

respective wafers were evaluated by taking and observing cross-sectional SEM photographs of the respective wafers. As a result, it was found that the etching was performed without causing an etching shape anomaly such as shoulder loss, bowing, mask deformation or hole clogging.

5 [0053] (Measurement of Iodine or Bromine on Wafer)

The wafer C was tested for the amount of metal adhered to the SiO₂ film-coated silicon wafer C. The etching conditions were the same as those in the etching shape evaluation test. After the etching, the wafer was subjected to ashing with an oxygen plasma. The measurement of the metal amount was carried out by a method specified in
 10 JIS K0160:2009. More specifically, a plastic beaker in which hydrofluoric acid was put was placed in a container of PFA (perfluoroalkoxy fluororesin) called a VPD (vapor phase decomposition) container. The wafer C after the etching was set on a wafer stand inside the PVD container. Then, the VPD container was closed. In this state, the SiO₂ film on the wafer substrate was subjected to decomposition with a vapor of the hydrofluoric acid for
 15 10 minutes. Subsequently, 100 μ L of a scan liquid (ultrapure water) was dropped onto a surface of the wafer after the decomposition of the SiO₂ film. The whole surface of the wafer was then scanned. After the scanning, the scanned liquid was entirely dried. The resulting residue was again dissolved in ultrapure water. The thus-obtained solution was analyzed by an ICP-MS (inductively coupled plasma-mass spectrometry). The analysis
 20 value was converted to the number of metal atoms per 1 cm² of the wafer on the basis of the amount of the solution and the surface area of the wafer. As a result, the analysis result of the remaining iodine atoms was found to be 1.2×10^{10} atoms/cm²; and the analysis result of the remaining bromine atoms was found to be 1.0×10^{10} atoms/cm².

[0054] [Examples 2 to 9]

25 The etching was performed under the same conditions as in Example 1, except that the mixing ratio of CF₃I, C₃F₆, C₃H₂F₄ and Ar was changed to different values.

[0055] [Examples 10 and 11]

The etching was performed under the same conditions as in Example 1, except that C₂F₅I or CF₂Br₂ was used in place of CF₃I.

30 [0056] [Examples 12 and 13]

The etching was performed under the same conditions as in Example 1, except that C₄F₆ (hexafluoro-1,3-butadiene) or C₅F₈ (octafluoro cyclopentadiene)

was used in place of C_3H_6 .

[0057] [Example 14]

The etching was performed under the same conditions as in Example 1, except that, in place of $C_3H_2F_4$ (trans-1,3,3,3-tetrafluoropropene), 2,3,3,3-tetrafluoropropene
 5 which is a structural isomer of $C_3H_2F_4$ was used.

[0058] [Comparative Example 1]

The etching was performed under the same conditions as in Example 1, except that C_3F_6 and $C_3H_2F_4$ were not used.

[0059] [Comparative Example 2]

10 The etching was performed under the same conditions as in Example 1, except that C_3F_8 (perfluoropropane) was used in place of C_3H_6 .

[0060] [Comparative Examples 3 and 4]

The etching was performed under the same conditions as in Example 1, except that $C_3H_2F_6$ (1,1,1,2,3,3-hexafluoropropane) or $C_3H_2F_4O$ (hexafluoropropylene oxide) was
 15 used in place of $C_3H_2F_4$ (trans-1,3,3,3-tetrafluoropropene).

[0061] The results of the respective Examples and Comparative Examples are shown in TABLE 1. In the table, the amount of the remaining iodine or bromine atoms on the silicon wafer is shown in the column of "Atom Concentration on Wafer".

CLAIMS

1. A dry etching method for a substrate having a silicon compound film, comprising: plasmatizing a dry etching agent; and etching the silicon compound film with the plasmatized dry etching agent through a mask formed with a predetermined opening pattern on the silicon substrate film,

wherein the dry etching agent comprises all of the following first to fourth gases:

First gas: at least one compound selected from the group consisting of iodinated fluorocarbon compounds and brominated fluorocarbon compounds;

Second gas: an unsaturated fluorocarbon represented by C_nF_m where n is an integer of 2 to 5; and m is an integer of 2, 4, 6 or 8, excluding the combination of n:m = 2:6, 2:8, 3:2, 3:8 and 5:2;

Third gas: an unsaturated hydrofluorocarbon represented by $C_xH_yF_z$ where x is an integer of 2 to 4; and y and z are integers satisfying $y+z = 2, 4, 6$ or 8, excluding the combination of x: $y+z = 2:6, 2:8, 3:2$ and 3:8; and

Fourth gas: an oxidizing gas.

2. The dry etching method according to claim 1, wherein a number of iodine atoms and bromine atoms contained in the first gas is less than or equal to 2 times a number of hydrogen atoms contained in the third gas.

3. The dry etching method according to claim 1 or 2, wherein a volume of the first gas in the dry etching agent is in a range of 0.01 to 2 times a sum of volumes of the second and third gases in the dry etching agent.

4. The dry etching method according to any one of claims 1 to 3, wherein a volume ratio of the second gas and the third gas is 1: 0.05 to 20.

5. The dry etching method according to any one of claims 1 to 4, wherein an amount of the oxidizing gas in the dry etching agent is larger than or equal to 1 vol% and smaller than or equal to 50 vol% based on a total amount of the dry etching agent.

6. The dry etching method according to any one of claims 1 to 5,
wherein the unsaturated fluorocarbon is at least one selected from the group consisting of C_3F_6 , C_4F_6 and C_5F_8 , and
wherein the unsaturated hydrofluorocarbon is $C_3H_2F_4$.
7. The dry etching method according to claim 6,
wherein the unsaturated fluorocarbon is hexafluoropropene, and
wherein the unsaturated hydrofluorocarbon is trans-1,3,3,3-tetrafluoropropene.
8. The dry etching method according to any one of claims 1 to 7, wherein the oxidizing gas is at least one selected from the group consisting of O_2 , O_3 , CO , CO_2 , $COCl_2$, COF_2 and NO_2 .
9. The dry etching method according to any one of claims 1 to 8,
wherein the dry etching agent comprises an inert gas as a fifth gas, and
wherein the inert gas is at least one selected from the group consisting of He, Ne, Ar, Kr, Xe and N_2 .
10. The dry etching method according to any one of claims 1 to 9, wherein the silicon compound film is etched with the plasmatized dry etching agent under the application of a negative direct-current self-bias voltage whose absolute value is greater than or equal to 500 V.
11. The dry etching method according to any one of claims 1 to 10, wherein, after the etching of the silicon compound film, an amount of iodine atoms or bromine atoms remaining on a surface of the substrate with which the dry etching agent has come into contact is 1×10^{11} atom/cm² or less.
12. The dry etching method according to any one of claims 1 to 11, wherein the substrate is a silicon wafer.

13. The dry etching method according to any one of claims 1 to 11, wherein the substrate has a silicon film.
14. The dry etching method according to any one of claims 1 to 13, wherein the silicon compound film is one or more films selected from the group consisting of silicon oxide films and silicon nitride films.
15. A manufacturing method of a semiconductor device, comprising an etching step of etching a silicon compound film on a substrate by the dry etching method according to any one of claims 1 to 14.
16. The manufacturing method of the semiconductor device according to claim 15, comprising, after the etching step, a removing step of removing by ashing or thermal annealing the mask and/or a fluorocarbon polymerization film formed during the etching step.