Solution 3 |
|-------------------------------------------------------------------------------------------------|------------|------------|
| T0                                                                                              | 84.5       |            |
| 0.58h                                                                                           | /          | 85         |
| 1 hour                                                                                          | 79         | /          |
| 1.42h                                                                                           | 78         | /          |
| 2h                                                                                              | 76         | /          |
| 6.5h                                                                                            | 17         | /          |

As shown in the previous point, the chemical etching solution 3 leads to a higher copper attack speed. The chemical etching solution 3 will therefore load more quickly with copper and therefore destabilize more quickly.

- conclusion

The tribasic phosphate salt ( $K_3PO_4$ ) is preferred to the ammonium salt because its use allows etching of titanium more selectively with respect to other exposed materials.

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Example 3: effect of the concentration of tribasic potassium phosphate

Several etching solutions are prepared from:

- an aqueous solution of 30% by weight of hydrogen peroxide
- and an aqueous solution:
  - comprising 25% by mass of tribasic potassium phosphate ( $K_3PO_4$ ) and 0.4% by mass of diethylenetriamine-pentamethylenephosphonic acid (DTPMP)
  - or comprising 46% by mass of tribasic potassium phosphate ( $K_3PO_4$ ) and 0.74% by mass of diethylenetriamine-pentamethylenephosphonic acid (DTPMP).

The mass proportion, in the chemical etching solution, of the aqueous solution comprising  $K_3PO_4$  and DTPMP is 1.5%, 3%, 6% and 12%.

The stability of the chemical etching solution obtained is evaluated by measuring the

variation in the hydrogen peroxide content and the variation in pH according to the stability test described above. The results are listed in Table 4.

[Table 4]

|                                                                                                                                                                      | % by mass of the solution in the chemical etching solution | % by mass of $K_3PO_4$ in the chemical etching solution | % DTPMP in the chemical etching solution | $\Delta[H_2O_2]$ in absolute value after 16h at 65°C (%) | $\Delta[pH]$ in absolute value after 16h at 65°C | Etching speed Ti - nm/min) | Initial pH | stability |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|---------------------------------------------------------|------------------------------------------|----------------------------------------------------------|--------------------------------------------------|----------------------------|------------|-----------|
| Aqueous solution comprising 25% by mass of tribasic potassium phosphate ( $K_3PO_4$ ) and 0.4% by mass of diethylenetriamine-pentamethylenephosphonic acid (DTPMP)   | 1.5                                                        | 0.37                                                    | 0.006                                    | 49                                                       | 30                                               | 37                         | 6.9        | No        |
|                                                                                                                                                                      | 3                                                          | 0.75                                                    | 0.012                                    | 41                                                       | 15                                               | 52                         | 7.2        | No        |
|                                                                                                                                                                      | 6                                                          | 1.5                                                     | 0.024                                    | 31                                                       | 10                                               | 86                         | 7.8        | Yes       |
|                                                                                                                                                                      | 12                                                         | 3                                                       | 0.048                                    | 16                                                       | 6                                                | 125                        | 8.2        | Yes       |
| Aqueous solution comprising 46% by mass of tribasic potassium phosphate ( $K_3PO_4$ ) and 0.74% by mass of diethylenetriamine-pentamethylenephosphonic acid (DTPMP). | 1.5                                                        | 0.69                                                    | 0.011                                    | 33                                                       | 13                                               | 46                         | 7.5        | No        |
|                                                                                                                                                                      | 3                                                          | 1.38                                                    | 0.022                                    | 24                                                       | 8                                                | 74                         | 7.5        | Yes       |
|                                                                                                                                                                      | 6                                                          | 2.76                                                    | 0.044                                    | 18                                                       | 7                                                | 120                        | 7.9        | Yes       |
|                                                                                                                                                                      | 12                                                         | 5.52                                                    | 0.088                                    | 24                                                       | 5                                                | 200                        | 8.6        | Yes       |

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#### Example 4: effect of the nature of the complexing agent and its concentration

- on the stability of etching solutions

The 7 chemical etching solutions of the following composition (28.2% by mass of hydrogen peroxide; 1.5% tribasic potassium phosphate; 0.024% complexing agent, the remainder being water) are evaluated.

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Etching solutions differ by the nature of the complexing agent:

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- solution 1: glycine
- solution 2: histidine
- solution 3: ammonium citrate
- solution 4: 2,6 pyridine dicarboxylic acid (PDA)
- solution 5: N-(2-acetamino)-iminodiacetic acid (ADA)
- solution 6: diethylenetriamine-pentamethylenephosphonic acid (DTPMP),
- solution 7: aminotrimethylenephosphonic acid (ATMP)

The stability of the different etching solutions is evaluated according to the stability test detailed above.

Solution 1 and solution 2 are stable for 1 hour then are destabilized (uncontrolled peroxide degradation).

5 Solution 3 and solution 4 are stable for 4 hours.

Solution 5 is stable for 5.5 hours.

Solutions 6 and 7 are stable during the entire test (6 hours).

The stability of the etching solutions was also evaluated by multiplying by 4 and 8 the concentration of complexing agent in each of the solutions, the concentration of the other  
10 components remaining unchanged.

Solution 1 and solution 2 are then stable for 3 hours.

The stability of solutions 3 to 5 remains unchanged.

Solutions 6 and 7 remain stable throughout the entire test (6 hours).

- 15 • case of DTPMP: influence of the DTPMP concentration on the etching speed of titanium

The effect of the DTPMP concentration on the etching speed of titanium was evaluated for solutions of the following composition: 28.2% by mass of hydrogen peroxide; 1.5% tribasic potassium phosphate; 0.024/0.048/0.096/0.192% DTPMP, the remainder being water.

20 The etching speed is respectively 81 nm/min, 84 nm/min; 86 nm/min and 93 nm/min for DTPMP concentrations of 0.024/0.048/0.096/0.192%.

#### Example 5: stability of etching solutions – effect of adding an organic acid

The addition of an organic acid as a complexing agent, such as citric acid, is described as  
25 allowing to stabilize etching solutions and increase compatibility with copper – see US9845538 (WACO).

The stability of the following 2 chemical etching solutions is evaluated according to the stability test described above:

- 30 - solution 1 of composition: 28.2% hydrogen peroxide; 1.5% tribasic potassium phosphate; 0.024% diethylenetriamine-pentamethylenephosphonic acid (DTPMP)
- Solution 2 of composition: 28.2% hydrogen peroxide; 1.5% tribasic potassium phosphate; 0.024% diethylenetriamine-pentamethylenephosphonic acid (DTPMP); 2.36% citric acid; 1.63% KOH

The loss of mass in hydrogen peroxide is 31% for solution 1 and 40% for solution 2.

Adding citric acid results in a decrease in the stability of the chemical etching solution.

After loading the chemical etching solution with 10 copper patterned coupons of diameter 300 mm per liter for a time sufficient to remove the 100 nm layer of titanium present on the surface of the coupons, and aging at 50°C for 1 hour, the chemical etching solution 2 runs away and degrades (strong gas release). As illustrated by the data in Table 3, the etching speed of titanium remains unchanged with solution 1 for an aging duration of 2 hours.

#### 10 Example 6: effect of temperature on titanium etching

The chemical etching solution tested has the following composition; 28.2% hydrogen peroxide; 1.5% tribasic potassium phosphate; 0.024% complexing agent, the remainder being water.

The evolution of the thickness of the remaining titanium layer as a function of etching time is illustrated in Figure 2 for temperatures comprised between 25°C and 65°C.

The evolution of the etching speed as a function of the temperature of the chemical etching solution is illustrated in Figure 3.

The higher the temperature of the chemical etching solution, the faster the titanium etching. A high chemical etching solution temperature can lead to evaporation of a fraction of the water from the chemical etching solution and to an increase in the hydrogen peroxide concentration causing an acceleration in etching speed.

The chemical etching solution can be kept in a closed container in order to limit these phenomena with suitable ventilation.

#### 25 Example 7: effect of metal contamination on the etching speed of titanium

- contamination of the chemical etching solution by titanium:

The chemical etching solution tested has the following composition; 28.2% hydrogen peroxide; 1.5% tribasic potassium phosphate; 0.024% complexing agent, the remainder being water.

The chemical etching solution is loaded with titanium by immersing the equivalent of 10 full wafers with a diameter of 300 mm per liter for a sufficient time to remove the 100 nm layer of titanium present on the surface of the coupons.

The titanium etching speed is evaluated at  $t_0$  (before and after loading with titanium), then after different aging times at  $50^\circ\text{C}$  of the chemical etching solution loaded with titanium. The etching speed is comprised between 80 and 90 nm/min up to 6 hours of aging of the chemical etching solution.

5 The chemical etching solution is therefore stable for at least 6 hours at  $50^\circ\text{C}$ .

Figure 4 illustrates the effectiveness of cleaning the titanium layer of Cu pillars by etching solutions aged at  $50^\circ\text{C}$  for different durations:

- top left: use of a chemical etching solution aged for 5 min at  $50^\circ\text{C}$
- top right: use of a chemical etching solution aged for 1h30 at  $50^\circ\text{C}$
- 10 - bottom left: use of a chemical etching solution aged for 3 hours at  $50^\circ\text{C}$
- bottom right: use of a chemical etching solution aged for 6 hours at  $50^\circ\text{C}$

In each photo, the upper left part corresponds to a copper pad, the rest of the photo representing an area in which the titanium layer has been removed. The surface of the copper pads is not modified and no titanium residue is visible.

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- contamination of the chemical etching solution with titanium and other components:

Two etching solutions are tested:

- solution 1 of the following composition: 28.2% hydrogen peroxide; 1.5% tribasic potassium phosphate; 0.024% DTPMP, the remainder being water.
- 20 - solution 2 of the following composition: 28.2% hydrogen peroxide; 0.35% potassium hydroxide; 0.012% CDTA, the remainder being water.

According to this test, the chemical etching solution is loaded with metallic elements by immersing the equivalent of 10 wafers of patterned plates exposing the following materials (copper, polyimide) with a diameter of 300 mm per liter for a sufficient time to remove the  
25 100 nm layer of titanium present on the surface of the coupons.

The titanium etching speed is evaluated at  $t_0$  (after wafer loading) then after different aging times at  $50^\circ\text{C}$  of the aged chemical etching solution.

The test results are shown in Table 5.

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[Table 5]

| Etching speed of Ti in nm/min after different aging times of the chemical etching solution | Solution 1 at 50°C | Solution 2 at 50°C |
|--------------------------------------------------------------------------------------------|--------------------|--------------------|
| T0 (after loading)                                                                         | 85                 | 71                 |
| 1 hour                                                                                     | 79                 | 62                 |
| 1.42h                                                                                      | 78                 | 60                 |
| 2h                                                                                         | 76                 | 50                 |

Solutions 1 and 2 are stable for at least 2 h at 50°C. However, there is a significant reduction in the etching speed (-30%) with solution 2 compared to solution 1 (-11%).

The cleaning effectiveness of the titanium layer of Cu pillars by the chemical etching solution 1 aged at 50°C for up to 2 hours was evaluated. The surface of the copper pads is not modified and no titanium residue is visible.

Figure 5 shows the foot of a copper pillar etched using the etching solution loaded with wafers (photo on the left) and this same etching solution aged for 2 hours at 50°C (photo on the right). The etching profile is identical.

## CLAIMS

1. A solution for chemical etching of a titanium-based material comprising:
  - from 26% by weight to 39% by weight of hydrogen peroxide,
  - 5    - from 1% by weight to 6% by weight of tribasic potassium phosphate ( $K_3PO_4$ ),
  - from 0.015% by weight to 0.2% by weight of a compound selected from diethylenetriamine-pentamethylenephosphonic acid (DTPMP), aminotrimethylenephosphonic acid (ATMP) and mixtures thereof
  - water,
- 10    the percentages by weight being expressed relative to the weight of the chemical etching solution,  
       said solution having a pH of 6.5 to 8.6.
  
2. A method for chemically etching a layer of a titanium-based material on a microelectronic
   
15    device, said method comprising contacting said layer with the chemical etching solution according to claim 1 for a duration sufficient to eliminate said layer, said titanium-based material consisting of titanium, titanium nitride, titanium-tungsten or mixtures thereof, preferably titanium.
  
- 20    3. The method according to claim 2, wherein the chemical etching solution, after etching the microelectronic device, is reused to etch one or more other microelectronic devices.
  
4. The method according to claim 2 or claim 3, wherein the chemical etching solution is heated and contacted with the microelectronic device at a temperature of 20°C to 60°C,
   
25    preferably 35°C to 50°C.
  
5. A method for preparing a chemical etching solution according to claim 1 comprising the mixture:
  - of a composition comprising:
    - 30    ○ tribasic potassium phosphate ( $K_3PO_4$ ),
    - the compound selected from diethylenetriamine-pentamethylenephosphonic acid (DTPMP), aminotrimethylenephosphonic acid (ATMP) and mixtures thereof
    - water,
  - and of an aqueous solution of hydrogen peroxide at a mass concentration of hydrogen

peroxide of 30% by weight to 40% by weight relative to the weight of the aqueous solution.

to reach a pH of 6.5 to 8.6.

- 5    6. The method according to claim 5, wherein the solution is prepared using a point-of-use mixing technique consisting of mixing just before distributing the aqueous solution of hydrogen peroxide and the composition comprising the potassium phosphate salt, the compound selected from diethylenetriamine-pentamethylenephosphonic acid (DTPMP), aminotrimethylenephosphonic acid (ATMP) and mixtures thereof and water.