ETCHANT

TECHNOLOGICAL FIELD

The present invention relates to an etchant and more particularly, to an etching treatment agent used for fine treatment of insulating film such as silicon oxide or the like at a high speed and uniformity in the manufacturing process of semiconductor devices.

BACKGROUND ART

In association with the tendency for increasingly higher degree of high integration and higher capability of integrated circuits in the wet process of the manufacturing process for semiconductor integrated circuits, cleaning, etching, and patterning of a wafer surface and a finely-manufactured surface with higher cleanliness, higher precision, and more advanced performance are becoming more and more important.

Both a solution of hydrogen fluoride (HF) and a mixed solution (buffered hydrogen fluoride) of HF and ammonium fluoride (NH_4F) are applied for the purpose of cleaning and patterning as a surface treatment agent for fine surface treatment indispensable for this process, but in order to acquire submicron ultra high integration, progress of the high performance and high capability is increasingly required. Further, although the wafer currently in the mainstream is 8 inches, it is predicted that the wafer will be 12 inches by the year 2000.

The wet etching method for a wafer in the mainstream is a batch method for putting 25 to 50 sheets of wafer into a cassette soaking the whole cassette into an etching bath, and subjecting the cassette to etching treatment. Further, a cassette-less type of cleansing method is employed for preventing drag-in of a solution.

The batch method described above has an advantage in high throughput because of enabling concurrent etching onto a large number of wafers, but has a disadvantage in low uniformity of etching within each surface of the wafers. This low uniformity is more noticeable when a wafer size is larger, and when it is 12 inches in future, it is conceivably difficult to obtain etching uniformity within the surface of a wafer in this current batch method. In addition, the difficulty will be more serious in accordance with more progress of a fine device.

And for this reason, in order to enhance etching uniformity, a single wafer processing type etching method in which an etching solution is supplied onto a wafer being rotated has been considered. This method has an advantage in enhancement of the uniformity, but has a disadvantage in that a long time is required for the throughput.

Namely, the buffered hydrogen fluoride solution (BHF) having conventionally been applied is prepared for application usually by mixing 40 % NH_4F and 50 % HF in various mixing ratios (such as in a range of 400 : 1 to 6 : 1), and etching speeds to silicon oxide film by this BHF are in a range from 27 nm/min to 115 nm/min.

A time required for etching onto 50 sheets of wafer each with oxide film having a thickness of 500 nm in the batch method with BHF obtained by mixing HF and NH_4F in a ratio, for example, 7 : 1 is about 5 minutes, but if the treatment is carried out by the cut sheet type of method with this BHF, the treatment for only one sheet thereof requires about 5 minutes, and so it is understood that the treatment for 50 sheets thereof requires the time 50 times as much as that by the batch method, namely 250 minutes.

Such an enormous time is unrealistic for a line of mass-production facilities, and in order to introduce a single wafer processing type etching method into the line of mass-production facilities, the treatment time for one sheet has to be reduced. Herein, what level of the treatment capability is required for the cut sheet type thereof may be decided through designing of the entire semiconductor manufacturing process, but it is required, at least in order to make throughput maximum, to make wafer passing between devices for treatment smoother so that a retention time is made minimum. For the purpose of that, at least the same level of treatment capability as that of a dry etching device is required.

The current single wafer processing dry etching process has the capability of etching onto silicon oxide film having a thickness of 500 nm to 1000 nm by around 25 to 30 sheets/hour. Accordingly, an etching solution having the capability of treatment at etching speeds in excess of 200 nm/min is required.

However, the conventional type of etching solution, of which etching speeds are so quick, dissolves and separates the resist

at the same time, and for this reason it is difficult to execute high- speed treatment for a fine pattern on the insulating film.

Namely, conventionally there exists no such etching solution that etching treatment can be effected onto a fine pattern with high speed.

An object of the present invention is to provide, under the situation described above, an etching treatment agent which can etch an insulating film with high speed without giving damage on a resist pattern.

Namely, the object of the present invention is to provide an etching solution enabling treatment with realistic throughput when the insulating film etching process in the semiconductor manufacturing process is replaced with the single wafer processing etching treatment method.

Further, another object of the present invention is to provide an etching treatment liquid for preventing the surface of a semiconductor from its roughness after etching.

DISCLOSURE OF THE INVENTION

An etchant according to the present invention is applied for the purpose of etching treatment onto insulating film with a resist as a mask formed on a substrate, contains 8 through 19 weight % of hydrofluoric acid and 12 through 42 weight % of ammonium fluoride, and has hydrogen ion concentration of $10^{-6.0}$ through $10^{-1.8}$ mol/L. Further, concentration of the hydrofluoric acid is set not less than 15 weight %.

An etchant according to the present invention is applied for the purpose of etching onto silicon oxide film with a resist as a mask formed on a substrate, etching speeds to the silicon oxide film is 200 nm/min or more, and a film-reduction rate of the resist is 50 nm/min or less.

Preferably added to the etchant according to the present invention is 0.001 through 1 weight % of a surfactant.

BEST MODE FOR CARRYING OUT THE INVENTION

The etching liquid according to the present invention contains 8 thorough 19 weight % of HF, further contains 12 through 42 weight % of NH_4F, and has hydrogen ion concentration of $10^{-6.0}$ thorough $10^{-1.8}$ mol/L.

The concentration of HF as well as of NH_4F is set within the range described above, and etching speeds to, for example, silicon thermal oxide film can be set to 200 nm/min or more by adjusting the temperature in the etching solution. Also, by adjusting the hydrogen ion concentration within a range from $10^{-6.0}$ through $10^{-1.8}$ mol/L, the resist separation during the etching treatment can be prevented, and also a resist film-reduction speed can be suppressed to 50 nm/min or less. As a result, it is possible to make minimum an error of dimensions of a pattern on the insulating film due to the separation of as well as the thinner resist and to enhance uniformity on the wafer as a whole, so that a high yielding rate of devices with higher performance can be achieved.

It should be noted that crystals may be precipitated in the

etching solution depending on its composition, but even in that case, the etching solution may be used by heating it up to dissolve the crystals. Also, etching speeds can even more be enhanced by heating the solution, and the temperature in the solution of 45 °C or less will hardly affect the reduction of the resist film thickness. Especially, by setting the hydrofluoric acid concentration to 15 weight % and heating the solution up to the temperature of 35 °C to 45 °C or more, extremely high-speed etching can be realized.

The etching solution according to the present invention can be prepared by mixing NH_4F solution NH_4OH solution or NH_3 gas with HF solution in a specified ratio, and adding water or the like thereinto, to adjust the concentration and pH.

The etching solution according to the present invention can easily be obtained by mixing, for example, a 50 weight % HF solution with a 50 weight % NH_4F solution so that HF will be 8 through 19 weight %.

It is desirable to contain a surfactant in the etching liquid according to the present invention, and 0.001 through 1 weight % thereof is preferably contained therein. Addition of the surfactant in the liquid allows roughness on the surface of a semiconductor exposed after removal of insulating film to be suppressed. Further, when a pattern is finer, the etching liquid is hard to wet the insulating film, so that etching uniformity may be reduced, but addition of the surfactant thereinto allows the wet capability to be improved, thus the etching uniformity being enhanced.

It should be noted that the effect described above is hardly obtained with a rate of adding thereinto the surfactant of 0.001 weight % or less, and the same effect is obtained even with the rate of 1 weight % or more.

As a surfactant, aliphatic amine ($C_nH_{2n+1}NH_2$; n = 7 - 14), aliphatic carboxylic acid ($C_nH_{2n+1}COOH$; n = 5 - 11), and aliphatic alcohol ($C_nH_{2n+1}OH$; n= 6 - 12) are preferably applied. Those hydrocarbon sections may be a straight chain or a structure having branches. And also, it is especially preferable that at least two types among those three types of surfactant are mixed and that any of the types is selected for application depending on the concentration of NH_4F and HF.

The etching according to the present invention is treated as described below as an example.

The etching solution according to the present invention is heated up to a specified temperature so that crystals are not precipitated if it is necessary, sends the heated liquid to a nozzle, and supplies it from the nozzle onto a rotating wafer. The etching solution is supplied while the nozzle is moved between the center and the periphery of the wafer, so that the solution is supplied over the whole wafer. Also, the shift of the nozzle may be omitted by using an one-dimensional nozzle having a length by a radius of the wafer.

Further, it is preferable that a megasonic-ultrasonic oscillator is provided in the nozzle and the etching liquid is supplied while ultrasonic waves in a range from 500 kHz to several

MHz are irradiated onto a wafer. With those operations, etching speeds are even more increased.

As resist treatment before etching is treated with the etching liquid according to the present invention, it is preferable to irradiate ultraviolet rays onto a wafer after development of the resist, and then to subject the wafer to high-temperature baking. With those operations, a film- reduction rate can be more suppressed, and finer treatment can be applied with high uniformity.

As a condition of irradiation of ultraviolet rays, the wafer is irradiated with, for example, a UV lamp (220 to 320 nm) for 10 to 20 minutes under the condition of 5 to 15 mW/cm^2.

Also, high- temperature baking is executed preferably in an N_2 or Ar gas atmosphere for 10 to 30 minutes at the temperature of 110 to 250 °C. The baking temperature is more preferable to be 210 to 240 °C.

The etching solution according to the present invention can be applied for etching onto insulating film such as silicon oxide films containing P, B or As, oxide film such as tantalum oxide, and plasma silicon nitride film or the like in addition to silicon thermal oxidation film.

Embodiments

Described in detail hereinafter are embodiments of the present invention.

(Embodiment 1)

In this embodiment, in order to make clear a difference in

effects of etching solution composition, etching was carried out a batch soaking method, and comparison was made between an etching speed and a resist film-reduction rate.

At first, thermal oxidation film was formed on a silicon wafer by 1000 nm, and a photoresist was formed thereon by 1 μm. It should be noted that positive-type resists OFPR800 and TSMR8900 produced by Tokyo Oka were used for a resist.

The resists of various types of pattern having each width of O. 5 μm, I μm, and 10 μm respectively were exposed to light, and developed, and then subjected to post-bake treatment, for 30 minutes at the temperature of 130 °C. It should be noted that, for an etching solution having a pH of 2.4 or less, after the development, the resist was exposed by ultraviolet rays ($8W/cm^2$) for 15 minutes using a UV deuterium lamp, and high-temperature baking was executed to the resist in an N_2 atmosphere for 15 minutes at the temperature of 230 °C.

This resist was soaked in etching solutions each having a different composition and at a different temperature for 2 minutes, and an etching speed (nm/min) to silicon thermal oxide film and a resist film-reduction rate or the like were examined. Table 1 indicates the result. The resist film-reduction rates in Table I are obtained in relation to OFPR800, but substantially the same result was obtained with TSMR8900, so that TSMR is omitted herein. Peeling off the resist was herein observed with a microscope, and a film-reduction rate was measured with an optical film thickness gage.

It should be noted that each pH of the etching solution is measured at the temperature of 35 °C.

(TABLE 1)

Solution composition			Etching temperature					
			25℃		35℃		45℃	
HF wt%	NH_4F (wt%)	pH	Etch rate (nm/m)	Film-reduction rate (nm)	Etch rate (nm/m)	Film-reduction rate (nm)	Etch rate (nm/m)	Film-reduction rate (nm)
5	0	<0.8	300	1000	483	1000	724	1000
5	20	3.6	950	0	1986	0	2958	0
7	15	2.4	1290	0	2235	0	3316	0
7	20	3.8	1380	0	2400	0	3613	0
7	35	4.4	1250	0	2256	0	3200	0
8	5	<0.8	960	1000	2012	1000	2850	1000
8	10	1.6	1460	100	2530	* 300	3230	1000
8	12	1.8	1600	10	2780	10	4200	15
8	15	2.1	1750	0	3215	5	5360	5
8	35	4.2	1570	0	2750	0	4912	0
8	42	4.4	1420	0	2012	0	4570	0
10	0	<0.8	666	1000	1094	1000	1608	1000
10	5	<0.8	1396	1000	2337	1000	3578	1000
10	10	1.0	1978	1000	3303	1000	5475	1000
10	15	1.8	2233	5	3872	10	6251	10
10	18.5	2.4	2251	0	3783	0	6200	0
10	20	3.2	2185	0	3818	0	6122	0
10	24	3.6	2100	0	3639	0	6146	0
10	28	3.8	1959	0	3407	0	6008	0
10	32	4.0	1810	0	3164	0	5294	0
10	40	5.0	1760	0	2516	0	4623	0
15	20	<0.8	3750	1000	6495	1000	10377	1000
15	24	1.8	3817	5	6381	10	10541	10
15	27	2.0	—		6350	5	10341	5
15	27.8	2.4	—		6258	0	10079	0
15	35	3.6	3026	0	5435	0	9315	0

18	26.3	1.7	---		7437	* 300	12154	500
18	30	1.9	---		7213	5	11960	10
18	31	2.0	---		7130	5	12030	10
19	20	0.9	4530	** 500	7680	900	12690	1000
19	24	1.2	4732	* 500	7980	700	13340	1000
19	31	1.8	---		8016	10	13416	10
23	20	<0.8	5990	1000	10128	1000	15885	1000
25	20	<0.8	6510	1000	11264	1000	17514	1000
25	25	<0.8	6420	1000	10006	1000	15900	1000

In Table 1 , any etchant without description of an etch rate indicates a case where crystals were precipitated at the corresponding temperature. Also, the sign (*) indicates a case where a 0. 5 μm resist pattern was peeled off, and the sign (* *) indicates a case where a resist pattern of 1.0 μm or less was peeled off. The film-reduction rate having 1000 nm indicates a case where the resist was completely dissolved.

As is evident from Table 1, it is found that the etchant according to the present invention can realize high- speed etching, and in addition, the resist separation does not occur at all even on a fine pattern, and the film-reduction rate is extremely small.

In addition, in a case where the concentration of hydrofluoric acid is set to 1 5 weight % or more, etching can even more be speeded up, an etching speed of 1 μm/min or more at the temperature of 45 °C can be obtained and also the resist film-reduction rate be suppressed, which provides us the fact that the etchant is extremely excellent.

(Embodiment 2)

In this example, as a resist, a negative type resist (OMR83) produced by Tokyo Oka was used, and similarly to Embodiment 1, separation of the resist and a film- reduction rate were examined. Table 2 indicates the result. The film-reduction rates are obtained at the liquid temperature of 45 °C.

(TABLE 2)

HF concentration	NH_4F concentration	Film-reduction rate (nm)
10	0	1000
10	5	1000
10	10	1000
10	15	15
10	18.5	5
10	20	0
10	24	0
10	28	0
10	32	0

As shown in Table 2, substantially the same result as that of the positive resist is obtained in the case of the negative resist as well, and for this reason it is understood that the etching treatment agent according to the present invention has also less solubility to the negative resist.

(Embodiment 3)

In order to examine an effect of a surfactant, each silicon wafer was soaked in each of etching solutions heated up to 35 °C for 10 minutes, and surface roughness of each silicon surface exposed when silicon oxide film etched. Table 3 indicates the

result.

Herein, as a surfactant the mixture of $C_8H_{17}NH_2$ and $C_9H_{19}COOH$ in an equal molar ratio is added to each of the etching solutions in various of its concentrations. It should be noted that an atomic force microscope was used for measurement of the surface roughness Ra.

(TABLE 3)

HF concentration	NH_4F concentration	Addition (ppm)	Surface Roughness Ra(nm)
8	35	200	0.15
8	35	0	0.55
10	20	400	0.16
10	20	0	0.52
15	20	400	0.17
15	20	0	0.49
18	30	300	0.16
18	30	0	0.55
19	31	300	0.17
19	31	0	0.61

As is evident from Table 3, it is found that an initial value (0.15 to 0.17 nm) for each surface roughness after the soaking can be maintained by adding a surfactant to the etching solution, and that surface roughness can also be suppressed by the surfactant.

INDUSTRIAL APPLICABILITY

With an etching solution of the present invention, when etching is applied onto oxide film on a surface of a silicon wafer with a photoresist mask formed thereon, etching speeds onto the

oxide film can be achieved to 200 nm/min or more at the temperature of 35 °C and to 1 μm/min or more at the temperature of 45 °C depending on its composition.

As a result, although the time of around 300 minutes was required for etching by 500 nm onto 50 sheets of wafer in the cut sheet method by using the conventional type of 7 : 1 -BHF, the time required for the same treatment can be reduced to 30 minutes on condition that BHF as a high-speed etchant having etching speed of 1 μm/min at the temperature of 45 °C is used.

It is needless to say that, with this reduction, a shift of the etching process from the batch method based on the conventional technology to the cut sheet method can be made quicker, and also uniformity within an etching-treated surface as well as a level of throughput based on the wet process each required by the manufacturing process of a semiconductor device can remarkably be improved.

CLAIMS

1. An etching treatment agent which is an etchant for etching treatment onto an insulting film formed on a substrate with a resist as a mask, containing 8 through 19 weight % of hydrofluoric acid and 12 through 42 weight % of ammonium fluoride, and having a hydrogen ion concentration of $10^{-6.0}$ through $10^{-1.8}$ mol/L.

2. The etchant according to Claim 1 ; wherein concentration of said hydrofluoric acid is set to 15 weight % or more .

3. An etchant for etching treatment onto silicon oxide film formed on a substrate with a resist as a mask; wherein etching speeds to said silicon oxide film is 200 nm/min or more, and a film-reduction rate of said resist is 50 nm/min or less.

4. The etchant according to any of Claims 1 to 3 containing 0.001 through 1 weight % of a surfactant.

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ABSTRACT

An object of the present invention is to provide an etching treatment agent which can suppress an influence over a resist pattern and can etch onto insulating film with high speed.

An etchant for etching treatment onto insulting film with a resist as a mask formed on a substrate, which contains 8 through 19 weight % of hydrofluoric acid and 12 to 42 weight % of ammonium fluoride, and has hydrogen ion concentration of $10^{-6.0}$ through $10^{-1.8}$ mol/L. Further, an etchant for etching treatment onto silicon oxide film with a resist as a mask formed on a substrate, of which etching speed to the silicon oxide film is 200 nm/min or more and a film reduction rate of the resist is 50 nm/min or less.

CLAIMS

1. An etching treatment agent which is an etchant for etching treatment onto an insulating film formed on substrate with a resist as a mask, containing 15 to 19 weight % of hydrofluoric acid and 12 to 42 weight % of ammonium fluoride, and having a hydrogen ion concentration of $10^{-6.0}$ to $10^{-1.8}$ mol/L.

2. The etchant according to Claim 1 containing 0.001 to 1 weight % of a surfactant.

REPLACEMENT SHEET
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