1001039-8
IPOS copy.

ST 9710 /Dr. Ei

Process for etching semiconductor wafers

THIS SHEET HAS BEEN REPLACED

The invention relates to a process for etching semiconductor wafers by exposure to an etching mixture which is obtained by mixing nitric acid and hydrofluoric acid and optionally a surfactant.

Semiconductor wafers, such as, for example, silicon semiconductor wafers, as a base material for electronic components are obtained from a rod-shaped single crystal via a sequence of machining steps. First, the single crystal is sawn into wafers. The near-surface crystal regions of the resultant semiconductor wafers are damaged to a depth of approximately 80 μm by the wire or annular saws. This so-called "damage" is reduced, as a rule, by a mechanical surface treatment, for example by lapping or polishing the wafers. Wet-chemical removal of further silicon layers then results in almost complete removal of the damage and in the deliberate production of defined surface parameters, such as microroughness and reflectivity. The object of the etching is to obtain a wafer surface which is as plane-parallel and defect-free as possible and has a low microroughness and high reflectivity. If the etching process is performed in an acidic medium, nitric acid is frequently used as oxidizing agent and hydrofluoric acid as dissolving agent, optionally in conjunction with a surfactant. Such a process is described, for example, in US-5,451,267.

If said acids are used, it has to be borne in mind that the disposal of them as waste must be environmentally compatible and therefore generates substantial costs. The object was therefore to seek ways of being able to reduce the acid consumption without at the same time having to accept an impairment of the etching result.

The object is achieved by a process for etching semiconductor wafers with an etching mixture which is obtained by mixing nitric acid and hydrofluoric acid and optionally a surfactant and to which either further hydrofluoric acid or further hydrofluoric acid and nitric

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

acid is/are added, wherein nitric acid having a concentration of ≥ 70% by weight and hydrofluoric acid having a concentration of > 50% by weight, or nitric acid having a concentration of > 70% by weight and hydrofluoric acid having a concentration of ≥ 50% by weight are used to prepare the etching mixture.

By using an etching mixture which contains at least one of the acids used in a more concentrated form than was hitherto usual, it is possible to extend the bath life for etching appreciably. This means that substantially more semiconductor wafers can be etched before the etching mixture has to be replaced and disposed of as waste. This economizes on acids and the costs associated with the etching decrease although the expenditure on safety increases as a function of the acid concentration.

The term bath life is to be understood as meaning the time interval during which the etching mixture can be used to etch semiconductor wafers. This is the case for as long as the microroughness and the reflectivity of the etched semiconductor wafers are in a desired tolerance range and the contamination of the etching mixture with metals, particles and hexafluorosilicic acid does not exceed a predetermined value.

A lengthening of the bath life is possible, in particular, if nitric acid having a concentration of 73 to 98% by weight and hydrofluoric acid having a concentration of > 60 to 95% by weight are used to prepare the etching mixture.

In addition, it has emerged that the values for microroughness and reflectivity depend in the case of the etched semiconductor wafers on the concentration of the nitric acid used to prepare the etching mixture. They are all the more favorable, the more concentrated the nitric acid used is. Nevertheless, even if an etching mixture is used which contains nitric acid which is of relatively low concentration within the scope of the range specified above, semiconductor wafers having adequate roughness

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

values and brightness values are obtained. The use of as concentrated nitric acid as possible to prepare the etching mixture can therefore also be used to reduce the material removed per semiconductor wafer without the values for microroughness and reflectivity of the semiconductor wafers being thereby impaired compared with the customary ones. In total, an appreciable saving of semiconductor material is consequently possible. Particularly preferred is the use of an etching mixture which is obtained by mixing nitric acid having a concentration of 80% by weight and hydrofluoric acid having a concentration of 70% by weight. Using this etching mixture, semiconductor wafers can be obtained whose values for microroughness and reflectivity are equal to those for whose achievement by usual processes a material removal is necessary which is one third higher. Similarly good results in relation to the lengthening of the bath life, but not in relation to saving silicon, are obtained with an etching mixture which is obtained by mixing nitric acid having a concentration of 70% by weight and hydrofluoric acid having a concentration of 85% by weight.

To improve the etching further, it is proposed to add either further hydrofluoric acid or further nitric acid and hydrofluoric acid to the etching mixture. The further acid added preferably has the same concentration as the corresponding acid which has been used to prepare the etching mixture.

The nitric acid and hydrofluoric acid used in the etching mixture may be diluted by the further addition and by water formed during the etching. It is therefore particularly preferable to counteract this dilution effect in that further hydrofluoric acid or further hydrofluoric acid and nitric acid is/are added and the further acid added is 5 to 10% more concentrated than the corresponding acid which has been used to prepare the etching mixture. The concentrations of the acids for the etching mixture must, of course, be chosen in this case

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

so that it is still possible to add further more highly concentrated acids. Surprisingly, this measure not only lengthens the bath life, but also has a positive effect on the values for microroughness and reflectivity of the etched semiconductor wafers. The range of variation in these values becomes narrower and also qualitatively better. This effect can be increased still further by replacing a certain volume of the etching mixture in addition to further addition.

For a given surface state of the silicon wafers, values for the reflectivity are obtained with the procedure according to the invention which are between 28 and 40% depending on acid concentration. Values of between 0.15 µm and 0.13 µm are measured for the microroughness Ra. In the case of etching processes in accordance with the prior art, on the other hand, the semiconductor wafers have reflectivity values of only 15 to 20% and microroughnesses of 0.17 µm to 0.25 µm with the same etching removal but lower acid concentrations.

Two comparison examples in which silicon wafers were treated with an etching mixture in accordance with the prior art are contrasted below with an example of the treatment, according to the invention, of semiconductor wafers.

The reflectivity of the etched surfaces was determined with a reflectometer, a polished silicon wafer having a reflectivity of 100% serving as reference. The microroughness Ra was measured using a perthometer (0.8 µm filter, 4.8 µm measurement path). The measurements were made at each of three points over the isohypse of the wafer, the measured value being the mean value from five wafers.

Five semiconductor wafers were subjected in each case to three different etching processes. In these processes, the material removed by etching, the concentration of the nitric acid and the hydrofluoric acid were varied; the amount of surfactant added and also all the other processing parameters (temperature, time

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

etc.) were kept constant. The results are summarized in Table 1.

The measured values show that an increase in the reflectivity and a reduction in the microroughness can be achieved either by increasing the material removed by etching (compare Comparison Example 1 with Comparison Example 2) or, according to the invention, by using more highly concentrated acids or a more highly concentrated acid mixture (compare Comparison Example 2 with Example 3). With the process in accordance with the prior art, this result can be achieved only by means of increasing the material removed by etching. However, this should be avoided because of the loss therewith of ultrapure silicon and increased acid consumption. Comparison of the measured values of Comparison Example 2 with Example 3 shows a clear improvement in the reflectivity and microroughness in the case of the treatment, according to the invention, of the silicon wafers.

Table 1: Reflectivity and microroughness on varying the etching process

	Comparison Example 1	Comparison Example 2	Example 3
Concentration of HNO_3 for preparing the etching mixture [% by wt]	70	70	80
Concentration of HF for preparing the etching mixture [% by wt]	50	50	70
Material removed by etching z [μm]	30	20	20
Reflectivity [%]	38	18	37
Microroughness Ra [μm]	0.14	0.16	0.14

This Sheet Has Been Replaced

THIS SHEET HAS BEEN REPLACED

As a result of using the highly concentrated etching mixtures, the bath lives can be appreciably lengthened while surface quality remains constantly high owing to the lower amount of material removed by etching which thereby becomes possible. Depending on how high the concentrations are chosen, the bath life can be lengthened by a factor of 2 to 3 and the amount of silicon removed can be reduced by a third. This results in a large potential saving of ultrapure silicon and a marked reduction in the environmental pollution as a result of the lower acid consumption.

Table 2 shows eight examples (B1 to B8) of the treatment, according to the invention, of semiconductor wafers with different acid concentrations. An etching process in accordance with the prior art, in which nitric acid having a concentration of 70% by weight and hydrofluoric acid having a concentration of 50% by weight were mixed to prepare an etching mixture, served as comparison example (V).

The further addition was carried out in accordance with the stoichiometric consumption of acids and the amount lost when lifting the semiconductor wafers out of the etching bath.

This Sheet Has Been Replaced



Table 2: Lengthening of the bath life on using highly concentrated acids

	HNO_3 conc.* [% by wt]	HF conc.* [% by wt]	Conc. of further HNO_3* added [% by wt]	Conc. of further HF* added [% by wt]	Bath life lengthening factor
C	70	50	70	50	1
E1	70	70	70	70	1.6
E2	70	85	70	85	2
E3	70	100	70	100	2.5
E4	75	70	75	70	2.4
E5	85	50	85	50	2.4
E6	85	60	85	60	2.8
E7	85	70	85	70	3.9
E8	80	70	80	70	3.1

* as individual component

This Sheet Has Been Replaced

THIS SHEET HAS BEEN REPLACED

THIS SHEET HAS BEEN REPLACED

As becomes clear from Table 1 and Table 2, lengthened bath lives and improved surface properties accompanied by a simultaneously low amount of material removed by etching can be achieved with the process according to the invention.

This Sheet Has Been Replaced

THIS SHEET HAS BEEN REPLACED

Patent Claims

1. A process for etching semiconductor wafers with an etching mixture which is obtained by mixing nitric acid and hydrofluoric acid and optionally a surfactant and to which either further hydrofluoric acid or further hydrofluoric acid and nitric acid is/are added, wherein nitric acid having a concentration of ≥ 70% by weight and hydrofluoric acid having a concentration of > 50% by weight, or nitric acid having a concentration of > 70% by weight and hydrofluoric acid having a concentration of ≥ 50% by weight are used to prepare the etching mixture.

2. The process as claimed in claim 1, wherein nitric acid having a concentration of 73 to 98% by weight and hydrofluoric acid having a concentration of > 60 to 95% by weight are used to prepare the etching mixture.

3. The process as claimed in claim 1 or 2, wherein further hydrofluoric acid or further hydrofluoric acid and nitric acid is/are added and the further acid added has the same concentration as the corresponding acid which was used to prepare the etching mixture.

4. The process as claimed in claim 1 or 2, wherein further hydrofluoric acid or further hydrofluoric acid and nitric acid is/are added and the further acid added is 5 to 10% more concentrated than the corresponding acid which was used to prepare the etching mixture.

5. The process as claimed in any of claims 1 to 4, wherein a certain volume of the etching mixture is replaced in addition to the further addition.

CLMS

This Sheet Has Been Replaced