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**YOSHINO et al.**(10) **Pub. No.: US 2014/0061031 A1**(43) **Pub. Date: Mar. 6, 2014**(54) **PROCESSING METHOD UTILIZING  
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(57) **ABSTRACT**

A processing method having excellent processing performance at a low flow rate is provided. A method for processing a surface of a sample uses reactive clusters produced by adiabatic expansion of a gas mixture ejected from a nozzle into a vacuum processing chamber. The gas mixture contains a reactive gas chlorine trifluoride, a first inert gas argon, and a second inert gas xenon. The gas mixture in an inlet of the nozzle has a pressure of 0.4 MPa (abs) or more. The reactive gas constitutes 3% by volume or more and 10% by volume or less. The first inert gas constitutes 40% by volume or more and 94% by volume or less. The second inert gas constitutes 3% by volume or more and 50% by volume or less of the gas mixture.

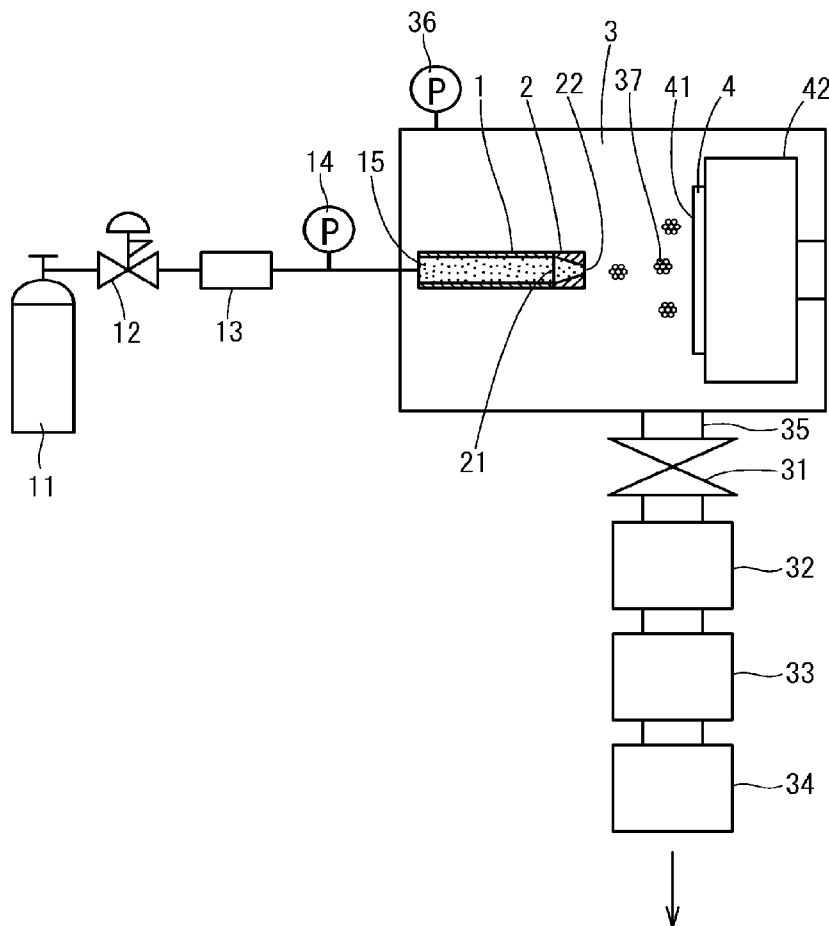


Fig. 1

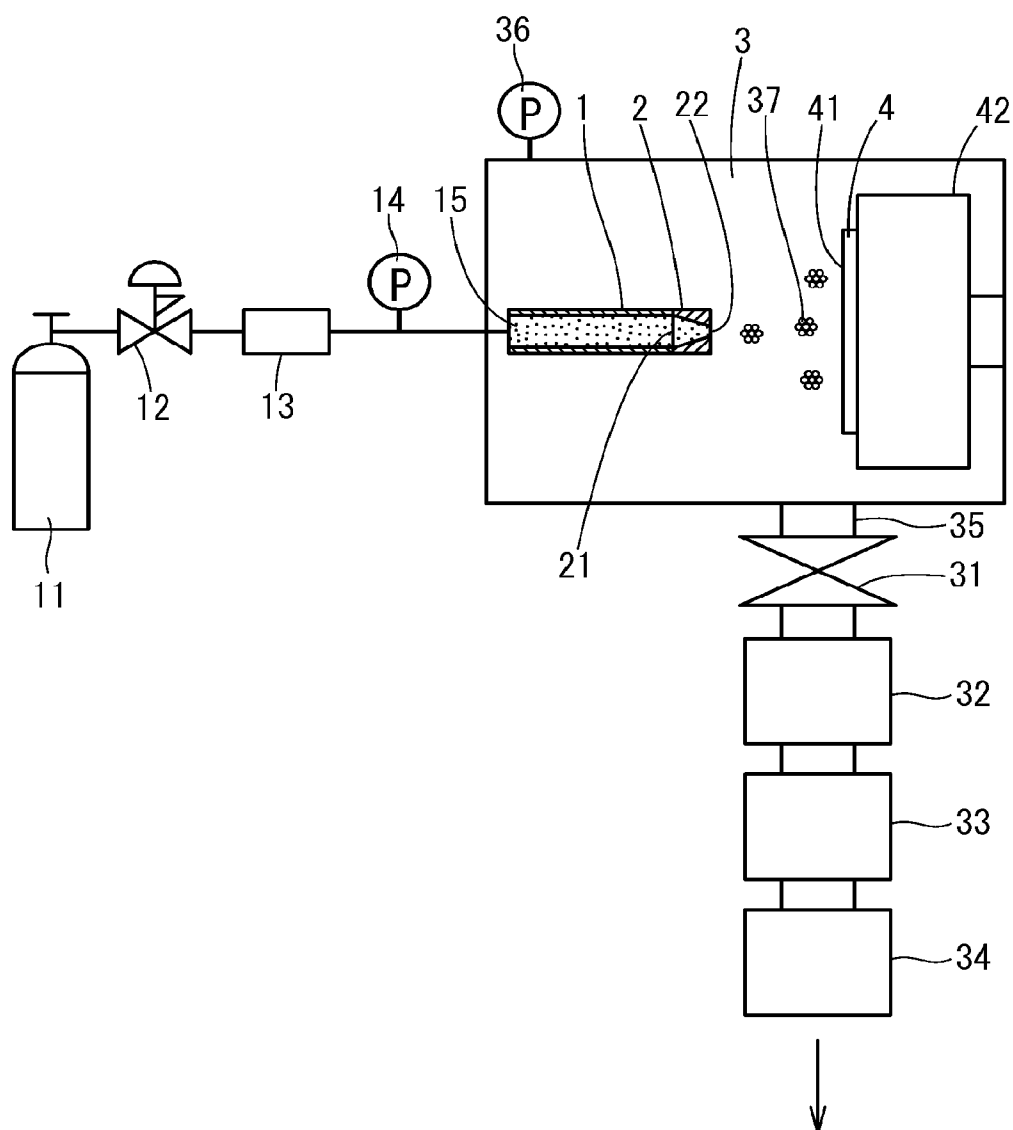


Fig. 2

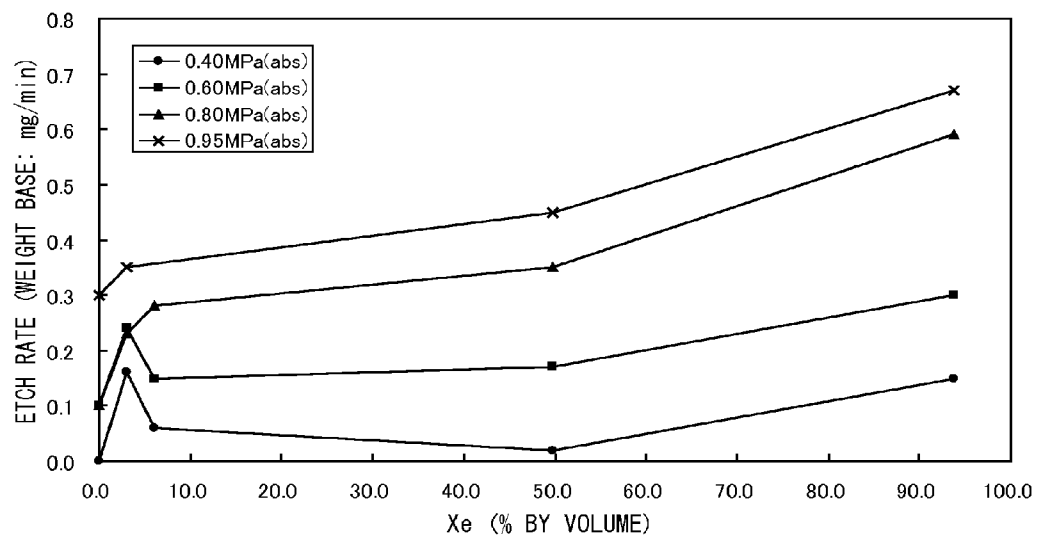


Fig. 3

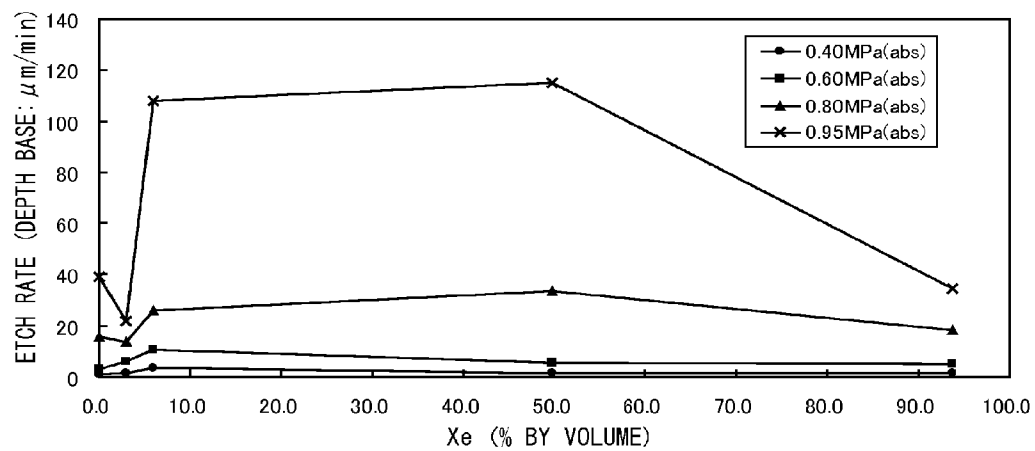


Fig. 4

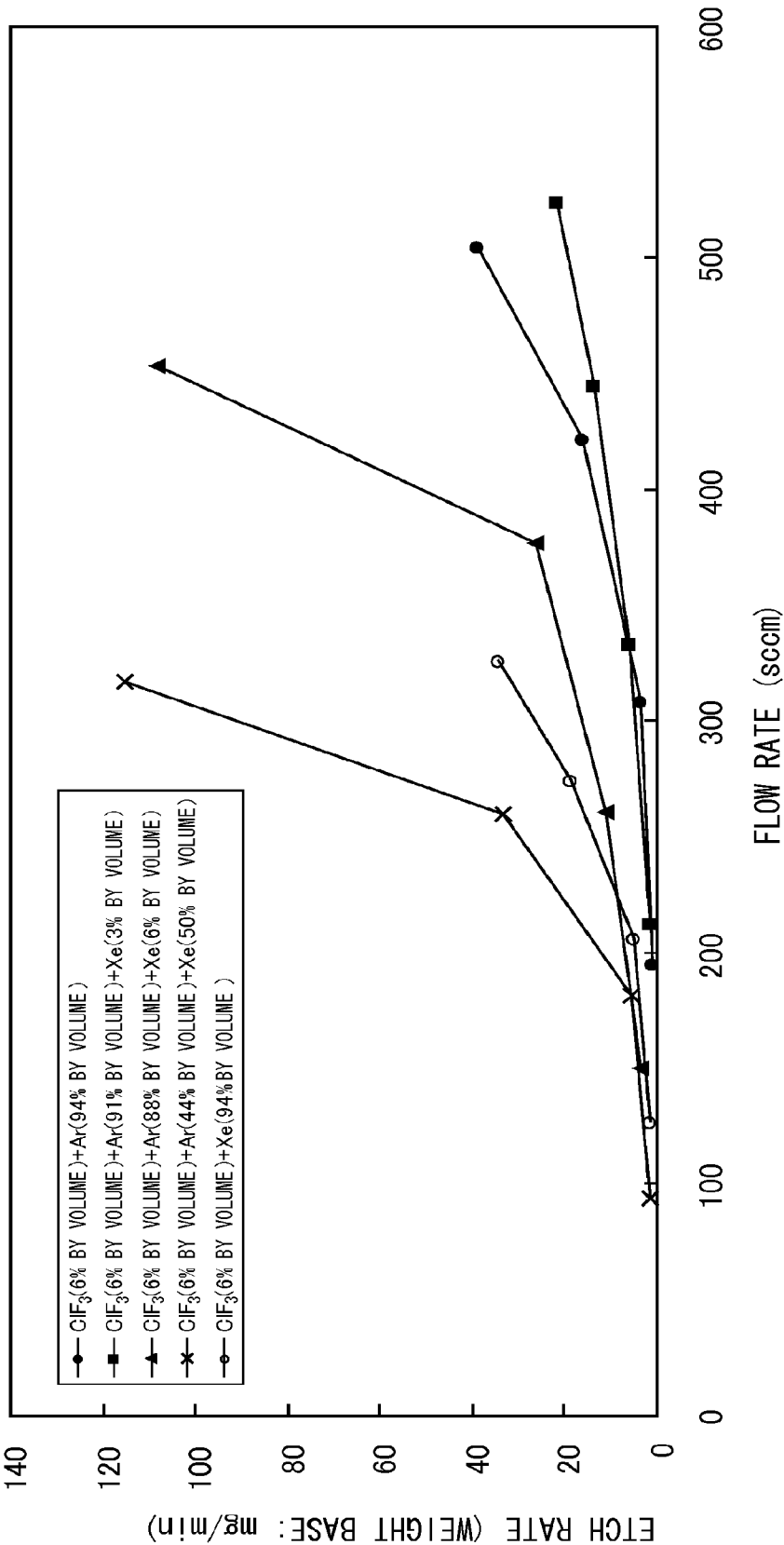
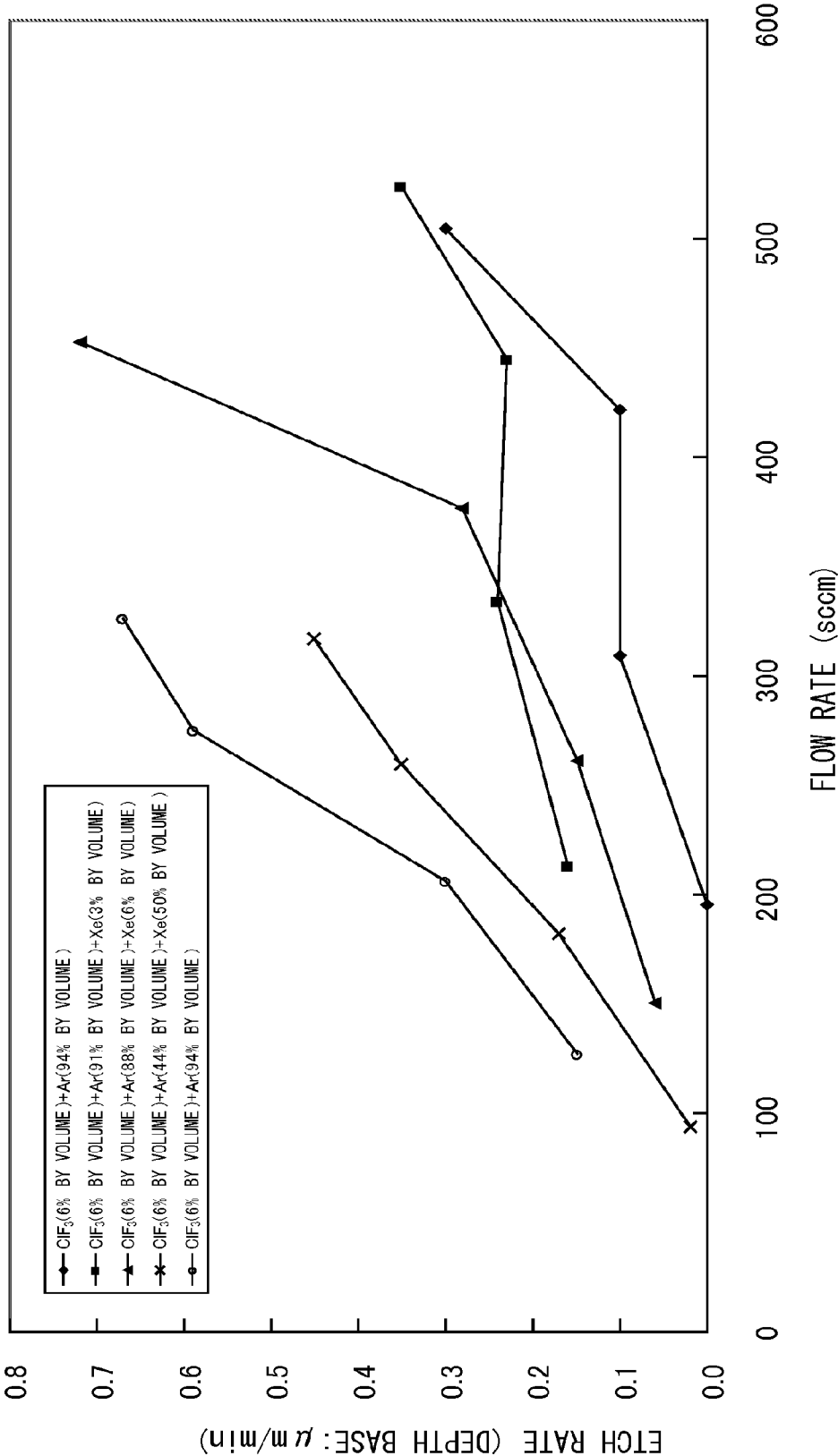


Fig. 5



## PROCESSING METHOD UTILIZING CLUSTER

### BACKGROUND OF THE INVENTION

**[0001]** 1. Field of the Invention

**[0002]** The present invention relates to a processing method for etching or cleaning a surface of a sample using reactive clusters produced from a reactive gas.

**[0003]** 2. Description of the Related Art

**[0004]** The present inventors have proposed a method utilizing neutral reactive clusters in order to solve problems associated with etching or cleaning of a sample using cluster ions (see, for example, WO 2010-021265).

**[0005]** In accordance with the method described in WO 2010-021265, a reactive gas and an additive gas that is inert to the reactive gas and has a lower boiling point than the reactive gas form neutral reactive clusters. The reactive clusters collide with a sample and react with the surface of the sample, thereby allowing anisotropic processing of the surface of the sample. The neutral reactive clusters are nonionized electro-neutral clusters and therefore advantageously cause no electrical damage to the sample.

**[0006]** However, this processing method has poor processing performance, such as a low etch rate.

**[0007]** In general, in order to improve the processing performance of clusters, it may be possible to increase the concentration or the supply pressure of a reactive gas before the formation of the clusters. When the reactive gas has a high boiling point, however, the reactive gas may become liquid before reaching a nozzle and not be able to form clusters by adiabatically expanding in the nozzle. Thus, the method has its limits.

**[0008]** Furthermore, treatment of a large area may require the use of a plurality of nozzles, which requires an increase in gas supply. Thus, a vacuum processing chamber must be evacuated of a large amount of gas in order to maintain a vacuum in the vacuum processing chamber. This is limited by exhaust capacity and may reduce processing capacity per nozzle. Thus, desired processing performance must sometimes be achieved with a small gas supply.

### SUMMARY OF THE INVENTION

**[0009]** In order to improve the poor processing performance of the method described in WO 2010-021265 in anisotropic etching using neutral clusters, it is an object of the present invention to provide a processing method having excellent processing performance at a low flow rate.

**[0010]** One aspect of the present invention is a method for processing a surface of a sample using reactive clusters produced by adiabatic expansion of a gas mixture ejected from a nozzle into a vacuum processing chamber. The gas mixture contains a reactive gas chlorine trifluoride, a first inert gas argon, and a second inert gas xenon. The gas mixture in an inlet of the nozzle has a pressure of 0.4 MPa (based on absolute pressure; hereinafter referred to simply as abs) or more. The reactive gas constitutes 3% by volume or more and 10% by volume or less. The first inert gas constitutes 40% by volume or more and 94% by volume or less. The second inert gas constitutes 3% by volume or more and 50% by volume or less of the gas mixture.

**[0011]** The pressure of the gas mixture and the concentration of the reactive gas in the nozzle inlet are in predetermined

ranges, and argon and xenon are used as inert gases. Under these conditions, excellent processing performance can be achieved at a low flow rate.

**[0012]** The gas mixture in the nozzle inlet may have a pressure of 0.6 MPa (abs) or more. The reactive gas may constitute 5% by volume or more and 7% by volume or less. The first inert gas may constitute 43% by volume or more and 89% by volume or less. The second inert gas may constitute 6% by volume or more and 50% by volume or less of the gas mixture.

**[0013]** This processing method has excellent processing performance particularly in the depth direction and is therefore very useful for applications requiring a high aspect ratio, such as micromachining.

### BRIEF DESCRIPTION OF THE DRAWINGS

**[0014]** FIG. 1 is a schematic explanatory view of a processing method utilizing clusters according to an embodiment of the present invention;

**[0015]** FIG. 2 is a graph of the relationship between the percentage of xenon and the etch rate (weight base) on a surface of a sample in a processing method utilizing clusters according to an embodiment of the present invention;

**[0016]** FIG. 3 is a graph of the relationship between the percentage of xenon and the etch rate (depth base) on a surface of a sample in a processing method utilizing clusters according to an embodiment of the present invention;

**[0017]** FIG. 4 is a graph of the relationship between the gas mixture flow rate and the etch rate (weight base) on a surface of a sample in a processing method utilizing clusters according to an embodiment of the present invention; and

**[0018]** FIG. 5 is a graph of the relationship between the gas mixture flow rate and the etch rate (depth base) on a surface of a sample in a processing method utilizing clusters according to an embodiment of the present invention.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0019]** Embodiments of the present invention will be described in detail below with reference to the accompanying drawings.

**[0020]** A processing method utilizing clusters according to an embodiment of the present invention will be described below with reference to a schematic explanatory view of FIG. 1.

**[0021]** In FIG. 1, reference numeral 1 denotes a gas mixture supply line, reference numeral 2 denotes a nozzle, reference numeral 3 denotes a vacuum processing chamber, and reference numeral 4 denotes a sample.

**[0022]** The gas mixture supply line 1 is connected to a gas cylinder 11 through a pressure-regulating valve 12 having a pressure-reducing function, a flowmeter 13, and a pressure gauge 14.

**[0023]** The gas cylinder 11 may contain a gas mixture 15 of a reactive gas, a first inert gas, and a second inert gas in a predetermined ratio at a predetermined pressure. The gas cylinder 11 may separately contain the reactive gas, the first inert gas, and the second inert gas in their respective containers and is controlled to supply the gas mixture 15 in a predetermined mixing ratio.

**[0024]** The reactive gas is chlorine trifluoride. Chlorine trifluoride has a high reactivity with silicon and is effective for a sample surface 41 made of a silicon single crystal.

[0025] The formation of reactive clusters requires a certain pressure. Because of its high boiling point, the reactive gas condenses (becomes liquid) and cannot be adiabatically expanded in the nozzle at high pressure. Thus, high pressure required for the formation of reactive clusters cannot be produced with the reactive gas alone.

[0026] The addition of an inert gas to the reactive gas can reduce the partial pressure of the reactive gas and prevent the reactive gas from becoming liquid, thereby producing primary pressure required for the formation of reactive clusters.

[0027] In the present embodiment, argon is used as a first inert gas, and xenon is used as a second inert gas.

[0028] The first inert gas and the second inert gas are inert to the reactive gas in the gas cylinder 11 and the gas mixture supply line 1. Thus, the first inert gas and the second inert gas do not react with the reactive gas in the gas cylinder 11 and the gas mixture supply line 1, allowing the stable formation of reactive clusters, and do not inhibit the processing of the sample surface 41.

[0029] Since processing results from a reaction between reactive clusters and the sample surface, the reactive clusters play the leading role in processing and, as described above, the inert gases only reduce the partial pressure of the reactive gas and prevent the reactive gas from becoming liquid, thereby producing primary pressure required for the formation of the reactive clusters. It is therefore supposed that the important thing is not the types of the inert gases but the partial pressure of the inert gases.

[0030] However, the experiments of the present inventors demonstrated that combined use of the first inert gas argon and the second inert gas xenon can improve processing performance (see examples described below).

[0031] In the present embodiment, the reactive gas constitutes 3% by volume or more and 10% by volume or less, the first inert gas constitutes 40% by volume or more and 94% by volume or less, and the second inert gas constitutes 3% by volume or more and 50% by volume or less of the gas mixture 15.

[0032] When the reactive gas constitutes less than 3% by volume of the gas mixture 15, this results in an insufficient reaction between the reactive gas and the sample. When the reactive gas constitutes 10% by volume of the gas mixture 15, the reactive gas may become liquid. The reactive gas preferably constitutes 5% by volume or more and 7% by volume or less.

[0033] When the first inert gas constitutes less than 40% by volume or more than 94% by volume, this results in high or low percentages of the reactive gas and the second inert gas. In both cases, it is difficult to control the percentages of the reactive gas and the second inert gas within the predetermined ranges. The first inert gas preferably constitutes 43% by volume or more and 89% by volume or less.

[0034] When the second inert gas constitutes less than 3% by volume, this results in insufficient effects of the second inert gas and an insufficient reaction between the reactive gas and the sample. When the second inert gas constitutes more than 50% by volume, this results in increased costs because of expensive xenon and reduces practicality. The second inert gas preferably constitutes 6% by volume or more and 50% by volume or less in terms of processing performance in the depth direction.

[0035] In the present embodiment, in order to achieve a certain level of processing performance, the gas mixture 15 in a nozzle inlet 21 has a pressure of 0.4 MPa (abs) or more. It is

difficult to form reactive clusters at a pressure of less than 0.4 MPa (abs). The gas mixture 15 in the nozzle inlet 21 preferably has a pressure of 0.6 MPa (abs) or more, more preferably 0.8 MPa (abs) or more. The maximum pressure of the gas mixture 15 in the nozzle inlet 21 is not particularly limited and may be 1 MPa (abs) or less in order to prevent an excessive load on the apparatus and the liquefaction of the reactive gas.

[0036] The adiabatic expansion of the gas mixture 15 ejected from a nozzle 2 into a vacuum processing chamber 3 will be described below.

[0037] The vacuum processing chamber 3 is connected to an outlet 35. The outlet 35 is connected to an abatement unit 34 for making the exhaust gas harmless through an open-close valve 31, a turbo-molecular pump 32, and a dry pump 33. Using the turbo-molecular pump 32 and the dry pump 33, the vacuum processing chamber 3 is maintained at a secondary pressure of approximately 10 Pa (abs).

[0038] The pressure of the vacuum processing chamber 3 is measured with a pressure gauge 36.

[0039] A differential pressure between the primary pressure of the nozzle inlet 21, for example, 0.68 MPa (abs) and the secondary pressure of the vacuum processing chamber 3, for example, 10 Pa (abs) allows the gas mixture 15 from the nozzle 2 to be adiabatically expanded to form reactive clusters 37.

[0040] In the present embodiment, in order to improve the processing performance of the reactive clusters 37, the gas mixture 15 of the reactive gas, the first inert gas, and the second inert gas ejected from the nozzle outlet 22 into the vacuum processing chamber 3 is adiabatically expanded to form the neutral reactive clusters 37.

[0041] The neutral reactive clusters 37 thus formed collide with the sample surface 41 in the vacuum processing chamber 3 to anisotropically process the sample surface 41 at a high speed.

[0042] A sample 4 is fixed at a predetermined position on a sample stage 42.

[0043] The following examples demonstrated that combined use of the first inert gas argon and the second inert gas xenon improved processing performance.

[0044] In the following examples, the etch rate (weight base) was calculated as a difference between the sample weights measured with a chemical balance "ER-182A" (manufactured by A&D Co., Ltd.) before and after one-minute processing. The etch rate (depth base) refers to the maximum etching depth in the one-minute processing. An etching depth of less than 60  $\mu\text{m}$  was measured with a stylus-based surface profiler "DekTak 3" (manufactured by Veeco Instruments Inc.). An etching depth of 60  $\mu\text{m}$  or more was measured with a scanning electron microscope "JSM-7505FS" (manufactured by JEOL Ltd.).

[0045] The gas mixture flow rate (sccm) is the volume flow rate of the gas mixture per minute. The volume flow rate is converted from the mass flow rate measured with the flow-meter 13 using the volume percentages and the molecular weights of the gas components of the gas mixture.

## EXAMPLES

[0046] The sample surface 41 to be processed with the reactive clusters 37 in the vacuum processing chamber 3 was made of a silicon single crystal. The gas mixture 15 contained chlorine trifluoride ( $\text{ClF}_3$ ) as the reactive gas, argon (Ar) as the first inert gas, and xenon (Xe) as the second inert gas.

[0047] The supply pressure (primary pressure) of the gas mixture **15** in the gas mixture supply line **1** was controlled with the pressure-regulating valve **12**. The internal pressure of the vacuum processing chamber **3** was maintained at approximately 10 Pa (abs) with the turbo-molecular pump **32** and the dry pump **33**.

[0048] The distance between the nozzle outlet **22** and the sample surface **41** was 13 mm. The irradiation time of the sample surface **41** with the reactive clusters **37** was 1 minute.

[0049] The primary pressure of the gas mixture **15** in the nozzle inlet **21** and the composition of the gas mixture **15** were changed.

[0050] More specifically, the primary pressure of the gas mixture **15** in the nozzle inlet **21** was 0.40, 0.60, 0.80, or 0.95 MPa (abs). The gas mixture **15** contained 6% by volume chlorine trifluoride, 0%, 3%, 6%, 50%, or 94% by volume xenon, and the remainder argon (100% by volume in total).

[0051] When the pressure of the gas mixture **15** in the nozzle inlet **21** was changed while the composition of the gas mixture **15** was fixed, the pressure of the gas mixture **15** having a predetermined composition was increased above the experimental pressure (0.95 MPa (abs)) in the gas cylinder **11** and was reduced to a predetermined pressure (0.40, 0.60, 0.80, or 0.95 MPa (abs)) with the pressure-regulating valve **12**.

[0052] Before an experiment using the gas mixture **15** having a different composition, the gas mixture **15** having the different composition was prepared in the gas cylinder **11**.

[0053] When xenon constituted 0% by volume, argon constituted 94% by volume, and when xenon constituted 94% by volume, argon constituted 0% by volume. In both cases, the gas mixture **15** contained only one inert gas, which is outside the scope of the present invention.

[0054] FIG. 2 is a graph of the relationship between the percentage of xenon (horizontal axis) and the etch rate (weight base: mg/min) on the sample surface **41** (vertical axis).

[0055] FIG. 3 is a graph of the relationship between the percentage of xenon (horizontal axis) and the etch rate (depth base:  $\mu\text{m}/\text{min}$ ) on the sample surface **41** (vertical axis).

[0056] FIG. 4 is a graph of the relationship between the gas mixture flow rate (horizontal axis) and the etch rate (weight base: mg/min) on the sample surface **41** (vertical axis).

[0057] FIG. 5 is a graph of the relationship between the gas mixture flow rate (horizontal axis) and the etch rate (depth base:  $\mu\text{m}/\text{min}$ ) on the sample surface **41** (vertical axis).

[0058] FIGS. 2 and 3 show that the addition of xenon improves processing performance. A high pressure of the gas mixture **15** in the nozzle inlet **21** tends to result in high processing performance.

[0059] FIGS. 4 and 5 show that the addition of xenon can achieve excellent processing performance as shown in FIGS. 2 and 3 at a reduced flow rate.

[0060] The excellent processing performance at a reduced flow rate indicates high reaction efficiency (a high percentage of reactive gas contributing to processing of the sample).

[0061] This can reduce the gas mixture flow rate per nozzle and ease exhaust capacity conditions for maintaining a vacuum in the vacuum processing chamber **3**. Thus, the number of nozzles can be increased to increase the gas mixture flow rate, which allows the processing method to be applied to large area processing and other applications.

[0062] The results of FIGS. 2 to 5 show that a pressure of 0.6 MPa (abs) or more and the presence of 6% to 50% by

volume xenon result in particularly excellent processing performance on the depth base. Thus, the processing method is very useful for applications requiring a high aspect ratio.

[0063] In order to clarify the excellent processing performance in the depth direction at a pressure (a pressure of the gas mixture in the nozzle inlet) of 0.6 MPa (abs) or more in the presence of 6% to 50% by volume xenon, the following table lists the specific numerical data of the graph of FIG. 3.

TABLE 1

Pressure (MPa (abs))	Xe (% by volume)	Etch rate (depth base: $\mu\text{m}/\text{min}$ )
0.60	0	3.3
	6	10.9
	50	5.4
0.80	0	16.0
	6	26.1
	50	33.5
0.95	0	33.0
	6	108
	50	115

[0064] Table 1 shows that the etch rate (depth base) for 6% or 50% by volume xenon is much higher than the etch rate for 0% by volume xenon at pressures of 0.6 MPa (abs) or more. This is particularly remarkable at a pressure of 0.8 MPa (abs) or more.

[0065] When xenon constitutes 3% by volume, processing performance on the depth base is not particularly high. However, this does not necessarily mean that the processing method has poor processing performance. The processing method may be preferred in wide and narrow processing. In other words, the processing method according to the present embodiment may be of technical value in changing the reactive processing performance of clusters using two inert gases argon and xenon.

[0066] Although the addition of 94% by volume xenon results in a high etch rate on the weight base, it is not advantageous from a practical standpoint because xenon is expensive. Furthermore, the processing method using 94% by volume xenon had a lower etch rate on the depth base than the processing method using argon and xenon according to the present embodiment.

[0067] In the present embodiment, the percentage of the reactive gas chlorine trifluoride is controlled so as to achieve a certain level of processing performance without causing the liquefaction of the reactive gas. On the basis of the results of the example in which the reactive gas chlorine trifluoride constitutes 6% by volume, the boiling point of chlorine trifluoride, and the reactivity of chlorine trifluoride with the sample, it is supposed by experience that use of 3% by volume or more and 10% by volume or less chlorine trifluoride can also result in a certain level of processing performance without causing the liquefaction of the reactive gas. Thus, combined use of argon and xenon can improve processing performance.

What is claimed is:

1. A method for processing a surface of a sample using reactive clusters produced by adiabatic expansion of a gas mixture ejected from a nozzle into a vacuum processing chamber, the gas mixture containing a reactive gas chlorine trifluoride, a first inert gas argon, and a second inert gas xenon, wherein



the gas mixture in an inlet of the nozzle has a pressure of 0.4 MPa (abs) or more, the reactive gas constitutes 3% by volume or more and 10% by volume or less, the first inert gas constitutes 40% by volume or more and 94% by volume or less, and the second inert gas constitutes 3% by volume or more and 50% by volume or less of the gas mixture.

**2.** The method according to claim 1, wherein the gas mixture in an inlet of the nozzle has a pressure of 0.6 MPa (abs) or more, the reactive gas constitutes 5% by volume or more and 7% by volume or less, the first inert gas constitutes 43% by volume or more and 89% by volume or less, and the second inert gas constitutes 6% by volume or more and 50% by volume or less of the gas mixture.

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