

ETCHANT COMPOSITION FOR SILICON NITRIDE LAYER

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of Korean Patent Application No. KR 10-2019-0009299, filed January 24, 2019, which is hereby incorporated by reference in its entirety into this application.

BACKGROUND OF THE INVENTION

1. Technical Field

[0002] The present invention relates to an etchant composition for a silicon nitride layer.

2. Description of the Related Art

[0003] 3D NAND flash memory may be manufactured by selectively removing only a nitride layer in a multilayer structure comprising an oxide layer and a nitride layer (wet removal of nitride). Complete removal of the nitride layer without damaging the oxide layer is the key technology of wet removal of nitride.

[0004] Typically, an etchant composition for use in wet removal of nitride comprises an additive having anti-corrosion capability in order to attain the effect of completely removing only a nitride layer without damaging an oxide layer.

[0005] Korean Patent Application Publication No. 10-2018-0004871 and Korean Patent No. 10-1769349 disclose an etchant composition that selectively etches only a silicon nitride layer among a silicon oxide layer and a silicon nitride layer. However, the above documents are disadvantageous in that gelation is more likely to occur due to the use of silica as an additive and in that solubility in water is low, making it difficult to solve problems in which particles may be generated and may remain during the rinsing process after etching.

[0006] [Citation List]

[Patent Literature]

(Patent Document 1) Korean Patent Application Publication No. 10-2018-0004871

(Patent Document 2) Korean Patent No. 10-1769349

SUMMARY OF THE INVENTION

[0007] The present invention has been made keeping in mind the problems encountered in the related art, and an objective of the present invention is to provide an etchant composition for a silicon nitride layer, which makes it easy to adjust the etching selectivity for a nitride layer so as to enable selective etching only of a nitride layer in a multilayer structure comprising an oxide layer and a nitride layer, and also in which a selectivity change is low even after processing a large number of sheets, thereby maintaining etching performance, and moreover, particles may be prevented from being generated and remaining during the rinsing process after etching.

[0008] In order to accomplish the above objective, the present invention provides an etchant composition for a silicon nitride layer, comprising (A) phosphoric acid, (B) silicone resin and (C) water.

[0009] According to the present invention, an etchant composition for a silicon nitride layer can selectively etch only a nitride layer by easily adjusting the etching selectivity for a nitride layer in a multilayer structure comprising an oxide layer and a nitride layer, and can exhibit a low selectivity change even after processing a large number of sheets, thereby maintaining etching performance, and moreover, is effective at preventing particles from being generated and remaining during the rinsing process after etching.

DESCRIPTION OF SPECIFIC EMBODIMENTS

[0010] The present invention pertains to an etchant composition for a silicon nitride layer, comprising (A) phosphoric acid, (B) silicone resin, and (C) water as a solvent.

[0011] The etchant composition is capable of selectively etching only a nitride layer in a multilayer structure comprising an oxide layer and a nitride layer, and moreover, facilitates the control of desired selectivity. For example, the oxide layer preferably comprises SiO_2 and the nitride layer preferably comprises SiN .

[0012] The etchant composition is used for the process of manufacturing 3D NAND flash memory, and is able to minimize defect problems in which side-reaction oxide remains and the oxide layer is damaged, occurring during the wet removal of nitride.

[0013] Also, the etchant composition comprises the silicone resin, thus exhibiting high solubility in water to thereby prevent particles from being generated and remaining during the rinsing process after etching.

[0014] Also, the etchant composition is able to maintain etching performance even after processing a large number of sheets, thereby increasing the lifespan of the composition.

[0015] Hereinafter, the phosphoric acid, silicone resin and water, which are comprised in the etchant composition according to the present invention, are described in detail.

[0016] (A) Phosphoric acid

[0017] In the etchant composition of the present invention, the phosphoric acid is the main component for etching a nitride layer, and may etch the nitride layer in the multilayer structure comprising the oxide layer and the nitride layer. Also, etching of the oxide layer of the multilayer structure may be prevented by the silicone resin, which will be described later, thus selectively etching only the nitride layer. Also, phosphoric acid may be added in the form of a phosphoric acid aqueous solution with water, which will be described later.

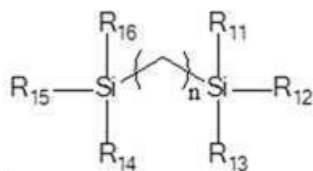
[0018] The amount of phosphoric acid is 60 to 95 wt%, and preferably 80 to 90 wt%, based on the total weight of the composition. When the amount of phosphoric acid that is added falls in the above range, an appropriate etching rate may be provided, and appropriate etching selectivity for the nitride layer in the multilayer structure comprising the oxide layer and the nitride layer may also be realized.

[0019] (B) Silicone resin

[0020] In the etchant composition of the present invention, the silicone resin is an anti-corrosive agent, and may be used to prevent the oxide layer of the multilayer structure comprising the oxide layer and the nitride layer from being etched by phosphoric acid.

[0021] The silicone resin may comprise at least one compound represented by Chemical Formula 1 and 2 below.

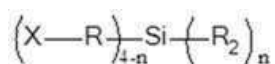
[Chemical Formula 1]



[0022] In Chemical Formula 1, R_{11} to R_{16} are each independently selected from the group consisting of hydrogen, halogen, C1-C10 alkyl group, C1-C4 alkoxy group and acetoxy group, and n may be an integer of 1 to 5.

[0023] Preferably, in Chemical Formula 1, R_{11} to R_{16} are each independently selected from the group consisting of hydrogen, halogen, C1-C5 alkyl group, methoxy, ethoxy, propoxy, isopropoxy and acetoxy group, and n is an integer of 1 to 5.

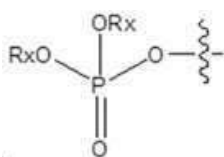
[Chemical Formula 2]



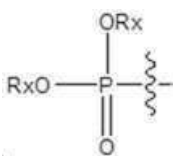
[0024] In Chemical Formula 2, R_2 is selected from the group consisting of hydrogen, halogen, C1-C10 alkyl group, C1-C4 alkoxy group and acetoxy group, R is selected from the group consisting of C1-C10 alkyl group, C2-C10 alkenyl group and C2-C10 alkynyl group, X comprises a functional group selected from the group consisting of hydrogen, halogen, hydroxyl group, ether group, ester group, amine group, phosphonate group, phosphate group, sulfonate group and sulfate group, and n may be an integer of 1 to 4.

[0025] Preferably, in Chemical Formula 2, R_2 is selected from the group consisting of hydrogen, halogen, C1-C5 alkyl group, methoxy, ethoxy, propoxy, isopropoxy and acetoxy group, R is selected from the group consisting of C1-C5 alkyl group, X is selected from the group consisting of compounds represented by Chemical Formulas 2-1 to 2-9 below, and n is an integer of 1 to 4.

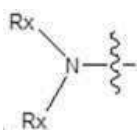
[Chemical Formula 2-1]



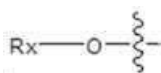
[Chemical Formula 2-2]



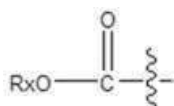
[Chemical Formula 2-3]



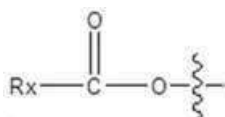
[Chemical Formula 2-4]



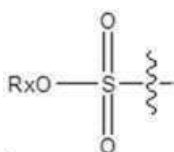
[Chemical Formula 2-5]



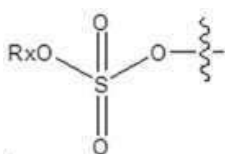
[Chemical Formula 2-6]



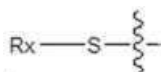
[Chemical Formula 2-7]



[Chemical Formula 2-8]



[Chemical Formula 2-9]



[0026] In Chemical Formulas 2-1 to 2-9, Rx may be each independently selected from the group consisting of hydrogen, C1-C10 alkyl group, C2-C10 alkenyl group, C2-C10 alkynyl group, and the alkyl group, the alkenyl group and the alkynyl group, each of which is substituted with a hydroxyl group.

[0027] The amount of the silicone resin is 0.0001 to 2.0 wt%, and preferably 0.001 to 1.0 wt%, based on the total weight of the composition. When the amount of the silicone resin falls in the above range, it is possible to adjust the etching selectivity for the nitride layer in the multilayer structure comprising the oxide layer and the nitride layer to thus selectively etch only the nitride layer, and moreover, gelation of the composition may be

prevented, thus improving etching performance. Furthermore, problems of low quality in which particles may be generated and remain during the rinsing process after etching may be prevented from occurring by virtue of the high solubility in water.

[0028] The silicone resin is a silicone polymer comprising at least one carbon, the properties of which are quite different from those of silica as inorganic particles represented by the chemical formula of SiO_2 . Unlike the etchant composition of the present invention comprising the silicone resin as the anti-corrosive agent, in the case in which silica in the form of inorganic particles is used as an anti-corrosive agent, the likelihood of silica not being dissolved in the composition and remaining as particles is high. Furthermore, even upon dissolution through surface modification or the like, gelation may occur and performance as the anti-corrosive agent may deteriorate, and particles may be formed during the water-rinsing process after etching due to the low solubility in water, and may thus be adsorbed to the surface of a semiconductor substrate, causing particle problems, undesirably resulting in low product quality.

[0029] In the present invention, the silicone resin may comprise a trifunctional and/or tetrafunctional silane compound having a network structure. Here, the number of functional groups of the silane compound may be determined based on the number of functional groups for a single silicon atom. For example, Chemical Formula 1 may be provided in the form of a trifunctional silane compound comprising two silicon atoms. In the case in which a siloxane polymer having a linear, branched or cross-linked structure is used, rather than a silicone resin having a network structure, the oxide layer may not be sufficiently protected, undesirably damaging the oxide layer when selectively etching only the nitride layer in the multilayer structure comprising the oxide layer and the nitride layer.

[0030] (C) Water

[0031] In the etchant composition of the present invention, the water may be deionized water for use in semiconductor processing, and is preferably deionized water of 18 $\text{M}\Omega/\text{cm}$ or more.

[0032] Here, the water may be added in a remaining amount such that the total weight of the composition, comprising the essential component of the present invention and the other components, is 100 wt%.

[0033] The water may be added in the form of a phosphoric acid aqueous solution together with phosphoric acid. For example, when it is added in the form of a 85% phosphoric acid aqueous solution, the amount of water may be 98% to 99.9999 wt% based on the total weight of the composition.

[0034] A better understanding of the present invention will be given through the following examples, which are merely set forth to illustrate the present invention but are not to be construed as limiting the scope of the present invention.

[0035] Preparation Examples: Preparation of silicone resin

[0036] With reference to Table 1 below, the compound represented by Chemical Formula 1 and/or Chemical Formula 2 was added to an aqueous solution in which a phosphoric acid catalyst was present (phosphoric acid was used as a catalyst in Preparation Examples of the present invention, but an acid or base catalyst may be selectively used, as necessary) to thus primarily form a silicone resin, and the silicone resin thus primarily formed was collected, dried, added to a 85% phosphoric acid aqueous solution, and secondarily treated at 90 to 200°C for 1 to 6 hr, thus preparing silicone resins of Preparation Examples 1 to 8.

[Table 1]

(amount: wt%)

No.	Compound of Chemical Formula 1 or 2											Phosphoric acid aqueous solution	Treatment conditions	
	1-a	1-b	1-c	2-a	2-b	2-c	2-d	2-e	2-f	2-g	2-h		Temp. (°C)	Time (hr)
Preparation Example 1	1											99	200	1
Preparation Example 2		1									14	85	150	2
Preparation Example 3			2						8			90	90	3
Preparation Example 4				1	9							90	90	3
Preparation Example 5				0.5	6.5			3				90	120	1.5
Preparation Example 6						15						85	90	4
Preparation		1								4		95	130	6

[0049] Examples and Comparative Examples: Preparation of etchant composition

[0050] With reference to Table 2 below, the etchant compositions of Examples and Comparative Examples were prepared.

[0051] In Comparative Examples 1 to 3, silica (SiO₂), poly(dimethylsiloxane) and tetraethyl orthosilicate (TEOS) were used, respectively, corresponding to the silicone resin according to the present invention. Specifically, the composition of Comparative Example 1 was prepared in a manner in which silica, available from Aldrich, was added in an amount of 1 wt% to a 85% phosphoric acid aqueous solution, heated at 180°C for 3 hr and then added again in an amount of 3.5 wt% to the 85% phosphoric acid aqueous solution, the composition of Comparative Example 2 was prepared by adding poly(dimethylsiloxane), available from Aldrich, in an amount of 0.5 wt% to a 85% phosphoric acid aqueous solution, and the composition of Comparative Example 3 was prepared by adding TEOS, available from Aldrich, in an amount of 0.1 wt% to a 85% phosphoric acid aqueous solution.

[Table 2]

(amount: wt%)

No.	Silicone resin		85% Phosphoric acid aqueous solution	Solubility after preparation of etchant
	Kind	Amount		
Example 1	Preparation Example 1	0.012	Remainder	Transparent
Example 2	Preparation Example 2	0.3	Remainder	Transparent
Example 3	Preparation Example 3	0.34	Remainder	Transparent
Example 4	Preparation Example 4	0.35	Remainder	Transparent
Example 5	Preparation Example 5	0.0005	Remainder	Transparent
Example 6	Preparation Example 5	0.52	Remainder	Transparent
Example 7	Preparation Example 5	2.5	Remainder	Transparent
Example 8	Preparation Example 6	0.11	Remainder	Transparent
Example 9	Preparation Example 7	0.12	Remainder	Transparent
Example 10	Preparation Example 8	0.46	Remainder	Transparent
Comparative Example 1	Silica (SiO ₂)	0.035	Remainder	Transparent
Comparative Example 2	Poly(dimethylsiloxane)	0.5	Remainder	Suspended
Comparative Example 3	Tetraethyl orthosilicate	0.1	Remainder	Generation of particles

[0052] The etchant composition of each of Examples and Comparative Examples prepared with reference to Table 2 was allowed to stand at 25°C for 1 hr. Thereafter, based on the results of observation of the state of dissolution thereof, the etchant compositions of Examples 1 to 10 and Comparative Example 1 remained transparent.

Particles were not observed in the etchant composition of Comparative Example 2 but a suspension was formed, and particles were observed in the etchant composition of Comparative Example 3.

[0053] Test Example

[0054] The etchant composition of Comparative Example 3 could not be used because particles were observed therein, and was thus excluded. The etchant compositions of Examples 1 to 10 and Comparative Examples 1 and 2 were evaluated for performance thereof as follows.

[0055] Evaluation 1: Measurement of etching rate of silicon nitride layer and silicon oxide layer

[0056] 200 g of the etchant composition of each of Examples and Comparative Examples was prepared in a 250 ml beaker and then heated to 158°C to 160°C, after which a silicon nitride layer having a thickness of 4500 Å and a silicon oxide layer having a thickness of 500 Å were immersed therein for 10 min and thus etched. After etching, water rinsing was performed at 25°C for 1 min, and the layer thickness was then measured using an ellipsometer to thus determine the etching rate (Å/min), which was then substituted into the following equation, thereby obtaining the selectivity (A). The results thereof are shown in Table 3 below.

[0057] Selectivity = Etching rate of silicon nitride layer/etching rate of silicon oxide layer

[0058] Evaluation 2: Measurement of etching rate of silicon nitride layer and silicon oxide layer

[0059] 200 g of the etchant composition of each of Examples and Comparative Examples was prepared in a 250 ml beaker and then heated to 158°C to 160°C, after which a silicon nitride layer having a thickness of 4500 Å and a silicon oxide layer having a thickness of 500 Å were immersed therein for 10 min and thus etched. In this way, etching of the silicon nitride layer and the silicon oxide layer in the same etching solution was repeated five times, after which the substrate was rinsed with water at 25°C for 1 min, and the layer thickness was then measured using an ellipsometer to thus determine the etching rate (Å/min), which was then substituted into the same equation as in Evaluation 1, thereby obtaining the selectivity (B). The results thereof are shown in Table 3 below.

[0060] Evaluation 3: Selectivity change depending on the number of processes of treating silicon nitride layer and silicon oxide layer

[0061] A selectivity change was calculated from the selectivity (A) and the selectivity (B) determined in Equations 1 and 2 using the following equation. The results thereof are shown in Table 3 below.

[0062] Selectivity change (%) = (B-A)/A x 100

[0063] A: Etching selectivity of silicon nitride layer and silicon oxide layer in the first process

[0064] B: Etching selectivity of silicon nitride layer and silicon oxide layer in the fifth process

[0065] Evaluation 4: Evaluation of solubility in water

[0066] The etchant composition of each of Examples and Comparative Examples was mixed with water at a mass ratio of 1:99, and was allowed to stand at 25°C for 1 hr, after which suspension and particle generation were observed.

[0067] ◎ transparency was maintained

[0068] ○: particles were not observed with the naked eye, but suspension occurred

[0069] △ particles were observed with the naked eye but were not precipitated and remained suspended

[0070] X: particles were observed with the naked eye and precipitated

[Table 3]

No.	Evaluation 1: Etching rate (Å/min)			Evaluation 2: Etching rate (Å/min)			Evaluation 3	Evaluation 4
	Si nitride layer	Si oxide layer	Selectivity (A)	Si nitride layer	Si oxide layer	Selectivity (B)	Selectivity change (%)	Solubility in water
Example 1	81.6	0.12	680.0	79.8	0.11	725.5	6.7	◎
Example 2	74.9	0.11	680.9	73.2	0.10	732.0	7.5	◎
Example 3	78.5	0.13	603.8	72.4	0.11	658.2	9.0	◎
Example 4	77.1	0.13	593.1	75.2	0.12	626.7	5.7	○
Example 5	86.2	0.31	278.1	84.6	0.29	291.7	4.9	◎
Example 6	69.8	0.17	410.6	67.2	0.15	448.0	9.1	◎
Example 7	62.0	0.06	1033.3	60.8	0.05	1216	17.7	△
Example 8	80.2	0.10	802.0	71.9	0.08	898.8	12.1	◎
Example 9	75.7	0.10	757.0	72.2	0.09	802.2	6.0	◎
Example 10	72.8	0.16	455.0	71.4	0.15	476.0	4.6	◎
Comparative	76.1	0.12	634.2	71.1	-0.03	-2370.0	-473.7	X

Example 1								
Comparative Example 2	73.5	0.68	108.1	70.1	0.63	111.3	2.94	X

[0071] As is apparent from Table 3, the use of the etchant compositions of Examples made it easy to adjust the selectivity and made it possible to process increased number of sheets by virtue of the low selectivity change. Moreover, because of the high solubility in water, particles were not generated and did not remain during the rinsing process after etching.

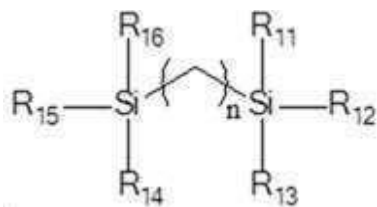
[0072] In contrast, when etching was performed five times using the etchant composition of Comparative Example 1 (Evaluation 2), the etching rate of the silicon oxide layer was measured to be $-0.03 \text{ \AA/min}$, which means that silica was adsorbed to the surface of the silicon oxide layer and thus the layer thickness was increased above the initial thickness, indicative of a very poor aspect in view of the number of sheets capable of being processed, thereby inducing generation of particles on the surface of the silicon oxide layer, resulting in a very great selectivity change. Moreover, because of the low solubility in water, particles were observed with the naked eye and precipitated, indicating that particles were generated during the rinsing process after etching and thus remained (adsorbed) on the surface of the substrate.

[0073] In the etchant composition of Comparative Example 2, the etching effect was exhibited both for the silicon nitride layer and for the silicon oxide layer, and thus there was no protection for the silicon oxide layer, from which the selectivity was evaluated to be very low. Moreover, particles were observed with the naked eye due to the low solubility in water, and precipitation occurred.

WHAT IS CLAIMED IS:

1. An etchant composition for a silicon nitride layer, comprising:
(A) phosphoric acid;
(B) silicone resin; and
(C) water,
wherein the silicone resin is polymerized by comprising at least one of the compounds represented by Chemical Formula 1 and Chemical Formula 2 below:

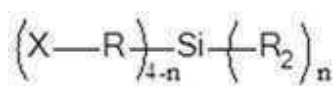
[Chemical Formula 1]



in Chemical Formula 1,

R₁₁ to R₁₆ are each independently selected from the group consisting of hydrogen, halogen, C1-C10 alkyl group, C1-C4 alkoxy group and acetoxy group, and n is an integer of 1 to 5,

[Chemical Formula 2]



in Chemical Formula 2,

R₂ is selected from the group consisting of hydrogen, halogen, C1-C10 alkyl group, C1-C4 alkoxy group and acetoxy group,

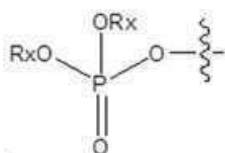
R is selected from the group consisting of C1-C10 alkyl group, C2-C10 alkenyl group and C2-C10 alkynyl group,

X comprises a functional group selected from the group consisting of hydrogen, halogen, hydroxyl group, ether group, ester group, amine group, phosphonate group, phosphate group, sulfonate group and sulfate group, and

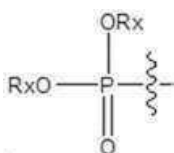
n is an integer of 1 to 4.

2. The etchant composition of claim 1, wherein, in Chemical Formula 2, X is selected from the group consisting of compounds represented by Chemical Formulas 2-1 to 2-9 below:

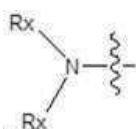
[Chemical Formula 2-1]



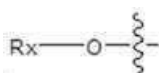
[Chemical Formula 2-2]



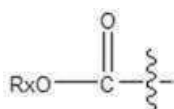
[Chemical Formula 2-3]



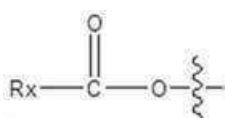
[Chemical Formula 2-4]



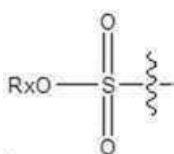
[Chemical Formula 2-5]



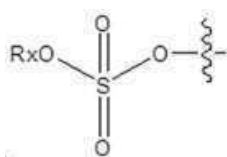
[Chemical Formula 2-6]



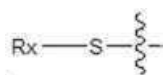
[Chemical Formula 2-7]



[Chemical Formula 2-8]



[Chemical Formula 2-9]



in Chemical Formulas 2-1 to 2-9,

Rx is each independently selected from the group consisting of hydrogen, C1-C10 alkyl group, C2-C10 alkenyl group, C2-C10 alkynyl group, and the alkyl group, the alkenyl group and the alkynyl group, each of which is substituted with a hydroxyl group.

3. The etchant composition of claim 1, wherein the etchant composition selectively etches a nitride layer only in a multilayer structure comprising an oxide layer and a nitride layer.

4. The etchant composition of claim 3, wherein the oxide layer comprises SiO_2 and the nitride layer comprises SiN .

5. The etchant composition of claim 1, comprising, based on a total weight of the composition:

- 60 to 95 wt% of phosphoric acid; and
- 0.0001 to 2.0 wt% of silicone resin.