TITLE OF THE INVENTION

ETCHING COMPOSITION AND METHOD FOR MANUFACTURING SEMICONDUCTOR DEVICE USING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to and the benefit of Korean Patent Application No. 10-2024-0016410 filed on February 2, 2024 and Korean Patent Application No. 10-2025-0013384 filed on February 3, 2025 with the Korean Intellectual Property Office, the entire disclosures of which are incorporated herein by reference.

TECHNICAL FIELD

The present invention relates to an etching composition and a method for manufacturing a semiconductor device using the same, and more particularly, to an etching composition for etching a nitride film and a method for manufacturing a semiconductor device using the same.

BACKGROUND ART

Recently, in accordance with the multifunctionalization of information and communication devices, semiconductor devices including memory devices have been required to have larger capacity and higher integration. With the reduction of memory cell size for higher integration, operation circuits and wiring structures included in a memory device for the operation and electrical connection of the memory device have also become more complicated. In a manufacturing process of a highly down-scaled semiconductor device, an oxide film and a nitride film, which are representative insulating films, may be used alone or alternately stacked, and a selective etching process of the nitride film formed in patterns of various shapes may be required in order to constitute a complicated and miniaturized structure, for example, an electronic device of a three-dimensional structure. In particular, an etching composition is required which can secure a sufficient etching selectivity of the nitride film without causing problems such as the generation of unnecessary particles during the etching process of the nitride film or

a phenomenon in which by-products abnormally grow undesirably on the surface of the oxide film.

In an integrated circuit (semiconductor) device, an oxide film such as a silicon oxide film (SiO2) and a nitride film such as a silicon nitride film (SiNx) are representative insulating films, and each has a structure in which the films are used alone or one or more layers of the films are alternately stacked. Such oxide films and nitride films are also used as hard masks for forming conductive patterns such as metal wirings.

In a wet etching process for removing the nitride film, an etching composition in which phosphoric acid and deionized water are mixed is generally used. At this time, the deionized water is added to prevent a decrease in the etching rate and a change in the etching selectivity with respect to the oxide film; however, there has been a problem in that defects occur due to minute changes in the amount of deionized water when removing the nitride film through the wet etching process, and as a result, there is a limitation in etching the nitride film to a required level.

In addition, recently, in the case of logic semiconductors, forming devices of a three-dimensional stacked structure in a vertical structure in order to increase the degree of integration beyond the planar architecture has been attracting attention, and in this case, a germanium-containing film, such as silicon-germanium (SiGe), is included.

Accordingly, in the case of the etching process of logic semiconductors, an etching composition is required which increases the etching rate of the silicon nitride film while keeping the etching rate of the germanium-containing film low within the process conditions, and in particular, the etching process is in some cases performed at a high temperature in the range of 130°C to 170°C; even in this case, in order to have a high etching selectivity of the nitride film with respect to the germanium-containing film, the selection of an additive material within a predetermined range is a very important task, and research thereon has been continued.

In addition, when an additive material is included in a nitride film etching solution, there has been a problem in that bubbles caused by gases such as H2 are generated in the etching solution itself and adsorbed onto the surface of the silicon wafer, causing a side effect of hindering the selective etching of the nitride film; thus, there has existed a need for additional means for solving this.

SUMMARY OF THE INVENTION

Problems to be Solved

The present invention has been devised to solve the above-described problems, and one embodiment of the present invention provides an etching composition capable of securing a sufficient etching selectivity of a nitride film with respect to a germanium-containing film without causing problems such as the generation of bubbles in the etching solution.

In addition, another embodiment of the present invention provides a method for manufacturing a semiconductor device capable of securing a sufficient etching selectivity of a nitride film with respect to a germanium-containing film optimized in a predetermined temperature range while etching nitride films of various shapes for realizing a complicated and miniaturized electronic device, in particular an electronic device having a three-dimensional stacked structure, thereby securing the stability and reliability of the nitride film etching process and improving the productivity of the semiconductor device manufacturing process.

In addition, another embodiment of the present invention provides a method for manufacturing an integrated circuit device.

In addition, another embodiment of the present invention provides an integrated circuit device.

The technical problems to be achieved by the present invention are not limited to the technical problems mentioned above, and other technical problems not mentioned will be clearly

understood by those of ordinary skill in the art to which the present invention pertains from the description below.

Means for Solving the Problems

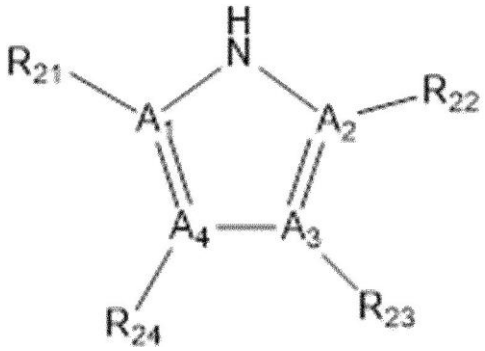
As a technical means for achieving the above-described technical problems, one aspect of the present invention

provides an etching composition comprising: an inorganic acid; a first etching inhibitor; and a remaining amount of a solvent, wherein the first etching inhibitor contains at least two nitrogen atoms and includes a heterocyclic ring structure containing at least one nitrogen atom.

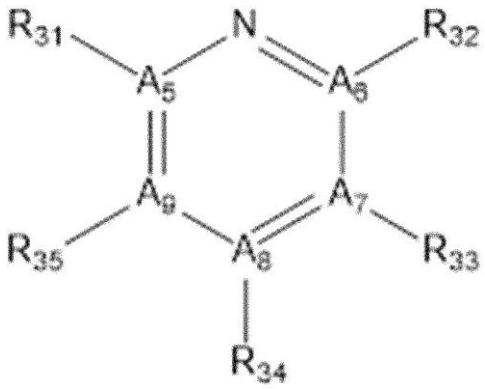
A second etching inhibitor may be further included, the first etching inhibitor may inhibit the etching of a germanium-containing film, and the second etching inhibitor may inhibit the etching of a silicon oxide film.

The first etching inhibitor may be represented by the following Chemical Formula 1 or Chemical Formula 2.

[Chemical Formula 1]



[Chemical Formula 2]

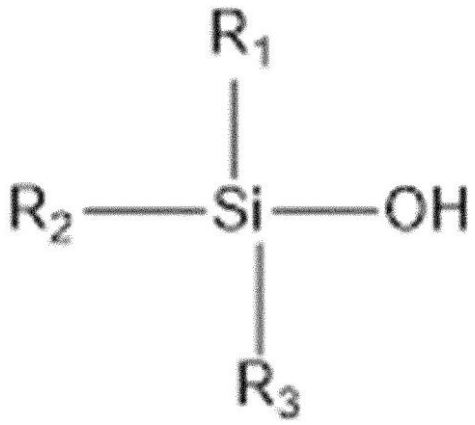


In Chemical Formula 1 or Chemical Formula 2, A1 to A9 are each independently carbon or nitrogen, and R21 to R24 and R31 to R35 are each independently any one selected from the group consisting of hydrogen, halogen, an amino group, an amide group, a hydroxy group, a thiol group (-SH or =S), -NO2, -NHCOR41 (R41 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), -CONHR42 (R42 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), -OCOR43 (R43 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms, a substituted or unsubstituted aminoalkyl group having 1 to 10 carbon atoms, a substituted or unsubstituted alkylamino group having 1 to 10 carbon atoms, and a substituted or unsubstituted heteroaryl group having 5 to 20 carbon atoms; in Chemical Formula 1, when A1 to A4 are all carbon, at least one of R21 to R24 is an amino group, an amide group, -NO2, -NHCOR51 (R51 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), -CONHR52 (R52 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), a substituted or unsubstituted aminoalkyl group having 1 to 10 carbon atoms, or a substituted or unsubstituted alkylamino group having 1 to 10 carbon atoms; or, in Chemical Formula 2, when A5 to A9 are all carbon, at least one of R31 to R35 may be an amino group, an amide group, -NO2, -NHCOR61 (R61 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), -CONHR62 (R62 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), a substituted or unsubstituted aminoalkyl group having 1 to 10 carbon atoms, or a substituted or unsubstituted alkylamino group having 1 to 10 carbon atoms.

The first etching inhibitor may be nicotinamide, pyrimidine, or imidazole.

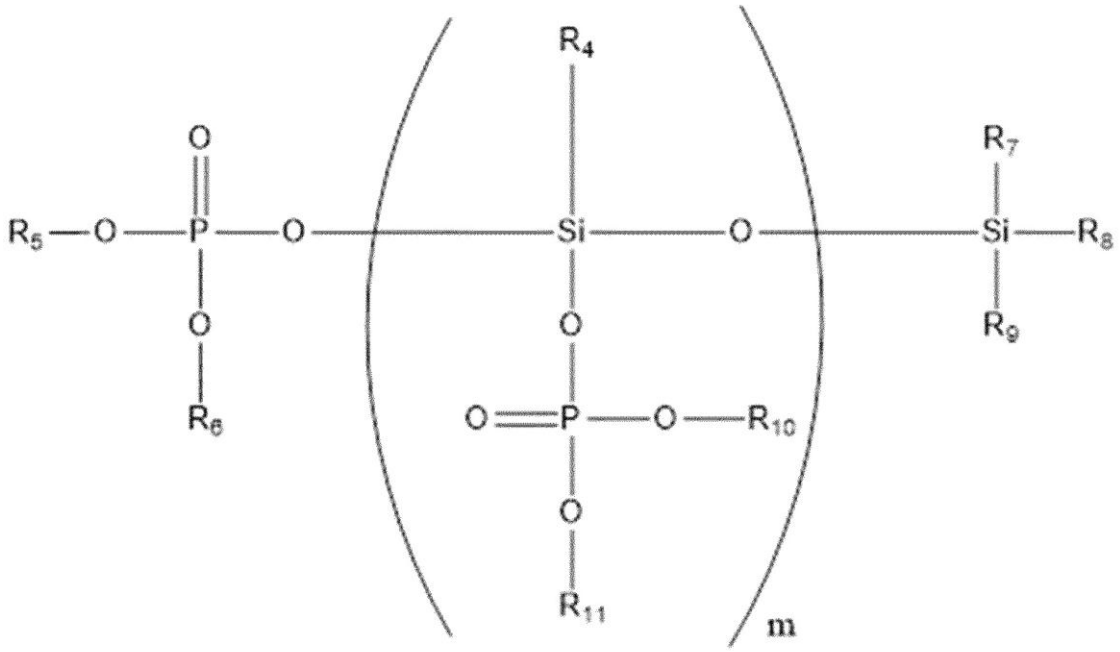
The second etching inhibitor may be represented by any one of Chemical Formulae 3 to 5 below.

[Chemical Formula 3]



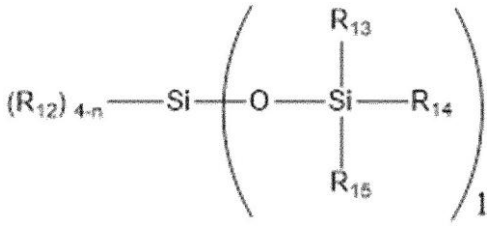
In Chemical Formula 3, R1 is selected from the group consisting of a substituted or unsubstituted aminoalkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted acetyloxy group, and a substituted or unsubstituted haloalkylacetyloxy group having 1 to 20 carbon atoms, and R2 and R3 may be hydroxy groups.

[Chemical Formula 4]



In Chemical Formula 4, R4 is selected from the group consisting of hydrogen, OH, a substituted or unsubstituted alkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted alkenyl group having 1 to 20 carbon atoms, a substituted or unsubstituted cycloalkyl group having 3 to 20 carbon atoms, a substituted or unsubstituted aminoalkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted amino(C1-C10)alkylamino(C1-C10)alkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted aryl group having 6 to 20 carbon atoms, a substituted or unsubstituted alkylcarbonyl group having 1 to 20 carbon atoms, a substituted or unsubstituted alkylcarbonyloxy group having 1 to 20 carbon atoms, and a cyano(C1-C10)alkyl group; R5 to R11 are each independently selected from the group consisting of hydrogen, OH, a substituted or unsubstituted alkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted alkenyl group having 2 to 20 carbon atoms, a substituted or unsubstituted cycloalkyl group having 3 to 20 carbon atoms, a substituted or unsubstituted aminoalkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted amino(C1-C10)alkylamino(C1-C10)alkyl group, a substituted or unsubstituted aryl group having 6 to 20 carbon atoms, a substituted or unsubstituted alkylcarbonyl group having 1 to 20 carbon atoms, a substituted or unsubstituted alkylcarbonyloxy group having 1 to 20 carbon atoms, and a cyano(C1-C10)alkyl group; m is an integer of 1 to 10; and when m is 2 or more, the plurality of respective R4, R10, and R11 may all be the same, or at least some of them may be different.

[Chemical Formula 5]



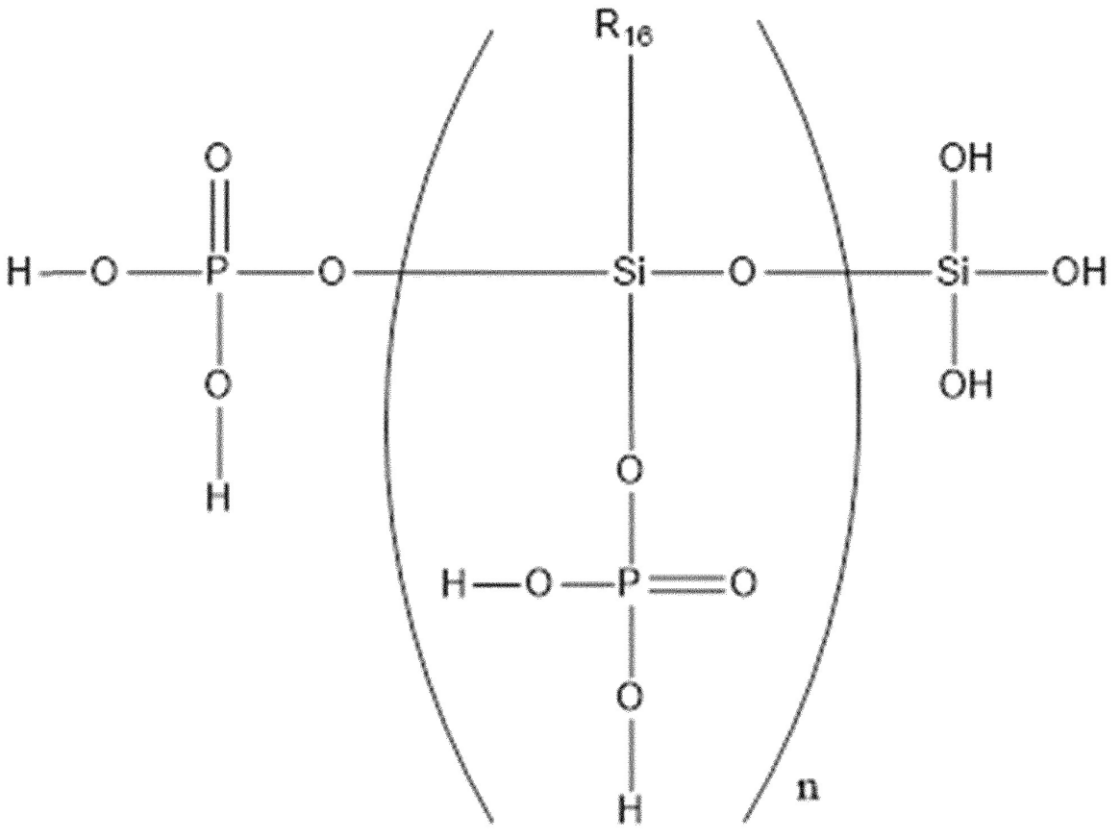
In Chemical Formula 5, R12 is hydrogen, an alkyl group, an aminoalkyl group, or an aminoalkoxy group; at least one of

R13, R14, and R15 is an aminoalkyl group or an aminoalkoxy group; and l may be 2 or 3.

The second etching inhibitor may be represented by Chemical Formula 4, and in Chemical Formula 4, R4 may be selected from the group consisting of a substituted or unsubstituted alkyl group having 1 to 3 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 3 carbon atoms, a substituted or unsubstituted alkenyl group having 1 to 3 carbon atoms, and a substituted or unsubstituted aminoalkyl group having 1 to 4 carbon atoms; R5, R6, R10, and R11 may each independently be selected from the group consisting of hydrogen, a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms, and a substituted or unsubstituted aminoalkyl group having 1 to 5 carbon atoms; R7 to R9 may each independently be selected from the group consisting of hydrogen, OH, a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms, and a substituted or unsubstituted aminoalkyl group having 1 to 5 carbon atoms; and m may be an integer of 1 to 5.

The second etching inhibitor may be represented by the following Chemical Formula 6:

[Chemical Formula 6]



In Chemical Formula 6, R16 is a methyl group, an ethyl group, or a propyl group; n is an integer of 1 to 5; and when n is 2 or more, the plurality of R16 may all be the same, or at least some of them may be different.

The etching composition may comprise, with respect to the entire etching composition, 7 to 85 wt% of the inorganic acid, 0.1 to 10 wt% of the first etching inhibitor, 0.1 to 10 wt% of the second etching inhibitor, and the remaining content of the solvent.

With respect to the total weight of the etching composition, the first etching inhibitor may be more than 0.1 wt% and 2 wt% or less.

With respect to the total weight of the etching composition, the second etching inhibitor may be more than 0.1 wt% and 3 wt% or less.

The inorganic acid may include at least one selected from the group consisting of sulfuric acid, nitric acid, phosphoric acid, silicic acid, hydrofluoric acid, boric acid, hydrochloric acid, and perchloric acid.

The etching composition may further include an ammonium-based compound.

The ammonium-based compound may include at least one of ammonium chloride, ammonium phosphate, ammonium acetate, ammonium sulfate, ammonium formate, and a metal ammine complex salt.

The etching composition may be characterized in that the etching selectivity of the silicon nitride film/germanium-containing material film of the etching composition is 50 or more.

The etching composition may be characterized in that the bubble height on the surface immediately after the preparation of the etching composition is 0.9 cm or less.

The etching composition may, with respect to an integrated circuit device including a silicon oxide film, a silicon nitride film, and a germanium-containing film, inhibit the

etching of the germanium-containing film and etch the silicon oxide film and the silicon nitride film.

The etching composition may, with respect to an integrated circuit device including a silicon oxide film, a silicon nitride film, and a germanium-containing film, inhibit the etching of the germanium-containing film and the silicon oxide film and etch the silicon nitride film.

Another aspect of the present invention

provides a method for manufacturing an integrated circuit device, comprising: a step of forming a structure by stacking a plurality of insulating films and a plurality of sacrificial films on a substrate; and a step of performing an etching process using the etching composition to remove the sacrificial films to form space regions.

The sacrificial films may include silicon nitride, and the insulating films may include a germanium-containing material or silicon oxide.

In the etching process, the sacrificial films may be characterized as having a higher etching rate than the insulating films.

In the step of performing the etching process to remove the sacrificial films to form the space regions, the space regions may be characterized as including gate regions formed between the insulating films and trenches connected to the gate regions.

The method may further comprise: forming openings penetrating the stack structure; and forming, in the openings, integrated circuit patterns spaced apart from the trenches, and the forming of the integrated circuit patterns may be performed before the forming of the trenches.

Another aspect of the present invention

provides an integrated circuit device comprising: a structure formed by stacking an insulating film and a sacrificial film; a space portion formed in the structure by the sacrificial film being etched by an etching composition; and a deposition

portion formed by depositing a conductive material or an insulating material in the space portion, wherein the etching composition comprises an inorganic acid, a first etching inhibitor, a second etching inhibitor, and a remaining amount of a solvent, and the first etching inhibitor contains at least two nitrogen atoms and includes a heterocyclic ring structure containing at least one nitrogen atom.

Effects of the Invention

According to one embodiment of the present invention, since the etching selectivity of the nitride film is high and the etching rate of the germanium-containing film is controlled, the effective oxide film height (EFH) can be easily controlled. In addition, the etching composition of the present invention prevents damage to the film quality of the germanium-containing film, deterioration of electrical characteristics due to the etching of the germanium-containing film, and generation of particles when removing the nitride film, thereby improving the reliability of the semiconductor device.

In addition, when etching the nitride film, even in the case where the nitride film and the germanium-containing film or the oxide film are alternately stacked or mixed, only the nitride film can be selectively etched with a relatively high etching selectivity between the nitride film and the germanium-containing film or the oxide film. Accordingly, while etching the nitride film formed in patterns of various shapes in order to constitute an electronic device having a complicated and miniaturized structure, a sufficient etching selectivity of the nitride film with respect to the oxide film or the germanium-containing film can be secured without causing the above-described problems, so that the stability and reliability of the nitride film etching process can be secured, and by preventing damage to the germanium-containing film or the oxide film exposed to the etching composition together with the nitride film, or deterioration of the electrical characteristics of the germanium-containing film or the oxide film, the productivity of the semiconductor device manufacturing process can be improved and the reliability of the semiconductor device can be improved.

Accordingly, the etching composition of the present invention can be usefully used in manufacturing processes of semiconductor devices in which the selective removal of a nitride film with respect to a germanium-containing film or an oxide film is required (for example, a fine etching process of devices such as logic semiconductor devices and image sensors, a device isolation process of flash memory devices, a pipe channel formation process of 3D flash memory devices, a diode formation process of phase-change memories, and the like), thereby contributing to improving the efficiency of the manufacturing process of semiconductor devices.

In addition, by containing an additive material capable of obtaining both the characteristics of improving the etching selectivity of the etching solution and exhibiting an optimized effect in a predetermined temperature range, an etching composition with high process utility can be provided.

In addition, the generation of bubbles caused by gases such as H2 that may occur during the process in the etching solution itself, and the phenomenon in which such bubbles are adsorbed onto the surface of the silicon wafer and hinder the selective etching of the nitride film, can be suppressed.

The effects of the present invention are not limited to the above-described effects, and should be understood to include all effects that can be inferred from the configuration of the invention described in the detailed description or the claims of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a plan view of a semiconductor device according to embodiments of the present invention.

FIGS. 2 to 8 are drawings for explaining a method for manufacturing a semiconductor device according to embodiments of the present invention.

FIG. 9 is an enlarged view of region A of FIG. 8.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Hereinafter, the present invention will be described in more detail. However, the present invention may be implemented in various different forms, and the present invention is not limited by the embodiments described herein, and the present invention is defined only by the claims to be described later.

In addition, the terms used in the present invention are used merely to describe specific embodiments and are not intended to limit the present invention. Singular expressions include plural expressions unless the context clearly indicates otherwise. Throughout the specification of the present invention, when a certain component is said to 'include' another component, this means that it does not exclude other components but may further include other components, unless specifically stated to the contrary.

As used herein, "silicon nitride film", "silicon nitride", and "SixNy" correspond not only to pure silicon nitride but also to impure silicon nitride containing hydrogen, carbon, and/or oxygen impurities in the crystal structure (where x and y are each independently a positive integer).

As used herein, "silicon oxide film" and "silicon oxide" mean a thin film made of silicon oxide (SiOx), for example, SiO2, "thermal oxide" (ThOx), and the like. Silicon oxide may be disposed on a substrate by any method, such as deposition through chemical vapor deposition from TEOS or another source, or thermal deposition. Silicon oxide may generally contain commercially useful low levels of other materials or impurities. Silicon oxide may be present as a feature of a microelectronic device as a part of the microelectronic device, for example, as an insulating layer.

As used herein, "at least partial removal of silicon nitride material" corresponds to the removal of at least a part of an exposed silicon nitride layer. For example, the partial removal of a silicon nitride film includes the anisotropic removal of a silicon nitride film (for example, an Si3N4 film) covering/protecting a gate electrode. It may be considered that the composition of the present invention can be used more generally to substantially remove silicon nitride relative to polysilicon and/or a silicon oxide film. In this context, "substantial removal" is defined as at least 90% in

one embodiment of the present invention and at least 95% in another embodiment, and in yet another embodiment, it may mean that at least 99% of the silicon nitride material is removed using the composition of the present invention.

In the present specification, "substituted or unsubstituted" may mean substituted or unsubstituted with one or more substituents selected from the group consisting of a hydrogen atom, a deuterium atom, a halogen atom, a cyano group, a nitro group, an amino group, a silyl group, a boron group, a phosphine oxide group, a phosphine sulfide group, a carboxyl group, an alkyl group, an alkenyl group, an aryl group, and a heterocyclic group. In detail, "substituted or unsubstituted" may mean substituted or unsubstituted with one or more substituents selected from the group consisting of a hydrogen atom, a deuterium atom, an alkyl group, an amino group, a silyl group, and an alkoxy group. In addition, each of the substituents exemplified above may be substituted or unsubstituted. For example, a methylamino group and an aminoalkylamino group may be interpreted as an amino group.

In the present specification, examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom.

In the present specification, the alkyl group may be a linear alkyl group, a branched alkyl group, or a cyclic alkyl group. The alkyl group may be a linear alkyl group, a branched alkyl group, or a cyclic alkyl group. Examples of the alkyl group include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, a t-butyl group, an i-butyl group, a 2-ethylbutyl group, a 3,3-dimethylbutyl group, an n-pentyl group, an i-pentyl group, a neopentyl group, a t-pentyl group, a cyclopentyl group, a 1-methylpentyl group, a 3-methylpentyl group, a 2-ethylpentyl group, a 4-methyl-2-pentyl group, an n-hexyl group, a 1-methylhexyl group, a 2-ethylhexyl group, a 2-butylhexyl group, a cyclohexyl group, a 4-methylcyclohexyl group, a 4-t-butylcyclohexyl group, an n-heptyl group, a 1-methylheptyl group, a 2,2-dimethylheptyl group, a 2-ethylheptyl group, a 2-butylheptyl group, an n-octyl group, a t-octyl group, a 2-ethyloctyl group, a 2-butyloctyl group, a 2-hexyloctyl group, a 3,7-dimethyloctyl

group, a cyclooctyl group, an n-nonyl group, and an n-decyl group, but are not limited thereto.

For example, the term "C1-C20 alkyl group" used in the specification refers to a linear or branched noncyclic saturated aliphatic hydrocarbon group having 1 to 20 carbon atoms. The term "C2-C20 alkenyl group" refers to a linear or branched noncyclic unsaturated aliphatic hydrocarbon group having 2 to 20 carbon atoms and having one or more double bonds between adjacent carbon atoms. The term "C2-C20 alkynyl group" may refer to a linear or branched noncyclic unsaturated aliphatic hydrocarbon group having 2 to 20 carbon atoms and having one or more triple bonds between adjacent carbon atoms. The term "C1-C20 alkoxy group" may refer to a linear or branched noncyclic saturated or unsaturated aliphatic hydrocarbon group having one or more ether groups and 1 to 20 carbon atoms.

In the present specification, the amino group may include an alkylamino group and an arylamino group. Examples of the amino group include a methylamino group, an ethylamino group, a dimethylamino group, a diethylamino group, and/or an ethylmethylamino group, but are not limited thereto.

In the present specification, the alkoxy group may include an alkyl alkoxy group and an aryl alkoxy group. Examples of the alkoxy group include a methoxy group, an ethoxy group, a propoxy group, a butoxy group, a pentoxy group, a hexyloxy group, a heptyloxy group, an octyloxy group, a nonyloxy group, and a decyloxy group, but are not limited thereto.

Unless otherwise stated, “%” used in the present specification may mean “% by weight” or “wt%” in terms of content.

Hereinafter, embodiments of the present invention will be described in detail so that those of ordinary skill in the art to which the present invention pertains can easily carry them out. However, the present invention may be implemented in various different forms and is not limited to the embodiments described herein.

Examples 1 to 6 and Comparative Examples 1 to 10. Preparation of etching compositions

As the compounds contained in the additives, the etching compositions were prepared by adding the first etching inhibitor according to the type and content shown in Table 1 below, and varying the type and content range of R16 of the second etching inhibitor represented by Chemical Formula 6 according to Table 1 below (n in Chemical Formula 6 was 1), with the balance being phosphoric acid.

[Table 1]

	Inorganic acid (type/content)		First etching inhibitor (germanium-containing film etching inhibitor)		Second etching inhibitor (silicon-based oxide film etching inhibitor)	
	85 wt% phosphoric acid aqueous solution	Content (wt%)	Type	Content (wt%)	Type (type of substituent of R16)	Content (wt%)
Example 1	Phosphoric acid	Balance	Nicotinamide	0.3	Methyl	0.3
Example 2	Phosphoric acid	Balance	Pyrimidine	0.5	Ethyl	0.5
Example 3	Phosphoric acid	Balance	Imidazole	0.8	Propyl	1
Example 4	Phosphoric acid	Balance	Nicotinamide	1	Methyl	2
Example 5	Phosphoric acid	Balance	Pyrimidine	1	Ethyl	3
Example 6	Phosphoric acid	Balance	Imidazole	2	Propyl	1
Comparative Example 1	Phosphoric acid	Balance	Nicotinamide	0.1	Methyl	0.3
Comparative Example 2	Phosphoric acid	Balance	Nicotinamide	3	Methyl	0.3
Comparative Example 3	Phosphoric acid	Balance	Pyrimidine	0.1	Ethyl	0.5
Comparative Example 4	Phosphoric acid	Balance	Pyrimidine	2.5	Ethyl	0.5
Comparative Example 5	Phosphoric acid	Balance	Nicotinamide	0.3	butyl	0.3

Comparative Example 6	Phosphoric acid	Balance	Pyrimidine	0.5	octyl	0.5
Comparative Example 7	Phosphoric acid	Balance	Imidazole	0.8	TEOS	1
Comparative Example 8	Phosphoric acid	Balance	1,3-diaminopropane	0.3	Methyl	0.3
Comparative Example 9	Phosphoric acid	Balance	Propylamine	0.5	Ethyl	0.5
Comparative Example 10	Phosphoric acid	Balance	4-methylpiperidine	0.8	Propyl	1

Experimental Example 1: Analysis of the bubble generation level of the etching compositions

The degree of bubble generation was checked using the Bubble Pour Method. The flow was carried out with N2 [0.5 L/min], and immediately after the preparation of the etching composition, it was placed in a container, the height of the bubbles was measured (cm), and then, after 60 seconds had elapsed, the height of the bubbles after defoaming had proceeded was measured, thereby evaluating the defoaming characteristics. The results are shown in Table 2 below.

[Table 2]

Category	Bubble height (cm)
Example 1	0.5
Example 2	0.6
Example 3	0.5
Example 4	0.6
Example 5	0.6
Example 6	0.7
Comparative Example 1	0.5
Comparative Example 2	10
Comparative Example 3	0.5

Comparative Example 4	3.8
Comparative Example 5	6
Comparative Example 6	15
Comparative Example 7	8
Comparative Example 8	5
Comparative Example 9	15
Comparative Example 10	12

According to Table 2, it could be confirmed that the etching compositions according to the Examples of the present invention formed bubbles at a low level, with a bubble height of less than 1.0 cm immediately after the formation of the composition. On the other hand, in the case of the Comparative Example compounds, the bubbles immediately after the preparation of the etching composition formed a high bubble layer, and it could be confirmed that the manner in which they were removed over time was also very slow. In the case of Comparative Examples 1 and 3, the bubble generation itself can be seen to appear at a level similar to that of the Examples, but reconsideration may be necessary in terms of basic performance. As described above and as will be described later regarding the etching selectivity and the like, such bubbles can be a factor that lowers the efficiency of the entire etching process; therefore, the etching composition according to one embodiment of the present application can be regarded as an invention that solves this problem by including the second etching inhibitor compound. This bubble removal effect is such that, by controlling the interfacial tension, the foam liquid has a relatively lower surface tension than the single layer in which it was generated, so that the foam easily spreads to the surroundings and becomes thinner, and it could be confirmed that the generation of bubbles is suppressed in the liquid itself. For this reason, it could be confirmed that, by suppressing the generation of bubbles in this way, the etching composition can remove the factors that hinder the etching of the nitride film.

Experimental Example 2. Measurement of etching rate and selectivity

Using the etching compositions prepared in each of the Examples and Comparative Examples, etching was performed on the nitride film and the oxide film at a process temperature of 165°C. The etching rates for the nitride film, the oxide film, the doped silicon film (doped-Si), and the silicon-germanium (SiGe) film were measured using an ellipsometer (NANO VIEW, SEMG-1000), which is a thin-film thickness measurement instrument, and are shown in Table 3 below. Specifically, the etching rates in Table 3 below are values calculated by etching each film for 300 seconds and then dividing the difference between the film thickness before the etching treatment and the film thickness after the etching treatment of each film by the etching time (minutes).

[Table 3]

	SiN etching rate (Å/min)	Oxide film etching rate (Å/min)	Nitride film/oxide film	SiGe etching rate (Å/min)	Nitride film/SiGe film	doped Si etching rate (Å/min)	Nitride film/doped Si film
Example 1	39.2	0.15	261.33	0.66	59.39	1.16	33.79
Example 2	37.9	0.12	315.83	0.6	63.17	1.03	36.80
Example 3	39	0.1	390.00	0.55	70.91	0.8	48.75
Example 4	39.4	0.08	492.50	0.5	78.80	0.72	54.72
Example 5	38.5	0.05	770.00	0.43	89.53	0.74	52.03
Example 6	39.1	0.09	434.44	0.62	63.06	0.43	90.93
Comparative Example 1	39	0.15	260.00	1.58	24.68	1.97	19.80
Comparative Example 2	38.7	0.13	297.69	0.58	66.72	0.85	45.53
Comparative Example 3	39.4	0.11	358.18	1.32	29.85	2.01	19.60

Comparative Example 4	41.8	0.12	348.33	0.55	76.00	0.67	62.39
Comparative Example 5	42.6	0.1	426.00	0.56	76.07	0.88	48.41
Comparative Example 6	43.1	0.12	359.17	0.6	71.83	0.74	58.24
Comparative Example 7	41.2	0.25	164.80	1.03	40.00	2.58	15.97
Comparative Example 8	40.6	0.16	253.75	2.56	15.86	9.86	4.12
Comparative Example 9	39.8	0.12	331.67	1.78	22.36	5.51	7.22
Comparative Example 10	39.5	0.09	438.89	1.32	29.92	3.14	12.58

According to Table 3 above, it can be confirmed that the nitride film:oxide film etching rate selectivities of the Examples corresponding to the etching composition of the present invention are at a relatively high level, but generally at a level similar to that of the Comparative Examples.

Specifically, compared with the Examples, in the case of Comparative Examples 1 and 3, in which the content of the first etching inhibitor was insufficient, it could be confirmed that the etching rate of the germanium film was not sufficiently suppressed, and accordingly, it can be seen that the nitride film/germanium film selectivity appeared to be less than 30. On the other hand, in the case of Comparative Examples 2 and 4, in which the content of the first etching inhibitor was relatively excessive, the overall selectivity aspect shows a level generally similar to that of the Examples when compared with the Examples, but as described above, it

has been confirmed that there is a process-impairing factor due to bubble formation.

In addition, in the case of the Example compositions satisfying the structure of the second etching inhibitor, it could be confirmed that the etching selectivities of the nitride film with respect to the oxide film, the germanium film, and the doped silicon film all appeared high. In addition, as described above, it has been confirmed that the generation of bubbles immediately after the preparation of the etching composition can also be suppressed.

Looking in more detail, in the case of Comparative Examples 5 and 6, as the number of carbon atoms of the alkyl group of Chemical Formula 6 exceeded 3, it was confirmed in Experimental Example 1 that the effect of suppressing bubble generation was impaired, and therefore it could be confirmed that there was a problem in processability. In addition, in the case of Comparative Example 7, the basic structure of the second etching inhibitor compound is different, and its effect differed from that of the Examples in that a sufficient nitride film/oxide film etching selectivity did not appear.

Meanwhile, as in Comparative Examples 8 to 10, when the type of the first etching inhibitor was different from the scope of the present invention, it was confirmed that a sufficient nitride film/germanium film selectivity was not secured, and as confirmed in Experimental Example 1, it was found that the bubble height was formed high immediately after the preparation of the etching composition, including a factor that hinders the process.

Hereinafter, before describing the first aspect of the present invention, the concept of the etching composition will be described.

The etching composition may be used for etching a silicon-containing material. For example, the etching composition may be used for etching a silicon nitride film, a germanium-containing film, or a silicon oxide film, which are insulating films. The etching of a silicon nitride film using the etching composition may proceed as in Reaction Scheme 1 below. The etching of a silicon oxide film using the silicon composition

may proceed as in Reaction Scheme 2 below. The etching of a germanium-containing film may include oxidizing silicon-germanium to form a semiconductor oxide, reacting the semiconductor oxide to form a water-soluble product, and removing the water-soluble product.

However, in the etching process using the etching composition, the etching rate of the silicon nitride film, which is the first insulating film, may be greater than the etching rates of the silicon oxide film, which is the second insulating film, and the germanium-containing film, which is the third insulating film. In the present specification, that a silicon nitride film is etched means that silicon nitride is removed, and that a silicon oxide film or a germanium-containing film is etched may mean that silicon oxide or a germanium-containing material is removed. Silicon nitride may be represented by SixNy. An oxide film may include silicon oxide (SixOy) or germanium oxide (for example, GeOy). (Here, x and y may each be an independent positive rational number. For example, x may be 2 and y may be 2.) The germanium-containing material may include silicon-germanium (SiGe).

[Reaction Scheme 1]

$$3Si_3N_4 + 4H_3PO_4 + 27H_2O \rightarrow 4(NH_4)_3PO_4 + 9SiO_2H_2O$$

[Reaction Scheme 2]

$$SiO_2 + 4H^+ + 4e^- \rightarrow Si + 2H_2O$$

Referring to Reaction Scheme 1 above, phosphoric acid may react with silicon nitride to remove the silicon nitride. At this time, the composition ratio of phosphoric acid as the inorganic acid may be 70 to 99 parts by weight. In the present specification, the composition ratio means the composition ratio with respect to the composition. When phosphoric acid is less than 70 parts by weight of the etching composition, it may be difficult for the silicon nitride film to be easily removed. Or, in the etching process, etching by-products may be formed. In one embodiment of the present application, the composition ratio of phosphoric acid may mean the composition ratio of an 85% phosphoric acid aqueous solution. That is, that the composition ratio of phosphoric acid is 65% may mean

that the 85% phosphoric acid aqueous solution is 65% of the etching composition.

Referring to Reaction Scheme 2, phosphoric acid may provide hydrogen ions and react with silicon oxide. When phosphoric acid exceeds 99 parts by weight of the etching composition, the reaction rate between phosphoric acid and silicon oxide may increase. Accordingly, in the etching process, it may be difficult for the silicon nitride film to have a sufficiently high etching selectivity with respect to the silicon oxide film.

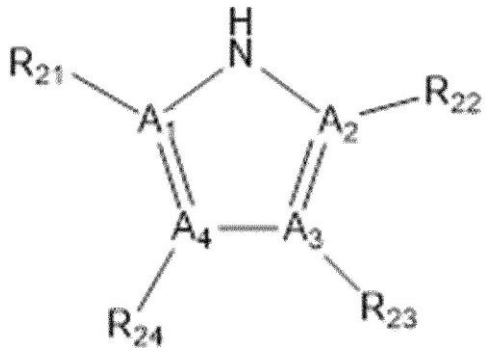
Hereinafter, the etching composition according to the first aspect of the present application will be described in detail.

The first aspect of the present application

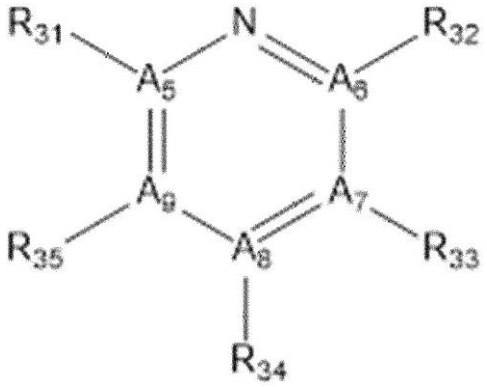
provides an etching composition comprising: an inorganic acid; a first etching inhibitor; and a remaining amount of a solvent, wherein the first etching inhibitor contains at least two nitrogen atoms and includes a heterocyclic ring structure containing at least one nitrogen atom.

In one embodiment of the present application, the first etching inhibitor may be represented by the following Chemical Formula 1 or Chemical Formula 2.

[Chemical Formula 1]



[Chemical Formula 2]



In Chemical Formula 1 or Chemical Formula 2, A1 to A9 are each independently carbon or nitrogen, and R21 to R24 and R31 to R35 are each independently any one selected from the group consisting of hydrogen, halogen, an amino group, an amide group, a hydroxy group, a thiol group (-SH or =S), -NO2, -NHCOR41 (R41 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), -CONHR42 (R42 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), -OCOR43 (R43 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms, a substituted or unsubstituted aminoalkyl group having 1 to 10 carbon atoms, a substituted or unsubstituted alkylamino group having 1 to 10 carbon atoms, and a substituted or unsubstituted heteroaryl group having 5 to 20 carbon atoms; in Chemical Formula 1, when A1 to A4 are all carbon, at least one of R21 to R24 is an amino group, an amide group, -NO2, -NHCOR51 (R51 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), -CONHR52 (R52 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), a substituted or unsubstituted aminoalkyl group having 1 to 10 carbon atoms, or a substituted or unsubstituted alkylamino group having 1 to 10 carbon atoms; or, in Chemical Formula 2, when A5 to A9 are all carbon, at least one of R31 to R35 may be an amino group, an amide group, -NO2, -NHCOR61 (R61 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), -CONHR62 (R62 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), a substituted or unsubstituted aminoalkyl group having 1 to 10

carbon atoms, or a substituted or unsubstituted alkylamino group having 1 to 10 carbon atoms.

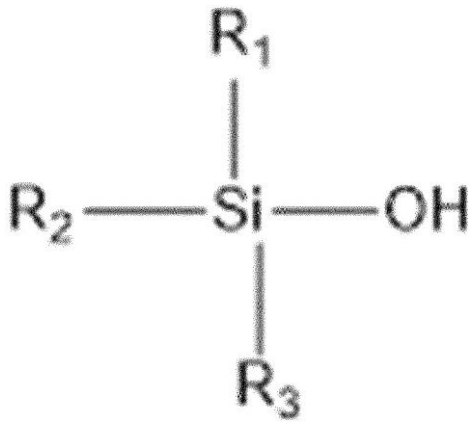
In one embodiment of the present application, preferably, the first etching inhibitor may be nicotinamide, pyrimidine, or imidazole.

In one embodiment of the present application, the first etching inhibitor may serve as an etching inhibitor for the germanium-containing film. For example, the first etching inhibitor may increase the etching selectivity of the silicon nitride film with respect to the germanium-containing film. The first etching inhibitor may be adsorbed onto germanium oxide formed during the etching process. Since the germanium oxide onto which the first etching inhibitor has been adsorbed can serve as a passivation film, the first etching inhibitor can accordingly inhibit the removal of the germanium oxide.

In one embodiment of the present application, the first etching inhibitor may be, with respect to the total weight of the etching composition, 0.01 wt% to 15 wt%, preferably 0.1 wt% to 10 wt%, and more preferably more than 0.1 and 2 wt% or less. When the content of the first etching inhibitor is less than the above-described range, the amine compound may be insufficient to adsorb the germanium oxide and further to inhibit the etching of the germanium-containing film. When the content of the first etching inhibitor exceeds the above-described range, the etching rate of the silicon oxide film may unnecessarily increase, or the etching rates of the nitride film, the oxide film, and the germanium-containing film may all decrease as a whole, and above all, it may become impossible to suppress the generation of bubbles occurring immediately after the preparation of the etching composition.

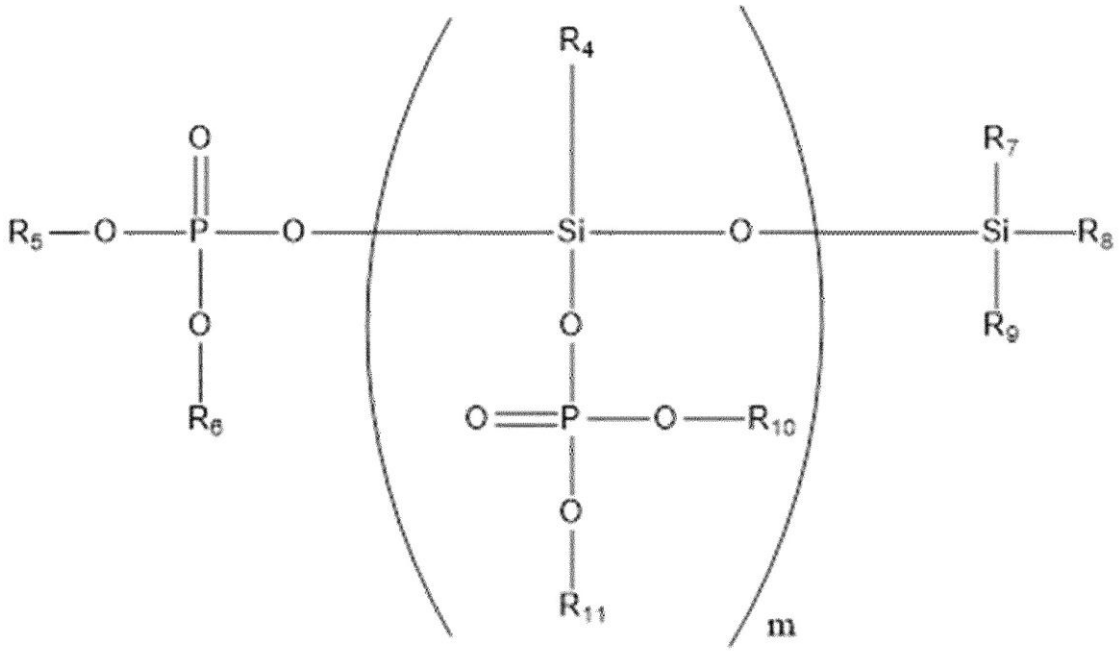
In one embodiment of the present application, a second etching inhibitor may be further included. The second etching inhibitor may be represented by any one of Chemical Formulae 3 to 5 below.

[Chemical Formula 3]



In Chemical Formula 3, R1 is selected from the group consisting of a substituted or unsubstituted aminoalkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted acetyloxy group, and a substituted or unsubstituted haloalkylacetyloxy group having 1 to 20 carbon atoms, and R2 and R3 may be hydroxy groups.

[Chemical Formula 4]



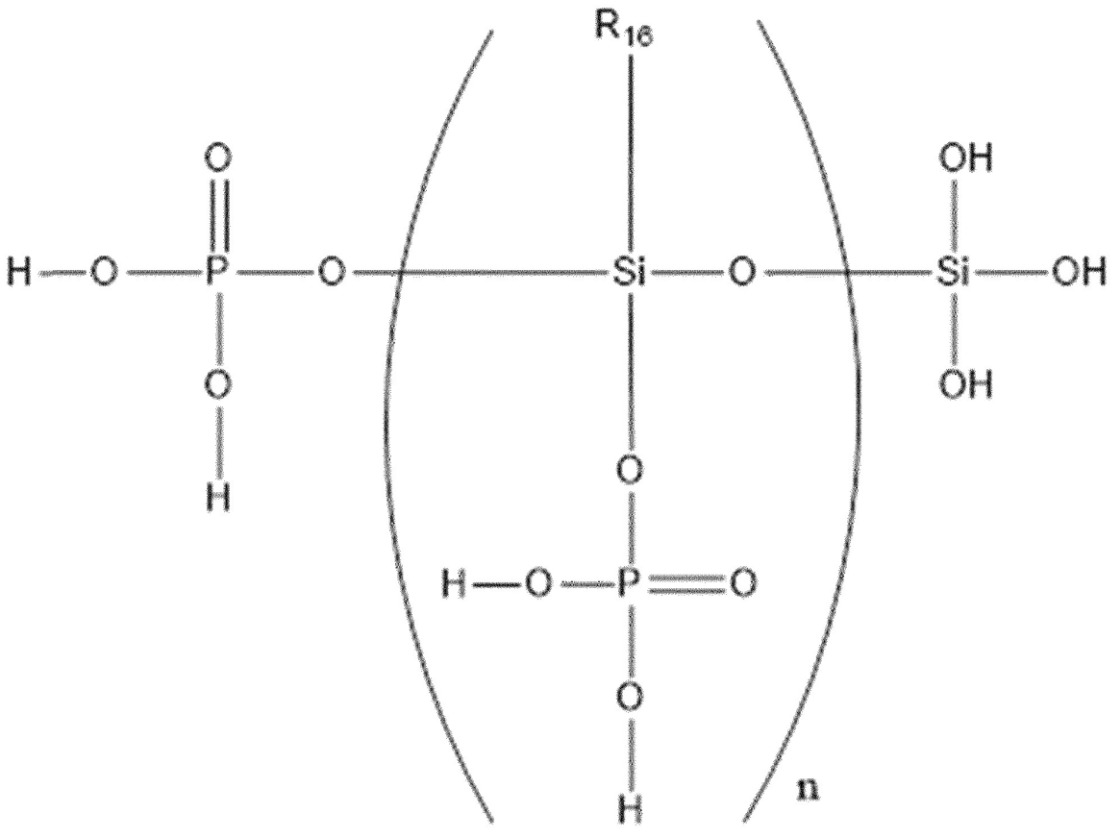
In Chemical Formula 4, R4 is selected from the group consisting of hydrogen, OH, a substituted or unsubstituted alkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted alkenyl group having 1 to 20 carbon atoms, a substituted or unsubstituted cycloalkyl group having 3 to 20 carbon atoms, a substituted or unsubstituted aminoalkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted amino(C1-C10)alkylamino(C1-C10)alkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted aryl group having 6 to 20 carbon atoms, a substituted or unsubstituted alkylcarbonyl group having 1 to 20 carbon atoms, a substituted or unsubstituted alkylcarbonyloxy group having 1 to 20 carbon atoms, and a cyano(C1-C10)alkyl group; R5 to R11 are each independently selected from the group consisting of hydrogen, OH, a substituted or unsubstituted alkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted alkenyl group having 2 to 20 carbon atoms, a substituted or unsubstituted cycloalkyl group having 3 to 20 carbon atoms, a substituted or unsubstituted aminoalkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted amino(C1-C10)alkylamino(C1-C10)alkyl group, a substituted or unsubstituted aryl group having 6 to 20 carbon atoms, a substituted or unsubstituted alkylcarbonyl group having 1 to 20 carbon atoms, a substituted or unsubstituted alkylcarbonyloxy group having 1 to 20 carbon atoms, and a cyano(C1-C10)alkyl group; m is an integer of 1 to 10; and when m is 2 or more, the plurality of respective R4, R10, and R11 may all be the same, or at least some of them may be different.

Preferably, the second etching inhibitor is represented by Chemical Formula 4, and in Chemical Formula 4, R4 is selected from the group consisting of a substituted or unsubstituted alkyl group having 1 to 3 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 3 carbon atoms, a substituted or unsubstituted alkenyl group having 1 to 3 carbon atoms, and a substituted or unsubstituted aminoalkyl group having 1 to 4 carbon atoms; R5, R6, R10, and R11 are each independently selected from the group consisting of

hydrogen, a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms, and a substituted or unsubstituted aminoalkyl group having 1 to 5 carbon atoms; R7 to R9 are each independently selected from the group consisting of hydrogen, OH, a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms, and a substituted or unsubstituted aminoalkyl group having 1 to 5 carbon atoms; and m may be an integer of 1 to 5.

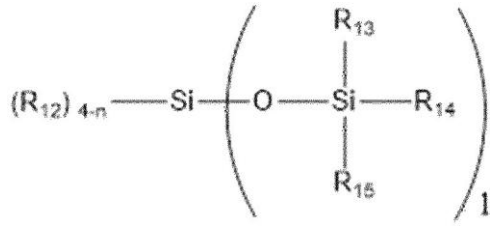
In a preferable embodiment, the second etching inhibitor may be represented by the following Chemical Formula 6:

[Chemical Formula 6]



In Chemical Formula 6, R16 is a methyl group, an ethyl group, or a propyl group; n is an integer of 1 to 5; and when n is 2 or more, the plurality of R16 may all be the same, or at least some of them may be different.

[Chemical Formula 5]



In Chemical Formula 5, R12 is hydrogen, an alkyl group, an aminoalkyl group, or an aminoalkoxy group; at least one of R13, R14, and R15 is an aminoalkyl group or an aminoalkoxy group; and l may be 2 or 3.

In one embodiment of the present application, the second etching inhibitor may be, with respect to the total weight of the etching composition, 0.01 wt% to 15 wt%, preferably 0.1 wt% to 10 wt%, and more preferably more than 0.1 and 3 wt% or less. When the above-described range is exceeded, it may itself act as an impurity and adversely affect the overall etching rate regardless of the type of film, and when it is less than the above-described range, it may be difficult to utilize the etching composition in a process in the temperature range described later, and it may be difficult to secure a sufficient nitride film etching selectivity.

In addition, in one embodiment of the present application, the etching composition may include a solvent. Specifically, the solvent may be water or deionized water (DIW). The solvent may constitute the balance of the composition, excluding 7 to 85 wt% of the inorganic acid, 0.1 to 10 wt% of the second etching inhibitor, and 0.1 to 10 wt% of the first etching inhibitor, with respect to 100 wt% of the entire etching composition.

In one embodiment of the present application, the inorganic acid included in the etching composition allows the etching composition to have an acidic pH (for example, pH 2 to 6) so

that the etching target (for example, an insulating film) can be etched.

Such an inorganic acid is not particularly limited, but may be at least one selected from the group consisting of sulfuric acid, nitric acid, phosphoric acid, silicic acid, hydrofluoric acid, boric acid, hydrochloric acid, and perchloric acid. Specifically, the inorganic acid may be phosphoric acid. When phosphoric acid is used as the inorganic acid and the etching targets are an oxide film and a nitride film, the etching selectivity of the nitride film with respect to the oxide film can be increased. In addition, when phosphoric acid is used as the inorganic acid, hydrogen ions are provided in the etching composition to promote etching.

In addition, when the inorganic acid is phosphoric acid, the etching composition according to one embodiment of the present application may further include sulfuric acid as an additive. The sulfuric acid can raise the boiling point of the etching composition including the phosphoric acid as the inorganic acid, thereby helping the etching of the nitride film.

In one embodiment of the present application, the etching composition may include 70 to 99 parts by weight of the inorganic acid. Specifically, the etching composition may include 70 to 90 parts by weight of the inorganic acid, and more specifically, the etching composition may include 75 to 85 parts by weight of the inorganic acid. When the content of the inorganic acid is less than 70 parts by weight, the etching (removal) of the nitride film is not easy or the utility at the predetermined temperature conditions described later is lowered, and when it exceeds 99 parts by weight, it is difficult to obtain a high etching selectivity for the nitride film.

In one embodiment of the present application, the etching composition may further include an ammonium-based compound. The ammonium-based compound may mean a compound that forms ammonium (NH_4^+) under aqueous solution conditions. The ammonium-based compound may include, for example, at least one of ammonia, ammonium chloride, ammonium phosphate, ammonium acetate, ammonium sulfate, ammonium formate, and a metal ammine complex salt. The metal ammine complex salt may

be a metal complex salt including at least one ammonia (NH3) ligand. When the etching process of the silicon nitride film is performed for a long time, the concentration of silicon ions may increase. As an example, the silicon ions may be formed by SiO2H2O, which is a product of Reaction Scheme 1. Abnormal growth of the silicon oxide film may occur due to the silicon ions. According to embodiments, in the etching process, the ammonium-based compound may dissociate to form ammonium (NH4+). The ammonium may react with the precursor of the silicon ions (for example, SiO2) to remove the precursor of the silicon ions. Accordingly, the abnormal growth of the silicon oxide film can be prevented. The ammonium-based compound can keep the etching rate constant over the etching time.

When the ammonium-based compound is less than 0.01 wt% of the etching composition, it may be difficult to prevent the silicon oxide film from growing abnormally or the etching selectivity of the silicon nitride film with respect to the silicon oxide film from changing over time. When the ammonium-based compound exceeds 10 wt% of the etching composition, the etching rates of the silicon nitride film and the silicon oxide film may change over time. According to an embodiment, the composition ratio of the ammonium-based compound may be 0.01 wt% to 10 wt%.

In addition, in one embodiment of the present application, the etching composition may further include any conventionally known additive to improve the etching performance. The additive may be a surfactant, a metal ion sequestering agent, a corrosion inhibitor, or the like.

As the etching composition of the present invention as described above optionally further includes an additive and an ammonium-based compound in addition to the inorganic acid, the second etching inhibitor, and the first etching inhibitor, it can exhibit a remarkably high etching selectivity of the nitride film with respect to the oxide film or the germanium-containing film. In addition, the etching composition prevents damage to the film quality of the oxide film or the germanium-containing film in the etching process of the nitride film, and deterioration of electrical characteristics

due to the etching of the germanium-containing film or the oxide film, and can minimize the generation of particles. Therefore, the etching composition of the present invention can be usefully used in etching processes in the manufacture of semiconductor devices.

In one embodiment of the present application, the etching composition may be characterized as being used for etching a silicon nitride film. As a preferable range, in this case, the silicon nitride film/oxide film etching selectivity may be characterized as being 250 or more, and the silicon nitride film/germanium-containing film etching selectivity of the etching composition may be 50 or more. In addition, the silicon nitride film/doped silicon film etching selectivity of the etching composition may be 30 or more.

In one embodiment of the present invention, the second etching inhibitor may be characterized as suppressing the generation of bubbles of the etching composition during the etching process. Specifically, in terms of preventing the adsorption of gas bubbles such as H2 onto the silicon surface, the second etching inhibitor can undergo hydrophobic interaction with the nonpolar silicon surface and, by imparting polarity to the silicon surface, can prevent the generation and adsorption of bubbles. As described above, in one embodiment of the present invention, the bubble generation rate of the etching composition may be characterized as being less than 1 cm. According to one embodiment of the present application, the bubble height on the surface immediately after the preparation of the etching composition may be characterized as being 0.9 cm or less. According to another embodiment of the present application, the bubble height on the surface after 60 seconds have elapsed since the formation of the etching composition may be characterized as being 0.9 cm or less. According to yet another embodiment of the present application, the bubble height on the surface immediately after the preparation of the etching composition may be 0.1 to 1.0 cm, and the rate of change of the bubble height on the surface after 60 seconds have elapsed may be characterized as being 50% or more.

In one embodiment of the present application, the etching composition may, with respect to an integrated circuit device

including a silicon oxide film, a silicon nitride film, and a germanium-containing film, inhibit the etching of the germanium-containing film and etch the silicon oxide film and the silicon nitride film. This may be an effect of the first etching inhibitor.

In one embodiment of the present application, the etching composition may, with respect to an integrated circuit device including a silicon oxide film, a silicon nitride film, and a germanium-containing film, inhibit the etching of the germanium-containing film and the silicon oxide film and etch the silicon nitride film. The above-described effect may be an effect of the first and second etching inhibitors.

Method for manufacturing semiconductor device

The second aspect of the present application

provides a method for manufacturing an integrated circuit device, comprising: a step of forming a structure by stacking an insulating film and a sacrificial film on a substrate; and a step of performing an etching process using the etching composition to remove the sacrificial film to form a space region.

Detailed descriptions of parts overlapping with the first aspect of the present application have been omitted; however, the contents described with respect to the first aspect of the present application can be equally applied to the second aspect even if the description thereof is omitted.

Hereinafter, the method for manufacturing a semiconductor device according to the second aspect of the present application will be described in detail.

The “space” in the terms “space region” and “space portion” used in the present specification collectively refers to a space formed by removing a sacrificial film in the etching process of a semiconductor device, and as non-limiting examples, a trench, a channel, a gate, a spacer, and the like may be included.

In addition, the “deposition portion” used in the present specification means one including a portion formed by

depositing a conductive material or an insulating material in the above-described space region or space portion, and may be configured in a patterned manner.

FIG. 1 of the present application is a plan view of a semiconductor device according to embodiments. FIGS. 2 to 8 are drawings for explaining a method for manufacturing a semiconductor device according to embodiments, and correspond to cross-sections taken along line I-I' of FIG. 1. Hereinafter, contents overlapping with those described above will be omitted.

Referring to FIGS. 1 and 2 of the present application, a stack structure (200) may be formed on a substrate (100). The substrate (100) may be a bulk silicon substrate, a silicon-on-insulator (SOI) substrate, a germanium substrate, a germanium-on-insulator (GOI) substrate, a silicon-germanium substrate, or a substrate of an epitaxial thin film obtained by performing selective epitaxial growth (SEG). A first direction (D1) and a second direction (D2) may be parallel to an upper surface (100a) of the substrate (100). The second direction (D2) may intersect the first direction (D1). A third direction (D3) may be perpendicular to the upper surface (100a) of the substrate (100).

In one embodiment of the present application, the stack structure (200) may include sacrificial films (SC) and insulating films (IL). The formation of the stack structure (200) may include alternately and repeatedly forming the sacrificial films (SC) and the insulating films (IL) on the substrate (100). The sacrificial films (SC) may be formed between the insulating films (IL). The sacrificial films (SC) may have etching selectivity with respect to the insulating films (IL). The sacrificial films (SC) may include, for example, silicon nitride (for example, SixNy). The insulating films (IL) may include a germanium-containing film (for example, SiGe) or silicon oxide (for example, SixOy). The insulating films (IL) may be formed using tetraethoxysilane (TEOS), and tetraethoxysilane may be represented by $(C_2H_5O)_4Si$.

In embodiments of the present invention, the sacrificial films (SC) may have substantially the same thicknesses as each

other. Alternatively, the lowermost sacrificial film (SC) and the uppermost sacrificial film (SC) among the sacrificial films (SC) may be formed thicker than the sacrificial films (SC) positioned therebetween. In addition, the insulating films (IL) may have the same thicknesses as each other, or the thicknesses of at least two of the insulating films (IL) may be different from each other. The lowermost one of the insulating films (IL) may have a thickness thinner than the sacrificial films (SC) and the insulating films (IL) formed thereon. The lowermost one of the insulating films (IL) may also be a silicon oxide film formed through a thermal oxidation process. In the present specification, the thickness of a certain component may mean the distance of the component in the third direction (D3).

Referring to FIGS. 1 and 3 of the present application, openings (210) and vertical structures (300) may be formed in the stack structure (200). Forming the openings (210) may include forming, on the stack structure (200), a mask pattern (not shown) defining the planar positions of the openings (210), and etching the stack structure (200) using the mask pattern as an etching mask. The etching of the stack structure (200) may be performed by an anisotropic etching process.

In one embodiment of the present application, the openings (210) may penetrate the stack structure (200). The sidewalls of the openings (210) may expose the sacrificial films (SC) and the insulating films (IL). The openings (210) may expose the substrate (100). While forming the openings (210), the upper surface (100a) of the substrate (100) may be over-etched. In this case, the upper surface (100a) of the substrate (100) exposed by the openings (210) may be recessed to a predetermined depth.

In one embodiment of the present application, each of the openings (210) may be formed in the form of a cylindrical or rectangular parallelepiped hole. The lower portions of the openings (210) may have smaller widths than the upper portions thereof. As shown in FIG. 1, the openings (210) may form columns parallel to the second direction (D2) from a planar viewpoint. The openings (210) between two adjacent columns may be arranged in a zigzag form in the second direction (D2).

Unlike FIG. 1, the openings (210) may form an array aligned along the first direction (D1) and the second direction (D2). For example, the openings (210) of two adjacent columns may be aligned in the first direction (D1) to form an array.

In one embodiment of the present application, first dielectric patterns (310) may be formed in the openings (210). The first dielectric patterns (310) may cover the sidewalls of the openings (210). The first dielectric patterns (310) may expose the upper surface (100a) of the substrate (100). The first dielectric pattern (310) may include a single-layer insulating layer or multi-layer insulating layers. The first dielectric pattern (310) may function as a part of the data storage film of a charge-trap type flash memory transistor. Exemplary embodiments of the first dielectric pattern (310) will be described later in the description of FIG. 9.

In one embodiment of the present application, semiconductor patterns (320) may be formed in the openings (210). The semiconductor patterns (320) may include, for example, silicon (Si), germanium (Ge), or a mixture thereof. The semiconductor patterns (320) may have a crystal structure including at least one of single-crystal, amorphous, and polycrystalline. The semiconductor patterns (320) may further include a doped impurity. As another example, the semiconductor patterns (320) may be an intrinsic semiconductor in an undoped state. The semiconductor patterns (320) may be formed using thermal chemical vapor deposition (Thermal CVD), plasma enhanced CVD, or atomic layer deposition (ALD) technology.

In one embodiment of the present application, the semiconductor patterns (320) may be formed on the sidewalls of the openings (210) to cover the first dielectric patterns (310). The semiconductor patterns (320) may extend onto the substrate (100) and contact a part of the upper surface (100a) of the substrate (100) exposed by the openings (210). Each of the semiconductor patterns (320) may be formed in a pipe shape, a hollow cylindrical shape, or a cup shape in each corresponding opening (210). The semiconductor patterns (320) may define empty regions (321) in the central portions of the openings (210).

In one embodiment of the present application, buried insulating patterns (330) may be filled in the empty regions (321), respectively. The buried insulating patterns (330) may be formed of an insulating material having excellent gap-fill characteristics. The buried insulating patterns (330) may be formed of, for example, a high-density plasma oxide film, an SOG film (Spin On Glass layer), an ALD oxide film, and/or a CVD oxide film.

In one embodiment of the present application, pads (340) may be formed on the vertical structures (300). The pads (340) may be made of a conductive material such as a semiconductor material doped with impurities or a metal. The lower surfaces of the pads (340) may be disposed at a level higher than the upper surface of the uppermost sacrificial film (SC). A lower capping film (510) may be formed on the upper surfaces of the vertical structures (300) and the stack structure (200). The lower capping film (510) may include an insulating material such as silicon oxide, silicon nitride, and/or silicon oxynitride.

Referring to FIG. 4 of the present application, trenches (600) may be formed to penetrate the stack structure (200) and the lower capping film (510). Forming the trenches (600) may include forming, on the lower capping film (510), a mask pattern (not shown) defining the planar positions of the trenches (600), and etching the stack structure (200) using the mask pattern as an etching mask. The etching of the stack structure (200) may be performed by an anisotropic etching process.

In one embodiment of the present application, the trenches (600) may be formed between adjacent vertical structures (300). The trenches (600) may be spaced apart from the vertical structures (300) and expose the sidewalls of the sacrificial films (SC) and the sidewalls of the insulating films (IL). The upper portions of the trenches (600) may have larger widths than the lower portions thereof. The trenches (600) may expose the upper surface (100a) of the substrate (100). While forming the trenches (600), the upper surface (100a) of the substrate (100) exposed by the trenches (600) may be recessed to a predetermined depth by over-etching. As

shown in FIG. 1, the trenches (600) may have long axes parallel to the second direction (D2) from a planar viewpoint. The trenches (600) may be spaced apart from each other in the first direction (D1).

Referring to FIG. 5 of the present application, the sacrificial films (SC) may be etched to form gate regions (250). The gate regions (250) may be voids, and may be regions in which gate electrode patterns (450) are formed in FIG. 7. The gate regions (250) are formed between the insulating films (IL) and may be connected to the trenches (600). The gate regions (250) may expose portions of the sidewalls (300c) of the vertical structures (300). The thicknesses of the gate regions (250) may be substantially the same as the thicknesses of the removed sacrificial films (SC). The etching of the sacrificial films (SC) may be performed by an etching process using the etching composition. The etching process may be a wet etching process.

In one embodiment of the present application, the etching composition may include an inorganic acid such as phosphoric acid, an ammonium-based compound, and a first etching inhibitor such as a compound represented by Chemical Formula 1. Since the sacrificial films (SC) include silicon nitride, they can be etched by phosphoric acid as in Reaction Scheme 1.

In one embodiment of the present application, for example, the etching composition at 130°C to 170°C may be supplied onto the substrate (100). Below 130°C, the etching rate of the silicon nitride film is too low to be applied, and at a temperature exceeding 170°C, uniform etching may not be achieved due to an excessively fast etching rate.

Under the above temperature conditions, phosphoric acid may further etch not only the sacrificial films (SC) but also silicon oxide or the germanium-containing film. The insulating films (IL) may include silicon oxide or a germanium-containing film. According to embodiments, the etching composition includes an oxide film etching inhibitor and an amine-based compound as additive materials, so that the etching of the insulating films (IL) by phosphoric acid can be prevented/reduced. For example, in the etching process,

the oxygen of the silicon-containing compound may be bonded to the surfaces of the insulating films (IL) to protect the insulating films (IL). Accordingly, during the etching process, the insulating films (IL) may exhibit a low etching rate. The oxygen atoms of the silicon-containing compound may not interact (for example, hydrogen bonding) with the surfaces of the sacrificial films (SC). Accordingly, the etching selectivity of the sacrificial films (SC) with respect to the insulating films (IL) may be increased. If the silicon-containing compound is unstable, by-products are formed, and the by-products may form particles. The by-products and/or particles may cause defects in the manufacturing process of the semiconductor device. For example, the by-products and/or particles may be adsorbed onto the insulating films (IL). Since the bond between the silicon atom and the oxygen atom of the silicon-containing compound is stable, the formation of by-products can be prevented in the etching process. The sacrificial films (SC) may be etched to form silicon ions (for example, SiO_2H_2O). The ammonium-based compound can remove the silicon ions generated while etching the sacrificial films (SC). Accordingly, the abnormal growth of the insulating films (IL) due to the silicon ions can be prevented/reduced.

In one embodiment of the present application, in the etching process, the etching composition may be applied onto the substrate (100) by a method of coating, dipping, spraying, or jetting. When the etching composition is applied by the dipping method, a batch-type apparatus may be used in the etching process. When the etching composition is sprayed onto the substrate (100), a single wafer type apparatus may be used in the etching process. After the etching process, a cleaning process using ultrapure water or the like and a drying process may be performed on the substrate (100). Ultrapure water may mean water having impurities of 100 ppb or less.

Referring to FIG. 6 of the present application, a second dielectric pattern (410) and a gate conductive film (451) may be formed on the stack structure (200) and in the trenches (600). The second dielectric pattern (410) may be formed substantially conformally on the stack structure (200) and in

the trenches (600). The second dielectric pattern (410) may extend into the trenches (600) and the gate regions (250). The second dielectric pattern (410) may substantially conformally cover the upper surface of the uppermost insulating film (IL) among the insulating films (IL), the sidewalls of the insulating films (IL) exposed by the trenches (600), the upper and lower surfaces of the insulating films (IL) exposed by the gate regions (250), the sidewalls (300c) of the vertical structures (300) exposed by the gate regions (250), and the upper surface (100a) of the substrate (100). The second dielectric pattern (410) may be formed by a deposition process. The deposition method and deposition conditions may be adjusted so that the second dielectric pattern (410) is formed to have good step coverage. For example, the deposition process of the second dielectric pattern (410) may be performed by chemical vapor deposition or atomic layer deposition. The second dielectric pattern (410) may include a single layer or a plurality of layers. The second dielectric pattern (410) may be a part of the data storage film (DS) of a charge-trap type flash memory transistor. Exemplary embodiments of the second dielectric pattern (410) will be described later in the description of FIG. 9. The gate conductive film (451) may be formed on the second dielectric pattern (410). The gate conductive film (451) may fill at least a part of each of the trenches (600) and the gate regions (250). Unlike shown, the gate conductive film (451) may completely fill each of the trenches (600). Although not shown, a barrier metal film and a metal film may be sequentially deposited to form the gate conductive film (451). The barrier metal film may include, for example, a metal nitride such as titanium nitride (TiN), tantalum nitride (TaN), or tungsten nitride (WN). The metal film may include, for example, tungsten (W), aluminum (Al), titanium (Ti), tantalum (Ta), cobalt (Co), or copper (Cu).

Referring to FIGS. 1 and 7 of the present application, the gate conductive film (451) may be patterned so that gate electrode patterns (450) are formed in the gate regions (250), respectively. The patterning of the gate conductive film (451) may proceed by an etching process. At this time, the second dielectric pattern (410) may be further etched. In the etching

process of the gate conductive film (451), the gate conductive film (451) on the substrate (100) may be removed. The etching of the gate conductive film (451) may proceed until portions of the gate conductive film (451) on the sidewalls of the insulating films (IL) are removed and the sidewalls of the insulating films (IL) are exposed. Accordingly, the gate electrode patterns (450) and the second dielectric pattern (410) are localized in the gate regions (250), and gate structures (400) may be formed. Each of the gate structures (400) may be formed between two adjacent trenches (600). The sidewalls of the gate structures (400) may be exposed to the trenches (600). The gate structures (400) may expose the upper surface (100a) of the substrate (100) in the trenches (600). The exposed upper surface (100a) of the substrate (100) may be further etched. As shown in FIG. 1, the gate structures (400) may have long axes parallel to the second direction (D2) from a planar viewpoint. The gate structures (400) may be spaced apart from each other in the first direction (D1).

In one embodiment of the present application, each of the gate structures (400) may include the stacked gate electrode patterns (450), the second dielectric pattern (410), and the insulating films (IL). In each of the gate structures (400), the gate electrode patterns (450) may be interposed between the insulating films (IL). The gate electrode patterns (450) may be used as a string selection line, a ground selection line, and word lines. For example, the uppermost one and the lowermost one of the stacked gate electrode patterns (450) may be used as a string selection line and a ground selection line, respectively. The gate electrode patterns (450) between the uppermost and lowermost gate electrode patterns (450) may be used as word lines.

In one embodiment of the present application, in the gate structures (400), the second dielectric pattern (410) may be interposed between the gate electrode patterns (450) and the insulating films (IL) and between the vertical structure (300) and the insulating films (IL).

In one embodiment of the present application, common source regions (CSR) may be formed in the substrate (100) exposed by the trenches (600). The common source regions (CSR) may be

spaced apart from each other in the second direction (D2). The common source regions (CSR) may be formed through an ion implantation process using the gate structures (400) as an ion mask. The common source regions (CSR) may overlap a part of the lower portion of the gate structures (400) from a planar viewpoint due to the diffusion of impurities. The common source regions (CSR) may have a conductivity type different from the conductivity type of the substrate (100). As another example, the common source regions (CSR) may be formed after the formation of the trenches (600) of FIG. 4.

Referring to FIGS. 1 and 8 of the present application, spacers (550) and common source plugs (CSP) may be formed in the trenches (600), respectively. The spacers (550) may cover the sidewalls of the gate structures (400). The spacers (550) may include an insulating material. The spacers (550) may be formed of, for example, silicon oxide, silicon nitride, silicon oxynitride, or a low-k material. Forming the spacers (550) may include depositing a spacer film (not shown) with a uniform thickness on the substrate (100) to cover the gate structures (400), and performing an etch-back process on the spacer film to expose the common source regions (CSR).

In one embodiment of the present application, common source plugs (CSP) may be formed on the spacers (550) to fill the trenches (600). The common source plugs (CSP) may be connected to the common source regions (CSR), respectively. Forming the common source plug (CSP) may include depositing a barrier metal film (not shown) covering the sidewalls of the spacers (550), and depositing a metal film (not shown) on the barrier metal film. The barrier metal film may include, for example, at least one of tantalum (Ta), tantalum nitride (TaN), titanium (Ti), titanium nitride (TiN), tungsten (W), tungsten nitride (WN), and combinations thereof. The metal film may include tungsten (W), aluminum (Al), titanium (Ti), tantalum (Ta), cobalt (Co), or copper (Cu). As shown in FIG. 1, from a planar viewpoint, the long axes of the common source plugs (CSP) may extend parallel to the second direction (D2).

In one embodiment of the present application, an upper capping film (520) may be formed on the lower capping film (510) to cover the upper surfaces of the common source plugs (CSP).

The upper capping film (520) may include an insulating material.

In one embodiment of the present application, bit line contact plugs (530) may be formed in the upper capping film (520). The bit line contact plugs (530) may penetrate the upper capping film (520) and the lower capping film (510) and be connected to the pads (340), respectively. The bit line contact plugs (530) may be electrically connected to the vertical structures (300) (for example, the semiconductor patterns (320)), respectively, through the pads (340). Bit lines (BL) may be formed on the upper capping film (520) and connected to the bit line contact plugs (530). As shown in FIG. 1, the bit lines (BL) may extend in the first direction (D1) from a planar viewpoint. The bit line contact plugs (530) and the bit lines (BL) may include a conductive material such as a metal. Accordingly, the manufacture of the semiconductor device (1) can be completed. The semiconductor device (1) may be a three-dimensional memory device.

FIG. 9 of the present application is a drawing for explaining insulating patterns of a semiconductor device according to embodiments, and shows an enlarged view of region A of FIG. 8. Hereinafter, in the description of FIG. 9, for simplification of the description, a single insulating film, a single gate electrode pattern, and a single vertical structure will be described.

Referring to FIGS. 8 and 9 of the present application, the first dielectric pattern (310) may include a tunnel insulating film (311), a charge storage film (312), and a first blocking insulating film (313). The tunnel insulating film (311) may extend along the vertical structure. The charge storage film (312) and the first blocking insulating film (313) may be stacked on the tunnel insulating film (311). The tunnel insulating film (311) may be formed of a material having a lower dielectric constant than the first blocking insulating film (313). The tunnel insulating film (311) may include, for example, at least one selected from oxide, nitride, oxynitride, and the like. Alternatively, the tunnel insulating film (311) may include a high-k material. The high-k material means an insulating material having a higher

dielectric constant than silicon oxide, and may include zirconium oxide, aluminum oxide, and/or hafnium oxide, and the like. The charge storage film (312) may be interposed between the tunnel insulating film (311) and the first blocking insulating film (313). The charge storage film (312) may include at least one of a charge-trap insulating film, a floating gate electrode, or conductive nano dots. The first blocking insulating film (313) may include a high-k material.

In one embodiment of the present application, the second dielectric pattern (410) may include a second blocking insulating film. The second blocking insulating film may be interposed between the gate electrode pattern (450) and the first dielectric pattern (310) and between the gate electrode pattern (450) and the insulating film (IL). The second blocking insulating film may include a high-k material. As an example, the first blocking insulating film (313) may include a high-k material, and the second blocking insulating film may be a material having a smaller dielectric constant than the first blocking insulating film (313). As another example, the second blocking insulating film may be one of high-k materials, and the first blocking insulating film (313) may be a material having a smaller dielectric constant than the second blocking insulating film.

In one embodiment of the present application, the first dielectric pattern (310) and the second dielectric pattern (410) may function as a data storage film. Data stored in the data storage film may be changed using Fowler-Nordheim tunneling, and the Fowler-Nordheim tunneling may be induced by a voltage difference between the vertical structure (300) and the gate electrode pattern (450).

In one embodiment of the present application, unlike shown, the second dielectric pattern (410) may not be formed. As another example, the first blocking insulating film (313) may not be formed.

Integrated circuit device

The third aspect of the present application

provides an integrated circuit device comprising: a structure formed by stacking an insulating film and a sacrificial film; a space portion formed in the structure by the sacrificial film being etched by an etching composition; and a deposition portion formed by depositing a conductive material or an insulating material in the space portion, wherein the etching composition comprises an inorganic acid, a first etching inhibitor, a second etching inhibitor, and a remaining amount of a solvent, and the first etching inhibitor contains at least two nitrogen atoms and includes a heterocyclic ring structure containing at least one nitrogen atom.

Detailed descriptions of parts overlapping with the first aspect and the second aspect of the present application have been omitted; however, the contents described with respect to the first aspect and the second aspect of the present application can be equally applied to the third aspect even if the description thereof is omitted.

The foregoing description of the present invention is for illustrative purposes, and those of ordinary skill in the art to which the present invention pertains will understand that the present invention can be easily modified into other specific forms without changing the technical spirit or essential features of the present invention. Therefore, the embodiments described above should be understood as illustrative in all respects and not restrictive. For example, each component described in a single form may be implemented in a distributed manner, and likewise, components described as distributed may also be implemented in a combined form.

INDUSTRIAL APPLICABILITY

According to one embodiment of the present invention, since the etching selectivity of the nitride film is high and the etching rate of the germanium-containing film is controlled, the effective oxide film height (EFH) can be easily controlled. In addition, the etching composition of the present invention prevents damage to the film quality of the germanium-containing film, deterioration of electrical characteristics due to the etching of the germanium-containing film, and generation of particles when removing

the nitride film, thereby improving the reliability of the semiconductor device.

In addition, when etching the nitride film, even in the case where the nitride film and the germanium-containing film or the oxide film are alternately stacked or mixed, only the nitride film can be selectively etched with a relatively high etching selectivity between the nitride film and the germanium-containing film or the oxide film. Accordingly, while etching the nitride film formed in patterns of various shapes in order to constitute an electronic device having a complicated and miniaturized structure, a sufficient etching selectivity of the nitride film with respect to the oxide film or the germanium-containing film can be secured without causing the above-described problems, so that the stability and reliability of the nitride film etching process can be secured, and by preventing damage to the germanium-containing film or the oxide film exposed to the etching composition together with the nitride film, or deterioration of the electrical characteristics of the germanium-containing film or the oxide film, the productivity of the semiconductor device manufacturing process can be improved and the reliability of the semiconductor device can be improved.

Accordingly, the etching composition of the present invention can be usefully used in manufacturing processes of semiconductor devices in which the selective removal of a nitride film with respect to a germanium-containing film or an oxide film is required (for example, a fine etching process of devices such as logic semiconductor devices and image sensors, a device isolation process of flash memory devices, a pipe channel formation process of 3D flash memory devices, a diode formation process of phase-change memories, and the like), thereby contributing to improving the efficiency of the manufacturing process of semiconductor devices.

In addition, by containing an additive material capable of obtaining both the characteristics of improving the etching selectivity of the etching solution and exhibiting an optimized effect in a predetermined temperature range, an etching composition with high process utility can be provided.

In addition, the generation of bubbles caused by gases such as H2 that may occur during the process in the etching solution itself, and the phenomenon in which such bubbles are adsorbed onto the surface of the silicon wafer and hinder the selective etching of the nitride film, can be suppressed.

For the above-described reasons, the etching composition according to one embodiment of the present invention, the method for manufacturing an integrated circuit device including performing an etching process using the same, and the integrated circuit device manufactured thereby can be regarded as industrially applicable.

CLAIMS

1. An etching composition comprising:

an inorganic acid;

a first etching inhibitor; and

a remaining amount of a solvent,

wherein the first etching inhibitor contains at least two nitrogen atoms and includes a heterocyclic ring structure containing at least one nitrogen atom.

2. The etching composition according to claim 1, further comprising:

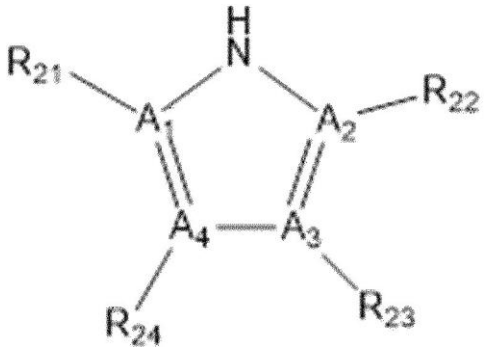
a second etching inhibitor,

wherein the first etching inhibitor inhibits etching of a germanium-containing film, and

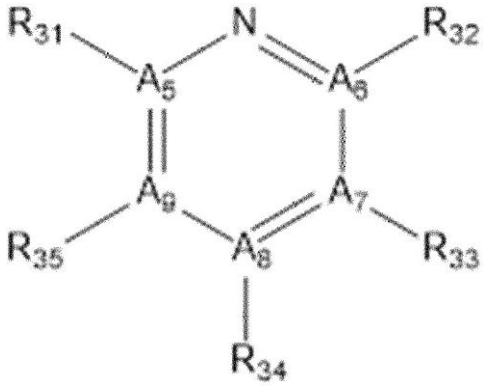
the second etching inhibitor inhibits etching of a silicon oxide film.

3. The etching composition according to claim 1, wherein the first etching inhibitor is represented by the following Chemical Formula 1 or Chemical Formula 2.

[Chemical Formula 1]



[Chemical Formula 2]



(In Chemical Formula 1 or Chemical Formula 2,

A1 to A9 are each independently carbon or nitrogen,

R21 to R24 and R31 to R35 are each independently any one selected from the group consisting of hydrogen, halogen, an amino group, an amide group, a hydroxy group, a thiol group (-SH or =S), -NO2, -NHCOR41 (R41 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), -CONHR42 (R42 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), -OCOR43 (R43 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms, a substituted or unsubstituted aminoalkyl group having 1 to 10 carbon atoms, a substituted or unsubstituted alkylamino group having 1 to 10 carbon atoms, and a substituted or unsubstituted heteroaryl group having 5 to 20 carbon atoms,

in Chemical Formula 1, when A1 to A4 are all carbon, at least one of R21 to R24 is an amino group, an amide group, -NO2, -NHCOR51 (R51 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), -CONHR52 (R52 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), a substituted or unsubstituted aminoalkyl group having 1 to 10 carbon atoms, or a substituted or unsubstituted alkylamino group having 1 to 10 carbon atoms, or

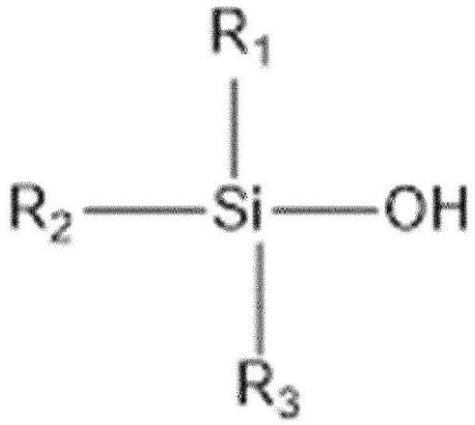
in Chemical Formula 2, when A5 to A9 are all carbon, at least one of R31 to R35 is an amino group, an amide group, -NO2, -NHCOR61 (R61 being a substituted or unsubstituted alkyl group

having 1 to 10 carbon atoms), -CONHR62 (R62 being a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms), a substituted or unsubstituted aminoalkyl group having 1 to 10 carbon atoms, or a substituted or unsubstituted alkylamino group having 1 to 10 carbon atoms.)

4. The etching composition according to claim 1, wherein the first etching inhibitor is nicotinamide, pyrimidine, or imidazole.

5. The etching composition according to claim 2, wherein the second etching inhibitor is represented by any one selected from the following Chemical Formula 3 to Chemical Formula 5.

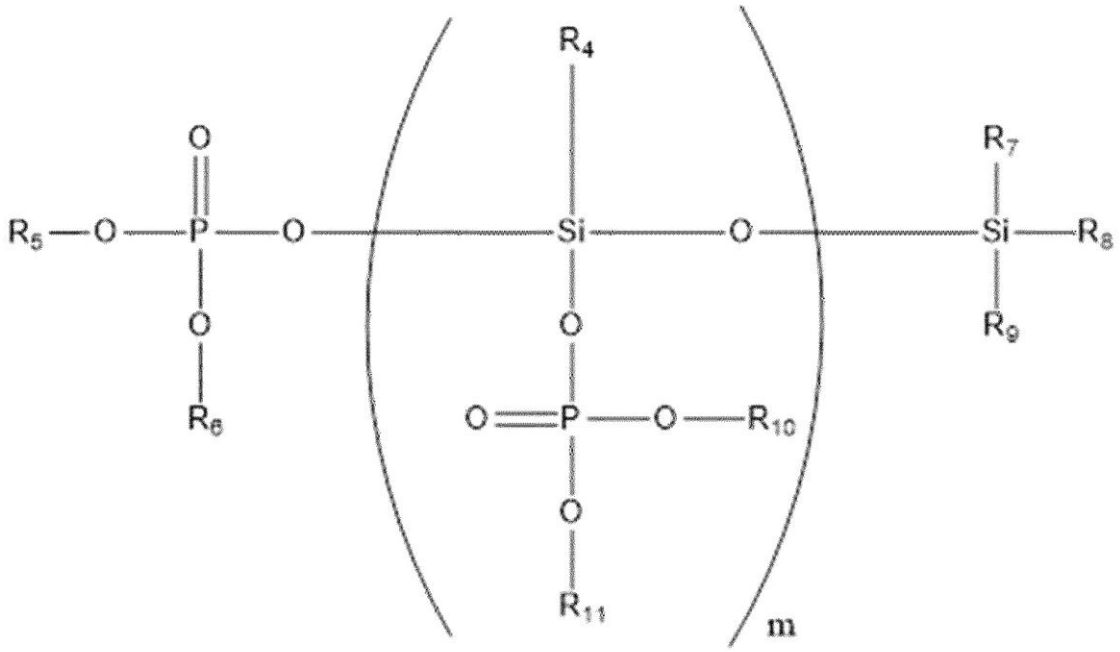
[Chemical Formula 3]



(In Chemical Formula 3,

R1 is selected from the group consisting of a substituted or unsubstituted aminoalkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted acetyloxy group, and a substituted or unsubstituted haloalkylacetyloxy group having 1 to 20 carbon atoms, and R2 and R3 are hydroxy groups.)

[Chemical Formula 4]



(In Chemical Formula 4,

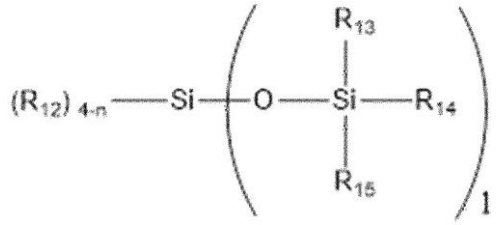
R4 is selected from the group consisting of hydrogen, OH, a substituted or unsubstituted alkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted alkenyl group having 1 to 20 carbon atoms, a substituted or unsubstituted cycloalkyl group having 3 to 20 carbon atoms, a substituted or unsubstituted aminoalkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted amino(C1-C10)alkylamino(C1-C10)alkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted aryl group having 6 to 20 carbon atoms, a substituted or unsubstituted alkylcarbonyl group having 1 to 20 carbon atoms, a substituted or unsubstituted alkylcarbonyloxy group having 1 to 20 carbon atoms, and a cyano(C1-C10)alkyl group,

R5 to R11 are each independently selected from the group consisting of hydrogen, OH, a substituted or unsubstituted alkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted alkenyl group having 2 to 20 carbon atoms, a substituted or unsubstituted cycloalkyl group having 3 to 20 carbon atoms, a substituted or unsubstituted aminoalkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted amino(C1-C10)alkylamino(C1-C10)alkyl group, a substituted or unsubstituted aryl group having 6 to 20 carbon atoms, a substituted or unsubstituted alkylcarbonyl group having 1 to 20 carbon atoms, a substituted or unsubstituted alkylcarbonyloxy group having 1 to 20 carbon atoms, and a cyano(C1-C10)alkyl group,

m is an integer of 1 to 10, and

when m is 2 or more, the plurality of respective R4, R10, and R11 are all the same, or at least some of them are different.)

[Chemical Formula 5]



(In Chemical Formula 5,

R12 is hydrogen, an alkyl group, an aminoalkyl group, or an aminoalkoxy group,

at least one of R13, R14, and R15 is an aminoalkyl group or an aminoalkoxy group, and

l is 2 or 3.)

6. The etching composition according to claim 5, wherein the second etching inhibitor is represented by Chemical Formula 4,

in Chemical Formula 4, R4 is selected from the group consisting of a substituted or unsubstituted alkyl group having 1 to 3 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 3 carbon atoms, a substituted or unsubstituted alkenyl group having 1 to 3 carbon atoms, and a substituted or unsubstituted aminoalkyl group having 1 to 4 carbon atoms,

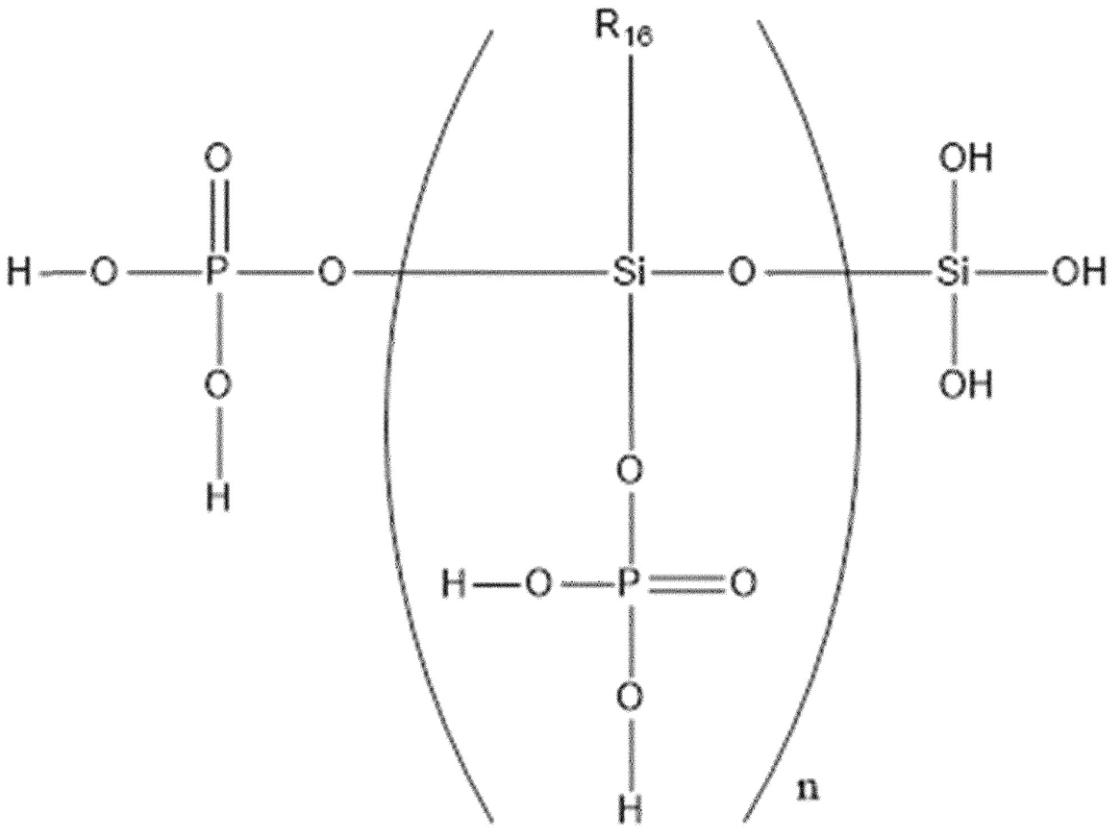
R5, R6, R10, and R11 are each independently selected from the group consisting of hydrogen, a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms, and a substituted or unsubstituted aminoalkyl group having 1 to 5 carbon atoms,

R7 to R9 are each independently selected from the group consisting of hydrogen, OH, a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms, and a substituted or unsubstituted aminoalkyl group having 1 to 5 carbon atoms, and

m is an integer of 1 to 5.

7. The etching composition according to claim 5, wherein the second etching inhibitor is represented by the following Chemical Formula 6.

[Chemical Formula 6]



(In Chemical Formula 6, R16 is a methyl group, an ethyl group, or a propyl group,

n is an integer of 1 to 5, and

when n is 2 or more, the plurality of R16 are all the same, or at least some of them are different.)

8. The etching composition according to claim 2, wherein the etching composition comprises, with respect to the entire etching composition, 7 to 85 wt% of the inorganic acid, 0.1 to 10 wt% of the first etching inhibitor, 0.1 to 10 wt% of the second etching inhibitor, and the remaining content of the solvent.

9. The etching composition according to claim 2, wherein, with respect to the total weight of the etching composition, the first etching inhibitor is more than 0.1 wt% and 2 wt% or less.

10. The etching composition according to claim 2, wherein, with respect to the total weight of the etching composition, the second etching inhibitor is more than 0.1 wt% and 3 wt% or less.

11. The etching composition according to claim 1, wherein the inorganic acid comprises at least one selected from the group consisting of sulfuric acid, nitric acid, phosphoric acid, silicic acid, hydrofluoric acid, boric acid, hydrochloric acid, and perchloric acid.

12. The etching composition according to claim 1, wherein the etching composition further comprises an ammonium-based compound.

13. The etching composition according to claim 12, wherein the ammonium-based compound comprises at least one of ammonium chloride, ammonium phosphate, ammonium acetate, ammonium sulfate, ammonium formate, and a metal ammine complex salt.

14. The etching composition according to claim 1, wherein the etching composition is used for etching a silicon nitride film.

15. The etching composition according to claim 1, wherein an etching selectivity of a silicon nitride film/germanium-containing material film of the etching composition is 50 or more.

16. The etching composition according to claim 1, wherein a bubble height on a surface immediately after preparation of the etching composition is 0.9 cm or less.

17. A method for manufacturing an integrated circuit device, comprising:

a step of forming a structure by stacking an insulating film and a sacrificial film on a substrate; and

a step of performing an etching process using the etching composition according to claim 1 to remove the sacrificial film to form a space region.

18. The method for manufacturing an integrated circuit device according to claim 17, wherein the sacrificial film comprises silicon nitride, and the insulating film comprises a germanium-containing material or silicon oxide.

19. The method for manufacturing an integrated circuit device according to claim 17, wherein, in the etching process, the sacrificial film has a higher etching rate than the insulating film.

20. The method for manufacturing an integrated circuit device according to claim 17, wherein, in the step of performing the etching process to remove the sacrificial film to form the space region, the space region comprises a gate region formed between the insulating films and a trench connected to the gate region.

21. The method for manufacturing an integrated circuit device according to claim 20, further comprising: forming openings penetrating the structure; and forming, in the openings, a semiconductor pattern spaced apart from the trench, wherein the forming of the semiconductor pattern is performed before the forming of the trench.

22. An integrated circuit device comprising:

a structure formed by stacking an insulating film and a sacrificial film;

a space portion formed in the structure by the sacrificial film being etched by an etching composition; and

a deposition portion formed by depositing a conductive material or an insulating material in the space portion,

wherein the etching composition comprises an inorganic acid, a first etching inhibitor, a second etching inhibitor, and a remaining amount of a solvent, and the first etching inhibitor contains at least two nitrogen atoms and includes a heterocyclic ring structure containing at least one nitrogen atom.