ACID ETCHING MIXTURE HAVING REDUCED WATER CONTENT

Background of the Invention

The invention relates to an acid etching mixture having reduced water content. In particular said water content can be reduced by adding fluorosulfonic acid to acidic compositions containing water. Said etching mixture is useful in etching silicon. For example silicon wafers can be etched in spray etching processes or spin etching processes. In said new acid etching mixture, water content affecting etching quality can be advantageously regulated and can be kept constant during the etching process.

Silicon is a very important material because of its semiconducting properties. For example it is used in the manufacture of solar cells and integrated circuits.

However these applications require surface treatment of the structural components made from silicon. Mostly said treatment is carried out mechanically and/or by means of an etching agent or an etching mixture which may be adjusted to obtain specific surface properties, wherein the end use determines the structure to be created.

For the etching of silicon for application in solar cells typically basic etching mixtures are used. However for the manufacture of silicon discs as carriers of integrated circuits (silicon wafers) in particular acid etching mixtures are used.

It is known to carry out the etching process of silicon wafers by means of acid etching mixtures containing hydrogen fluoride and one or more acids selected from sulfuric acid, hydrochloric acid, nitric(v) acid, orthophosphoric acid, perchloric acid, hydrobromic acid, hydriodic acid or periodic acid (US 5,300,463).

Furthermore it is well known, too, to use aqueous mixtures of acids, which contain hydrogen fluoride and organic acids with at least two carbon atoms, in particular acetic acid and propionic acid (US 6,162,739).

There are fundamentally two types of applications in which silicon is etched with an acid etching mixture.

In one of these applications the backsides of structural elements made from silicon are etched. In said etching process predetermined amounts of silicon are removed from the surface in an anisotropic manner, which means predominantly in one direction, to achieve a rough, or textured, surface structure. The textured surface is extremely important for subsequent processes with other structural elements or materials, in which, for example the backside of said structural element may be metallized or bonded. This anisotropic etching process is known as "texture etching."

The other application relates exclusively to the manufacture of very thin structural elements with application in multi chip packages or flexible carriers, as for example smart cards. In said application the wafers are first ground down mechanically. Afterwards the damaged and uneven areas are etched in a chemical etching process isotropically, what means regular to all space directions, to provide polished surfaces.

It is well known to use for both above-described applications the acids and combinations of acids of the prior art as etching agents and etching mixtures. In particular etching mixtures are applied consisting mainly of mixtures of sulfuric acid and hydrogen fluoride or aqueous hydrogen fluoride. Optionally nitric(v) acid and orthophosphoric acid can be added. The prior art has attempted to improve the selectivity and the etching rate of the etching process by modification of the relative ratios of the ingredients used.

Etching agents or etching mixtures which are preferably useful in producing textured surfaces typically contain more than 80 % of sulfuric acid, up to 10 % of nitric(v) acid and up to 5 % of hydrogen fluoride, wherein the total amount of all compounds being present in the etching mixture is 100 % (% by weight). Said etching mixtures are known as texture etching agents.

Etching agents that produce an extended degradation with formation of a polished surface must have a clearly reduced amount of sulfuric acid of from 10 to 20 % and approximately an amount of orthophosphoric acid of from 10 % to 20 %. However said etching mixtures must have a considerably increased amount of nitric(v) acid in the range of from 20 to 50 %. The content of hydrogen fluoride can be between 2 and 20 % (% by weight). Said etching mixtures are known as polishing etching agents.

The commercially available acids used in said etching mixtures typically contain water. Therefor the resulting etching mixtures contain water, too. In general polishing etching mixtures contain a higher amount of water than texture etching mixtures.

In industrial processes the desired surface structure must be reproducible. For instance in continuous process spraying etching plants it is extremely important to keep as constant as possible the chemical composition as well as the viscosity of the etching mixture being employed. Both parameters are decisive for the reactivity with respect to the etching rate and the selectivity of the etching process.

In particular the concentration of hydrogen fluoride has to be controlled carefully. Hydrogen fluoride is a volatile compound, vaporizing during the process and being transformed into volatile compounds during the etching process. Therefor it is used up and must be replaced. Said replacement can be carried out in a continuous or intermittent manner. Consequently the water content of said etching mixture is increasing steadily because said added hydrogen fluoride is applied as an aqueous solution. In addition water is formed from the reaction of the aqueous hydrogen fluoride with silicon dioxide, which is developed by oxidation of silicon on the surface of the wafer.

Because of said steadily increasing water content the chemical composition and viscosity of said etching mixture changes the properties thereby affecting etching. This effect has a great influence on the quality of the etching process. The etching rate and the resulting quality of the surface of the wafer is affected. Consequently the etching becomes uneven during the process and results in a surface structure steadily changing, what is extraordinarily disadvantageous. If the water content is increased over 40 % by weight, the etching process

can become completely irregular. In an extreme during texture etching of silicon wafers, a polished surface can result, which is a completely useless result.

Therefor it is extremely difficult to adjust the selectivity of the etching process relative to the etching rate with the aforementioned described etching mixtures of the prior art and at the same time keep the selectivity constant during the etching process. Normally the etching rate is low when the selectivity is high and vice versa. Said behavior is unsatisfactory for reproducible industrial production.

Detailed Description of Preferred Embodiment

It is one object of the invention to provide an acid etching mixture having reduced water content, with which the described disadvantages in the etching of silicon can be avoided. In particular, it is an object of the invention to maintain the water content of said etching mixture constant during the etching process. Moreover it is an object of the invention that said etching mixture not change significantly in chemical composition and viscosity, particularly in spray etching processes and spin etching processes even during prolonged processing periods. It is also an object of the invention to obtain etching mixtures that provide selective etching of silicon wafers in etching processes resulting in a constant and reproducible surface structure. It is another object of the invention to provide a method for preparing said acid etching mixtures having reduced water content.

These objects are achieved according to the invention by using fluorosulfonic acid to reduce the water content of acid etching mixtures.

By using fluorosulfonic acid an acid etching mixture can be prepared which is particularly well-suited for spray etching and spin etching processes. Said mixture does not change significantly either in its chemical composition or in its viscosity, even during prolonged working periods. It is possible to employ said new acid etching mixtures in manufacturing plant etching processes that, when applied to silicon wafers results in very constant and good reproducible surface properties. The properties of the new acid etching mixtures are extremely advantageous for industrial processing. It is even possible to provide an etching mixture which can be used selectively as a texture etching agent or polishing etching agent. Said selective adjustment, which is made possible only by the use of fluorosulfonic acid in said acid etching mixture, was not foreseeable and is therefor surprising.

Therefor according to one aspect of the present invention, a method is provided for preparing an acid etching mixture having reduced water content by adding fluorosulfonic acid to an acidic composition containing water. By means of this method said fluorosulfonic acid is hydrolyzed by said water to form a mixture having proportionately less water and more sulfuric acid and hydrofluoric acid than the acidic composition containing water.

According to another aspect of the present invention a process for the manufacture of an acid etching mixture is provided, characterized in that fluorosulfonic acid is reacted with an acidic composition containing water.

Still yet another aspect of the present invention provides an acid etching mixture, characterized in that said mixture is prepared by adding fluorosulfonic to an acidic composition containing water.

It is preferred that by the use of fluorosulfonic in said compositions the water content is reduced to an amount from 0 to about 40 % by weight, wherein the total amount of all components present in the etching mixtures is 100 % by weight. In said range it is possible to prepare acid etching mixtures that are particularly selective with respect to their texturing or polishing effect.

With regard to the invention, the fluorosulfonic acid for the reduction of the water content may be added in an amount from about 0.1 to about 60 % by weight of the acidic composition containing water, wherein the total amount of all components being used for the manufacture of said acid containing mixture is 100 % by weight.

Said acid etching mixtures can contain the acids of the prior art. Therefor said acid etching mixture can contain inorganic as well as organic acids.

Organic acids are for example acetic acid or propionic acid.

It is preferred that the acid etching mixtures of the invention contain nitric(v) acid, because said acid oxidizes silicon surfaces easily. Said property enables an easier processing. The silicon dioxide being formed during the oxidation can be reacted with other suitable acids to form volatile or soluble compounds, for example with hydrogen fluoride to form silicon tetrafluoride or siliconfluoric acid. Further nitric(v) acid is available in highly pure form, which is important for the quality of the silicon wafers.

Furthermore it is preferred that the acid etching mixtures of the invention contain sulfuric acid and aqueous hydrofluoric acid or hydrogen fluoride. In said etching mixtures said sulfuric acid is able to bind water to a limited extent. However said acid is also used for the adjustment of the viscosity necessary for spray etching and spin etching processes. The mechanism of the hydrofluoric acid during the etching process has been described aforementioned.

As it is known that fluorosulfonic acid reacts with water nearly quantitatively to form hydrofluoric acid and sulfuric acid, said acids can be regenerated if they are used up during the etching process. At the same time water is used up by the hydrolysis reaction. Hereby the water content of the etching mixture is reduced.

The acid etching mixture of the invention can contain orthophosphoric acid. With said acid the viscosity of said etching mixture can be adjusted.

Said acids are known products, which are manufactured commercially. They are readily available.

Commercially produced nitric(v) acid, sulfuric acid, hydrofluoric acid and orthophosphoric acid typically contain water and can be used in this form. Typical forms of said acids as delivered contain besides water about 70 % by weight of nitric(v) acid, about 96 % by weight of sulfuric acid, about 50 % by weight of hydrogen fluoride (aqueous hydrofluoric acid) and about 85 % by weight of orthophosphoric acid.

Hydrofluoric acid can be applied in water-free form as 100% hydrogen fluoride. However, because of the aggressive properties and the difficult handling of said chemical, costly equipment and special safety precautions are necessary. Moreover the addition of water-free hydrogen fluoride only avoids the further addition of water, whereas fluorosulfonic acid consumes water when added.

Preferably fluorosulfonic acid is provided in a concentrated form and is water-free to a large extent. However said acid can contain secondary amounts of sulfuric acid and hydrogen fluoride, as happens sometimes in the commercially available product.

The hydrolytic reaction of fluorosulfonic acid with water to form sulfuric acid and hydrofluoric acid or hydrogen fluoride allows in the manufacturing process of etching mixtures, which contain by nature sulfuric acid and hydrofluoric acid or hydrogen fluoride, the adjustment of the compositions, which is not possible when using the acids of the prior art alone.

For example, in a conventional water containing texture etching mixture made from sulfuric acid, nitric(v) acid and aqueous hydrofluoric acid, if the concentration of the aqueous hydrofluoric and nitric(v) acid is increased in order to increase the etching rate, automatically the water content is increased, too. Therefor one has to take into account that the texture properties will change.

However if applying fluorosulfonic acid nearly any mixtures with a very low content of water and clearly higher content of hydrogen fluoride can be prepared, which is extraordinarily advantageous.

For example, it is possible to prepare mixtures with nearly constant content of sulfuric acid and nitric(v) acid of from about 2.5 % to about 12 % by weight, wherein the water content of the mixtures can be reduced to a content of from about 0.1 to about 8 % by weight.

Texture etching agents that are produced with the acids of the prior art, however, the water content is already more than about 8 % by weight even when using a low concentration of aqueous hydrofluoric acid. Consequently with the addition of aqueous hydrofluoric acid, the water content increases disadvantageously.

However if using fluorosulfonic acid it is even possible to reduce the water amount to an extent which allows the production of nearly water-free etching mixtures. Therefor it is possible to adjust the water content of conventional etching mixtures, which strongly influences the texturing or polishing effect of said etching mixtures, to within a predetermined range by adding fluorosulfonic acid thereby keeping said water content constant during the etching process. This is extraordinarily advantageous.

If using fluorosulfonic acid in acid etching mixtures wherein said mixtures should still contain noticeable amounts of water, said fluorosulfonic acid is added in an amount so that it is consumed during the hydrolysis reaction, but wherein part of the water is not consumed. After said reaction said acid is not present in the etching mixture.

However in water-poor or water-free etching mixtures fluorosulfonic acid is stabile. In such mixtures said acid per se can take part in the etching process. Consequently it is possible to produce etching mixtures which contain an excess of fluorosulfonic acid. Therefor such mixtures possess an additional capacity for water-binding as well as a reservoir of unliberated hydrogen fluoride. For example it is possible to carry out etching processes in a controlled manner wherein one has to take into account the fast consumption of large amounts of water. Said property renders the acid etching mixture of the invention superior over the etching mixtures of the prior art.

When an excess of fluorosulfonic acid relative to water is used, an acid etching mixture can be obtained, containing fluorosulfonic acid, sulfuric acid, hydrofluoric acid, and either or both nitric(v) acid and orthophosphoric acid.

It is possible to produce by partial or total replacement of sulfuric acid with fluorosulfonic acid acid etching mixtures with different water contents but nearly constant concentrations of the rest of the components in the mixture. Said fluorosulfonic acid allows the adjustment of formulations to the requirements of the etching process to a broader range than is possible with the acids of the prior art alone. By varying the concentrations of the educts it is possible to prepare specific etching mixtures, which are suitable either as texture etching agents or as polishing agents. Intermediate blends are possible if desired. This variability and the application possibilities renders the mixture of the invention extraordinarily versatile.

The water content of the acid etching mixtures of the invention can vary within a relatively large range. However said content is preferably below about 40 % by weight, wherein the total amount of all components being present in the etching mixture is 100 % by weight. It is important that said water content can be kept relatively constant during the etching process.

If it is preferred to use the acid etching mixture of the invention as a polishing etching mixture it is advantageous to provide a higher water content in order to achieve sufficiently high etching rates. Then by applying fluorosulfonic acid the water content is preferably reduced to an amount from about 15 to about 35 %, and the content of acids present in the etching mixtures is preferably from about 20 to about 40 % nitric(v) acid, from about 5 to 35 % sulfuric acid, from about 5 to 25 % aqueous hydrofluoric acid, and from about 5 to about 20 % phosphoric acid, wherein the total amount of all components being present in the etching mixture is 100 % (% by weight).

If it is preferred to use the mixture of the invention as a texture etching agent however it is advantageous to choose a lower water content. Then by applying fluorosulfonic acid the

water content is preferably reduced to an amount of from about 0.1 to about 15 %, and the content of acids present in the etching mixtures is preferably from about 0.1 to about 10 % nitric(v) acid, from about 70 to about 95 % sulfuric acid, and from about 1 to about 15 % aqueous hydrofluoric acid, wherein the total amount of all components being present in the etching mixture is 100 % (% by weight).

If it is preferred to use acid etching mixtures that contain detectable amounts of fluorosulfonic acid, the resulting mixtures consequently are nearly water-free. Then by applying fluorosulfonic acid the water content is preferably reduced to an amount from about 0.01 to about 0.05 %, and the content of acids being present in the etching mixtures is preferably from about 0.1 to about 30 % fluorosulfonic acid, about 0.1 to about 50 % nitric(v) acid, from about 5 to about 90 % sulfuric acid, from about 5 to about 30 % hydrofluoric acid, and from 0 to about 30 % phosphoric acid, wherein the total amount of all components being present in the etching mixture is 100 % (% by weight).

The manufacture of said acid etching mixtures of the invention can be carried out in a manner that meters said fluorosulfonic acid to an acid etching mixture containing water. In particular, in continuous process spray etching plants or spin etching plants it is preferred to use this variant of the invention. One can proceed in a way that first uses an acid etching mixture containing essentially only the preferred acids, for example, sulfuric acid, hydrofluoric acid, nitric(v) acid, optionally orthophosphoric acid, and water. Hydrogen fluoride that vanishes from the system by vaporizing or reaction however will not be replaced by aqueous or anhydrous hydrofluoric acid, but by fluorosulfonic acid. Said acid will be metered into the etching mixture to the extent that the concentration of the hydrogen fluoride in the mixture has been diminished. In particular, using this method the concentration of acid and water can be kept constant during the etching process, because the water content being increased for the moment is reduced again, which provides very constant and advantageous etching processes for silicon wafers. Because of the aforementioned hydrolysis reaction of the fluorosulfonic acid into sulfuric acid and hydrofluoric acid the increase of the water content can be avoided in a prolonged process, thereby keeping the etching rate constant. Reconcentration with aqueous hydrogen fluoride as described in the prior art would result in a disadvantageous increase of the water content. Therefor with the new acid etching mixtures of the invention, the composition of the etching bath can be maintained for a longer period than with an etching mixture of the prior art. The parameters relevant for the etching process, for example the viscosity, can be kept constant, too.

This represents yet another embodiment of the present invention. That is, in a process of etching silicon or a silicon substrate using an aqueous acid etching mixture containing hydrofluoric acid, sulfuric acid and either or both nitric(v) acid or orthophosphoric acid, wherein during the process the concentration of hydrofluoric acid decreases and the concentration of water increases, the present invention provides an improvement in which the hydrofluoric acid is replenished while at the same time the water concentration is decreased. According to one aspect of this embodiment of the invention, this is accomplished by adding fluorosulfonic acid to the acid etching mixture, so that the fluorosulfonic acid hydrolyzes to form hydrofluoric acid and sulfuric acid, thereby consuming water to decrease the concentration thereof while increasing the concentration of hydrofluoric acid. The fluorosulfonic acid addition step can be performed periodically to maintain the water content of the etching mixture at an essentially constant level. This is particularly advantageous for continuous etching processes.

On the other hand it is possible to meter the fluorosulfonic acid and further acids mutually and then mix them by stirring.

But it is also possible to hydrolyze the fluorosulfonic acid first, wherein hydrofluoric acid and sulfuric acid are produced as hydrolysis products that are essentially anhydrous, or with a predetermined water content. The other acids, which should be present in the etching mixtures, for example nitric(v) acid and orthophosphoric acid, can be admixed into said mixture.

Therefor, according to yet another aspect of the present invention there is provided a process for the manufacture of an acid etching mixture, characterized in that the water content is reduced by the addition of fluorosulfonic acid wherein the fluorosulfonic acid is subsequently hydrolyzed. Said hydrolysis reaction can be carried out in the presence of further acids selected from at least one of nitric(v) acid, sulfuric acid, hydrofluoric acid, orthophosphoric acid.

Hydrofluoric acid can be employed in its aqueous form. But it is possible to use water-free hydrogen fluoride.

Consequently the invention provides an acid etching mixture, characterized in that said mixture is obtained by hydrolysis of fluorosulfonic acid, wherein the hydrolysis is carried out in the presence of one or more further acids selected from nitric(v) acid, sulfuric acid, hydrofluoric acid and orthophosphoric acid.

Furthermore, according to another aspect of the invention methods are provided in which the acid etching mixtures of the invention are used in the etching of silicon or silicon substrates.

In particular said acid etching mixtures, wherein the water content is reduced by fluorosulfonic acid, can be applied in spray etching processes or spin etching processes. Said processes can be carried out in spray etching plants or spin etching plants.

In an etching process of silicon or of a silicon substrate, for example a silicon wafers, one can proceed by first cutting the semiconductor crystal in thin slices followed by polishing the surfaces. In general this polishing process is carried out in two steps in a spray etching plant. The first step includes mechanical polishing by abrasion. For that the wafer is arranged on a rotating carrier and brought into contact with a contra-rotating tampon. Said mechanical polishing is performed by spraying the surface with an abrasive suspension. Afterwards said suspension can be replaced by the polishing etching mixture according to the invention, after which the polishing process can be finished by fine polishing. If necessary the wafer will have to undergo a second etching step or a cleaning step.

Because of constantly increasing disc diameters, single-disc processes are carried out to an increasing degree in spin etching plants. For that wafers of a thickness of, for example, 750 μm are ground down mechanically to a thickness of approximately 250 μm followed by chemical etching down to about 40 μm. Said etching process can be carried out in several steps, first with a fast acting etching mixture, which takes away from about 50 to about 100 μm, followed by slow polishing with a slow acting etching mixture, which takes away of from about 5 to about 30 μm.

During the etching process the temperature is preferably from about 20 to about 50°C. Lower temperatures mostly result in higher selectivity and decreased etching rate. Higher temperatures mostly result in higher etching rates and decreased selectivity.

The invention is now explained with examples but not limited thereto.

Examples

Etching mixtures were prepared by mixing commercial sulfuric acid (96 % by weight in water), nitric(v) acid (70 % by weight in water), aqueous hydrofluoric acid (50 % by

weight in water), orthophosphoric acid (85 % by weight in water), and fluorosulfonic acid (100 % by weight). The amounts of acids and the compositions of the mixtures with water content are listed in the following tables. The compositions of the mixtures were checked according to standard methods, for example the water content with the well known titration according to Karl Fischer.

Table 1 shows the acids used as starting material and the amounts of said acids for texture etching agents, table 2 the resulting compositions.

The mixture of the comparison example was prepared without the use of fluorosulfonic acid.

One can see clearly how the water content can be decreased by using increasing amounts of fluorosulfonic acid in the examples 1 to 4 compared to comparison example 1, wherein the content of sulfuric acid is nearly constant and the amount of hydrofluoric acid is increased advantageously.

Table 1: starting material (amount in % by weight)

		H_2SO_4 96%	HNO_3 70%	HF 50%	FSO_3H 100%
comparison example	1	87.50	6.57	5.60	0
example	1	78.13	5.43	6.40	10.00
	2	67.71	5.43	6.80	20.00
	3	57.29	5.43	7.20	30.00
	4	46.88	5.43	7.60	40.00

Table 2: composition of the etching mixtures [% by weight]

		H_2SO_4	HNO_3	HF	H_2O
comparison example	1	84.00	4.60	2.80	8.27
example	1	84.80	3.80	5.20	6.15
	2	84.60	3.80	7.40	4.14
	3	84.40	3.80	9.60	2.12

	4	84.20	3.80	11.80	0.11

Table 3 shows the acids used as starting material and the amounts of said acids in polishing etching agents, table 4 the resulting compositions.

The mixture of the comparison example was prepared without the use of fluorosulfonic acid.

Here one can see clearly, too, how in examples 5 to 9 the water content of the etching mixtures can be limited or decreased advantageously with increasing amounts of fluorosulfonic acid compared to comparison example 2 despite the relative high amount of aqueous hydrofluoric acid and nitric(v) acid.

Table 3: starting material (amount in % by weight)

		H_2SO_4 96%	HNO_3 70%	HF 50%	H_3PO4 85%	FSO_3H 100%
comparison example	2	15.63	40.00	30.00	14.12	0.00
example	5	11.98	40.00	28.00	14.12	5.00
	6	8.02	40.00	26.00	14.12	10.00
	7	4.17	40.00	24.00	14.12	15.00
	8	2.08	40.00	20.00	14.12	20.00
	9	0.00	37.86	20.00	12,94	25.00

Table 4: composition of the etching mixtures in % by weight

		H_2SO_4	HNO_3	HF	H_3P04	H_2O
comparison example	2	15.00	28.00	15.00	12.00	29.74
example	5	16.40	28.00	15.00	12.00	27.70
	6	17.50	28.00	15.00	12.00	25.64
	7	18.70	28.00	15.00	12.00	23.59
	8	21.60	28.00	14.00	12.00	20.60
	9	24.50	26.50	15.00	11.00	18.80

CLAIMS

1. A method for preparing an acid etching mixture having reduced water content comprising adding fluorosulfonic acid to an aqueous acid-containing composition.

2. The method as claimed in claim 1, characterized in that said water content is reduced from a higher concentration to an amount from 0 to about 40 % by weight, wherein the total amount of all components of said etching mixture is 100 % by weight.

3. The method as claimed in claim 1, characterized in that said fluorosulfonic acid is added to said acid-containing composition containing water in an amount from about 0.1 to about 60 % by weight, wherein the total amount of all components of the etching mixture is 100 % by weight.

4. The method as claimed in claim 1, characterized in that said acid etching mixture comprises sulfuric acid, hydrofluoric acid, and one or more acids selected from the group consisting of fluorosulfonic acid, nitric(v) acid and orthophosphoric acid, and said aqueous acid-containing composition comprises one or more acids selected from the group consisting of hydrofluoric acid, sulfuric, nitric(v) acid and orthophosphoric acid.

5. In a process for etching silicon or a silicon substrate using an aqueous acid etching mixture comprising hydrofluoric acid, sulfuric acid and either or both nitric(v) acid or orthophosphoric acid, wherein during said process the concentration of said hydrofluoric acid decreases and the concentration of water increases, the improvement comprising replenishing said hydrofluoric acid and simultaneously decreasing said water concentration.

6. The process of claim 5, wherein said hydrofluoric acid is replenished while decreasing said water concentration by adding fluorosulfonic acid to said acid etching mixture, so that said fluorosulfonic acid hydrolyzes to form hydrofluoric acid and sulfuric acid, thereby

consuming water to reduce the concentration thereof while increasing said concentration of hydrofluoric acid.

7. The process of claim 6, wherein said fluorosulfonic acid is added periodically in quantity that maintains the water content of said acid etching mixture essentially constant.

8. The process of claim 5, wherein said process is a continuous process.

9. An acid etching mixture prepared by adding fluorosulfonic acid to an aqueous acid-containing composition.

10. The acid etching mixture as claimed in claim 9, characterized in that the water content is reduced from a higher concentration to an amount from about 15 to about 35%, and said mixture further comprises nitric(v) acid in an amount from about 20 to about 40%, sulfuric acid in an amount from about 5 to about 35%, hydrofluoric acid in an amount from about 5 to about 25%, and orthophosphoric acid in an amount from about 5 to about 20%, wherein the total amount of all components present in said etching mixture is 100% (by weight).

11. The acid etching mixture as claimed in claim 9, characterized in that the water content is reduced from a higher concentration to an amount from about 0.1 to about 15%, and said etching mixture further comprises nitric(v) acid in an amount from about 0.1 to about 10%, sulfuric acid in an amount from about 70 to about 95%, and hydrofluoric acid in an amount from about 1 to about 15%, wherein the total amount of all components present in said etching mixture is 100% (by weight).

12. The acid etching mixture as claimed in claim 9, characterized in that the water content is reduced from a higher concentration to an amount from about 0.01 to about 0.05%, and said etching mixture further comprises fluorosulfonic acid in an amount from about 0.1 to about 30%, nitric(v) acid in an amount from about 0.1 to about 50%, sulfuric acid in an

amount from about 5 to about 90%, hydrofluoric acid in an amount from about 5 to about 30%, and orthophosphoric acid in an amount from 0 to 30%, wherein the total amount of all components present in said etching mixture is 100% (by weight).

13. A method for etching silicon or a silicon substrate comprising contacting said silicon or silicon substrate with an acid etching mixture prepared according to the process as claimed in claim 6.

14. The method as claimed in claim 13, characterized in that said method is a spray etching or a spin etching process.