

ETCHANT COMPOSITION AND METHOD OF SELECTING SILANE-BASED COUPLING AGENT CONTAINED THEREIN

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of Korean Patent Application No. KR 10-2018-0125172, filed October 19, 2018, 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 and a method of selecting a silane-based coupling agent contained therein.

2. Description of the Related Art

[0003] FIG. 1 shows part of the process of manufacturing 3D NAND flash memory. 3D NAND flash memory may be manufactured by selectively removing only a nitride layer from a multilayer structure including 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 includes 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] However, when trying to completely remove the nitride layer within a range that does not damage the oxide layer, an additive having strong anti-corrosion capability is used, thus causing a process defect (FIG. 2) in which the nitride layer is not completely removed.

[0006] Alternatively, when trying to completely remove the nitride layer, an additive having weak anti-corrosion capability is used, and thus the nitride layer is completely removed, but a process defect in which the oxide layer is damaged may occur (FIG. 3).

[0007] Conventionally, the selection of an additive having an appropriate level of anti-corrosion capability for completely removing only a nitride layer from a multilayer structure including an oxide layer and a nitride layer is confirmed experimentally depending on the kind and concentration of the additive. Without such experimental confirmation, the selection of additives is impossible in practice, and thus there is a problem in which excessive time and expenses are incurred in order to develop etchant compositions.

[0008] U.S. Patent Application Publication No. 2013-0092872 discloses an etchant composition, which selectively etches only a silicon nitride layer among a silicon oxide layer and a silicon nitride layer during the manufacture of 3D NAND flash memory. However, in order to determine the kind and concentration of components, testing the etching performance of the etchant composition is inevitable. As described above, the problem of excessive time and expenses incurred in finding components appropriate for the etchant composition still remains.

[0009] [Citation List]

[Patent Literature]

(Patent Document 1) U.S. Patent Application Publication No. 2013-0092872

SUMMARY OF THE INVENTION

[0010] 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, which includes a parameter for selecting a silane-based coupling agent as an additive having anti-corrosion capability and an effect of selectively etching only a nitride layer from a multilayer structure including an oxide layer and a nitride layer, even without additional experimental confirmation, and thus includes a silane-based coupling agent based on the parameter.

[0011] Another objective of the present invention is to provide an etchant composition, which is capable of selectively etching only a nitride layer from a multilayer structure including an oxide layer and a nitride layer.

[0012] Still another objective of the present invention is to provide an etching method using the etchant composition.

[0013] Yet another objective of the present invention is to provide a method of selecting a silane-based coupling agent contained in the etchant composition.

[0014] In order to accomplish the above objectives, the present invention provides an etchant composition, including phosphoric acid, a silane-based coupling agent and water, in which the silane-based coupling agent has an A_{eff} value ranging from 2.2 to 4.0, the A_{eff} value being obtained by dividing the number of active sites of the silane-based coupling agent by the molecular weight of a hydrolyzed form of the silane-based coupling agent and then multiplying by 96.1.

[0015] In addition, the present invention provides a method of selecting a silane-based coupling agent for use in an etchant composition that selectively etches only a nitride layer from a multilayer structure including an oxide layer and a nitride layer, the method including selecting a silane-based coupling agent having an A_{eff} value ranging from 2.2 to 4.0, the A_{eff} value being obtained by dividing the number of active sites of the silane-based coupling agent by the

molecular weight of a hydrolyzed form of the silane-based coupling agent and then multiplying by 96.1.

[0016] According to the present invention, an etchant composition includes a silane-based coupling agent having superior anti-corrosion capability and a high effect of selectively etching only a nitride layer from a multilayer structure including an oxide layer and a nitride layer, which can be selected without additional experimental confirmation.

[0017] Also, according to the present invention, the etchant composition is effective in selectively etching only the nitride layer without damaging the oxide layer.

BRIEF DESCRIPTION OF DRAWINGS

[0018] FIG. 1 shows part of the process of manufacturing 3D NAND flash memory;

[0019] FIGS. 2 and 3 show process defects occurring during the wet removal of nitride upon manufacturing the 3D NAND flash memory;

[0020] FIG. 4 shows an appropriate anti-corrosion capability range of a silane-based coupling agent that is able to minimize a residual level of side-reaction oxide and damage to an oxide layer, which are defects occurring during the manufacture of 3D NAND flash memory; and

[0021] FIG. 5 is a graph showing the correlation between the A_{eff} value of the silane-based coupling agent and the etching amount.

DESCRIPTION OF SPECIFIC EMBODIMENTS

[0022] The present inventors have ascertained that when an additive having anti-corrosion capability used for the etchant composition for wet removal of nitride satisfies a specific parameter value, the effects of selectively removing only a nitride layer from a multilayer

structure including an oxide layer and a nitride layer and preventing damage to the oxide layer may be maximized, thus culminating in the present invention.

[0023] The present invention pertains to a method of selecting an additive having a high ability to selectively remove only a nitride layer from a multilayer structure including an oxide layer and a nitride layer, an additive selected thereby, an etchant composition including the additive, and an etching method using the etchant composition.

[0024] In the present invention, a layer to be etched may be a nitride layer and a layer to be protected may be an oxide layer. The additive of the present invention may be a silane-based coupling agent.

[0025] <Etchant composition>

[0026] Specifically, the etchant composition of the present invention includes phosphoric acid, an additive and water, and the additive may be a silane-based coupling agent.

[0027] The additive of the present invention has a novel parameter value, A_{eff} , ranging from 2.2 to 4.0, the A_{eff} value being obtained by dividing the number of active sites of the additive by the molecular weight of a hydrolyzed form of the additive and then multiplying by 96.1, as represented by the following equation.

$$A_{\text{eff}} = (\text{number of active sites of additive} / \text{molecular weight of hydrolyzed form of additive}) \times 96.1$$

[0028] In the present invention, examples of the number of active sites of each additive and the molecular weight of a hydrolyzed form of the additive are shown in Table 3 below.

[0029] Also, examples of the A_{eff} value of each additive calculated therefrom and the etching amount are shown in Table 2 below. As is apparent from the above results, the A_{eff} value of the additive preferably falls in the range of 2.2 to 4.0, and more preferably 2.2 to 3.0.

[0030] With reference to FIG. 4, when the A_{eff} of the additive (silane-based coupling agent) is 3.0 or less, the defect in which the nitride layer is not completely removed due to the long residence time of side-reaction oxide may be minimized. On the other hand, when the A_{eff} of the silane-based coupling agent is 2.2 or more, the defect in which the oxide layer is damaged may be minimized. Therefore, the use of an additive having anti-corrosion capability with the A_{eff} ranging from 2 to 3.0 corresponding to the above overlapping range (Spec satisfaction zone) may minimize defects in which the nitride layer is not completely removed due to the long residence time of side-reaction oxide and in which the oxide layer is damaged.

[0031] When the A_{eff} value of the additive falls within the above range, the additive may have an appropriate level of anti-corrosion capability, thereby making it possible to select an additive such as a silane-based coupling agent having desired anti-corrosion capability, even without costly and time-consuming practical experiments.

[0032] The additive of the present invention, such as the silane-based coupling agent, is preferably added at a concentration that enables the etching amount (E/A) of the layer (oxide layer) to be protected to fall in the range of $-20 \text{ \AA}$ to $100 \text{ \AA}$. For example, when a multilayer structure including an oxide layer (e.g. SiO_2) and a nitride layer (e.g. SiN) on the oxide layer is treated with the additive at a concentration of 1000 ppm at 160°C for 10,000 sec, the additive is preferably added at a concentration that enables the etching amount (E/A) for oxide layer of the layer to be protected to fall in the range of $-20 \text{ \AA}$ to $100 \text{ \AA}$. The anti-corrosion capability of the additive according to the present invention is determined by multiplying the A_{eff} value of the additive with the concentration thereof, and may be represented as the etching amount (E/A). A positive value of the etching amount means an increase in the thickness after the etching process, and a negative value thereof means a decrease in the thickness.

[0033] The etchant composition is able to selectively etch only the nitride layer from the multilayer structure including the oxide layer and the nitride layer, and the oxide layer preferably includes SiO₂ and the nitride layer preferably includes SiN.

[0034] The etchant composition is used for the process of manufacturing 3D NAND flash memory, and is able to minimize the defect problems in which side-reaction oxide remains and the oxide layer is damaged, occurring during the wet removal of nitride.

[0035] The etchant composition of the present invention includes the additive selected as above, and upon selectively etching only the nitride layer from the multilayer structure including the oxide layer and the nitride layer using the same, process defects in which the nitride layer is not completely removed due to the long residence time of side-reaction oxide (FIG. 2) and in which the nitride layer is completely etched but the oxide layer is damaged (FIG. 3) may be minimized.

[0036] The defect in which the nitride layer is not completely removed due to the long residence time of side-reaction oxide occurs when the anti-corrosion capability of the additive is greater than an appropriate level, and the defect in which the oxide layer is damaged occurs when the anti-corrosion capability of the additive is less than the appropriate level.

[0037] Hereinafter, phosphoric acid, a silane-based coupling agent serving as an additive, and water, which are included in the etchant composition of the present invention, are described in detail.

[0038] (A) Phosphoric acid

[0039] In the etchant composition of the present invention, the phosphoric acid is the main oxidant, and may be used to oxidize the nitride layer.

[0040] The amount of phosphoric acid is 50 to 95 wt%, and preferably 80 to 90 wt%, based on the total weight of the composition. When the amount of phosphoric acid falls in the above range, an appropriate etching rate and high SiN/SiO₂ selectivity may result.

[0041] (B) Silane-based coupling agent

[0042] In the etchant composition of the present invention, the silane-based coupling agent is an anti-corrosive agent, and may be used to prevent the oxide layer of the multilayer structure including the oxide layer and the nitride layer from being oxidized by phosphoric acid.

[0043] The silane-based coupling agent preferably has an A_{eff} value ranging from 2.2 to 4.0, and more preferably from 2.2 to 3.0, the A_{eff} value being obtained by dividing the number of active sites of the silane-based coupling agent by the molecular weight of a hydrolyzed form of the silane-based coupling agent and then multiplying by 96.1.

[0044] The silane-based coupling agent is preferably added at a concentration that enables the etching amount (E/A) for oxide layer of the etchant composition to fall in the range of $\sim 20 \text{ \AA}$ to $100 \text{ \AA}$.

[0045] The silane-based coupling agent is preferably at least one selected from the group consisting of tetraethyl orthosilicate, bis(triethoxysilyl)methane, bis(triethoxysilyl)ethane, (triethoxysilyl)methanol, and (triethoxysilyl)methane, and is more preferably at least one selected from the group consisting of bis(triethoxysilyl)methane, (triethoxysilyl)methanol and (triethoxysilyl)methane. (Triethoxysilyl)methane and/or (triethoxysilyl)methanol are most preferably used.

[0046] The amount of the silane-based coupling agent is 0.01 to 10 wt%, and preferably 0.01 to 1.0 wt%, based on the total weight of the composition. When the amount of the silane-based coupling agent falls in the above range, gelation of the additive itself may be controlled, and appropriate SiO_2 anti-corrosion and SiN etching performance may result.

[0047] (C) Water

[0048] 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.

[0049] Here, the water may be added in a remaining amount such that the total weight of the composition, including the essential component of the present invention and the other components, is 100 wt%. Preferably, the water is added in an amount of 2 to 45 wt% based on the total weight of the composition of the present invention.

[0050] <Method of selecting additive, additive selected thereby and etching method using the same>

[0051] The present invention pertains to a method of selecting an additive for use in the etchant composition for selectively etching only a nitride layer from a multilayer structure including an oxide layer and a nitride layer, an additive selected thereby, and an etching method using the same. All of the details for additive selection and the like described in connection with the etchant composition above may be equally applied to the method of selecting an additive for use in the etchant composition for selectively etching only a nitride layer from a multilayer structure including an oxide layer and a nitride layer, the additive selected thereby, and the etching method using the same.

[0052] Specifically, the present invention addresses a method of selecting a silane-based coupling agent of the etchant composition for selectively etching only a nitride layer from a multilayer structure including an oxide layer and a nitride layer, a silane-based coupling agent selected thereby, and an etching method using the same.

[0053] The method of selecting the silane-based coupling agent includes selecting a silane-based coupling agent having an A_{eff} value ranging from 2.2 to 4.0, the A_{eff} value being obtained by dividing the number of active sites of the silane-based coupling agent by the molecular weight of a hydrolyzed form of the silane-based coupling agent and then multiplying by 96.1.

[0054] A better understanding of the present invention will be given through the following examples. However, these examples are merely set forth to illustrate the present invention but are not to be construed as limiting the scope of the present invention.

[0055] Examples and Comparative Examples: Preparation of etchant composition

[0056] With reference to the following Table 1 (wt%), the etchant compositions of Examples and Comparative Examples were prepared.

[Table 1]

	Phosphoric acid	Silane-based coupling agent		Water
		Kind	Amount	
Example 1	85	bis(triethoxysilyl)methane	0.1	Remainder
Example 2		bis(triethoxysilyl)ethane		
Example 3		tetraethyl orthosilicate		
Example 4		(triethoxysilyl)methanol		
Example 5		(trimethoxysilyl)methanol		
Example 6		(triacetoxysilyl)methanol		
Example 7		(triethoxysilyl)methane		
Example 8		(trimethoxysilyl)methane		
Example 9		(triethoxysilyl)ethane		
Example 10		(trimethoxysilyl)ethane		
Example 11		(triethoxysilyl)propane		
Example 12		(trimethoxysilyl)propane		
Example 13		(triethoxysilyl)ethanol		
Example 14		(trimethoxysilyl)ethanol		
Comparative Example 1		γ -aminopropyl triethoxysilane		
Comparative Example 2		allyltrimethylsilane		
Comparative Example 3		phenyltrimethoxysilane		
Comparative Example 4		1-[3-(trimethoxysilyl)propyl]urea		
Comparative Example 5		1-[3-(triethoxysilyl)propyl]urea		
Comparative Example 6		(3-((2-aminoethyl)amino)propyl)silanetriol		

Comparative Example 7	(trimethoxysilylpropyl)ethylenediamine		
Comparative Example 8	dimethyl 2-(trimethoxysilyl)ethyl phosphate		
Comparative Example 9	diethyl 2-(triethoxysilyl)ethyl phosphate		
Comparative Example 10	3-aminopropyl-ethyl-diethoxysilane		
Comparative Example 11	tris(trimethylsilyl) phosphate		

[0057] With reference to Table 2 below and FIG. 5, using the etchant composition of each of Examples and Comparative Examples, a multilayer structure including an oxide layer SiO₂ and a nitride layer SiN on the oxide layer, having a total thickness of 4000 Å, was treated as follows. When the multilayer structure was treated with a 0.1% silane-based coupling agent at 160°C for 10,000 sec, the A_{eff} value had a linear correlation with the etching amount (E/A).

[0058] Specifically, in Examples 1 to 14, including the silane-based coupling agent having the A_{eff} value ranging from 2.2 to 4.0, the etching amount (E/A) was appropriate, thus very effectively preventing defects in which the oxide layer was damaged and in which the nitride layer was not completely removed due to the long residence time of side-reaction oxide.

[0059] In contrast, in Comparative Examples 1 to 11, including the silane-based coupling agent having the A_{eff} value that fell out of the range of 2.2 to 4.0, the etching amount was inappropriate, and thus damage to the oxide layer occurred.

[Table 2]

	Silane-based coupling agent	A _{eff}	E/A (Å)
Example 1	bis(triethoxysilyl)methane	3.35	113.45
Example 2	bis(triethoxysilyl)ethane	3.10	92.43
Example 3	tetraethyl orthosilicate	4.0	140.01
Example 4	(triethoxysilyl)methanol	2.6	55.1
Example 5	(trimethoxysilyl)methanol	2.6	59.0
Example 6	(triacetoxysilyl)methanol	2.6	60.5

Example 7	(triethoxysilyl)methane	3.1	80.7
Example 8	(trimethoxysilyl)methane	3.1	83.5
Example 9	(triethoxysilyl)ethane	2.7	65.5
Example 10	(trimethoxysilyl)ethane	2.7	67.0
Example 11	(triethoxysilyl)propane	2.4	45.6
Example 12	(trimethoxysilyl)propane	2.4	48.2
Example 13	(triethoxysilyl)ethanol	2.3	42.0
Example 14	(trimethoxysilyl)ethanol	2.3	43.7
Comparative Example 1	γ -aminopropyl triethoxysilane	2.10	-71.93
Comparative Example 2	allyltrimethylsilane	2.10	-103.45
Comparative Example 3	phenyltrimethoxysilane	1.86	-161.31
Comparative Example 4	1-[3-(trimethoxysilyl)propyl]urea	1.60	-97.39
Comparative Example 5	1-[3-(triethoxysilyl)propyl]urea	1.60	-28.487
Comparative Example 6	(3-((2-aminoethyl)amino)propyl)silanetriol	1.60	-78.78
Comparative Example 7	(trimethoxysilylpropyl)ethylenediamine	1.60	-117.28
Comparative Example 8	dimethyl 2-(trimethoxysilyl)ethyl phosphate	1.53	-46.82
Comparative Example 9	diethyl 2-(triethoxysilyl)ethyl phosphate	1.53	-41.35
Comparative Example 10	3-aminopropyl-ethyl-diethoxysilane	1.42	-130.03
Comparative Example 11	tris(trimethylsilyl) phosphate	1.07	-232.07

[0060] For example, with reference to Table 3 below, the A_{eff} value of Example 1 including bis(triethoxysilyl)methane as the silane-based coupling agent may be obtained by dividing 6, which is the number of active sites, by 172.2, which is the molecular weight of a hydrolyzed form, and then multiplying by 96.1.

[Table 3]

	Silane-based coupling agent	Molecular weight (hydrolysis)	Number of active sites
Comparative Example 4	1-[3-(trimethoxysilyl)propyl]urea	181.2	3

Comparative Example 5	1-[3-(triethoxysilyl)propyl]urea	180.2	3
Example 1	bis(triethoxysilyl)methane	172.2	6
Example 3	tetraethyl orthosilicate	96.1	4
Example 4	(triethoxysilyl)methanol	110.1	3
Example 7	(triethoxysilyl)methane	94.1	3

[0061] Based on the experimental results of Examples and Comparative Examples according to the present invention, a new correlation between the A_{eff} value of the silane-based coupling agent and the selective anti-corrosion capability for a multilayer structure including an oxide layer and a nitride layer was derived.

WHAT IS CLAIMED IS:

1. An etchant composition, comprising phosphoric acid, a silane-based coupling agent and water,

wherein the silane-based coupling agent has an A_{eff} value ranging from 2.2 to 4.0, the A_{eff} value being obtained by dividing a number of active sites of the silane-based coupling agent by a molecular weight of a hydrolyzed form of the silane-based coupling agent and then multiplying by 96.1.

2. The etchant composition of claim 1, wherein the A_{eff} value of the silane-based coupling agent falls in a range of 2.2 to 3.0.

3. The etchant composition of claim 1, wherein the silane-based coupling agent is added at a concentration that enables an etching amount (E/A) for oxide layer of the etchant composition to fall in a range of -20 Å to 100 Å.

4. The etchant composition of claim 1, wherein the silane-based coupling agent is at least one selected from the group consisting of tetraethyl orthosilicate, bis(triethoxysilyl)methane, bis(triethoxysilyl)ethane, (triethoxysilyl)methanol, and (triethoxysilyl)methane.

5. The etchant composition of claim 1, wherein the etchant composition selectively etches only a nitride layer from a multilayer structure including an oxide layer and a nitride layer.

6. The etchant composition of claim 5, wherein the oxide layer includes SiO_2 and the nitride layer includes SiN .

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

50 to 95 wt% of phosphoric acid; and

0.01 to 10 wt% of the silane-based coupling agent.

8. A method of selecting a silane-based coupling agent for use in an etchant composition that selectively etches only a nitride layer from a multilayer structure including an oxide layer and a nitride layer, the method comprising:

selecting a silane-based coupling agent having an A_{eff} value ranging from 2.2 to 4.0, the A_{eff} value being obtained by dividing a number of active sites of the silane-based coupling agent by a molecular weight of a hydrolyzed form of the silane-based coupling agent and then multiplying by 96.1.