Etch Rate and Surface Morphology of Polycrystalline β-Silicon Carbide Using Chlorine Trifluoride Gas

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The etch rate of the polycrystalline β-silicon carbide (SiC) substrate in a wide range from less than one to more than ten μm/min is studied using chlorine trifluoride gas at concentrations of 10-100% in ambient nitrogen at 673-973K and atmospheric pressure in a horizontal reactor. The etch rate immediately increases at the substrate temperatures between 673 and 773K over the chlorine trifluoride gas concentrations used in this study. Additionally, the etch rate at higher than 773K is independent of the substrate temperature, similar to that at the chlorine trifluoride gas concentration of 100%. The etched surface tends to be smooth at high temperatures and high chlorine trifluoride gas concentrations. The polycrystalline β-SiC etch rate can be adjusted using the combination of the gas flow rate, chlorine trifluoride gas concentration and the substrate temperature in order to obtain surfaces suitable for various purposes.

KEYWORDS: silicon carbide, etching, surface roughness, surface morphology

1. Introduction

Silicon carbide (SiC) has various useful properties, such as high thermal conductivity, high chemical stability, high mechanical hardness, and low dielectric constant [1]. However, due to its chemically and mechanically stable nature, the preparation of the SiC substrate and its surface is often very difficult, particularly, for obtaining a smooth surface and removing the damaged layer caused by various mechanical processes of grinding and slicing.

For this purpose, the authors applied chlorine trifluoride gas, for the first time, as a polycrystalline β-SiC etchant [2], since this gas is very reactive at low temperatures with a very low global warming potential. As the maximum capability evaluation, they reported that the etch rate was greater than 20 μm/min at temperatures above 723K using the chlorine trifluoride gas concentration of 100%. Additionally, the surface having step-like hills was found to be rounded and smoothed.

The industrial processes of surface preparation, such as the etching over the entire SiC substrate and the removal of its damaged layer, often prefer a low etch rate, such as less than several μm/min. Therefore, the etch rate must be adjustable and stable from low to high which is suitable for each purpose. For these purposes, the following subjects should be studied.

(i) Temperature dependence of the etch rate over a wide concentration range of chlorine trifluoride gas.

(ii) Roughness of the surface etched using various chlorine trifluoride concentrations and temperatures.

Therefore, in this study, the etch rate and the etched surface morphology of a polycrystalline β-SiC substrate are studied in detail using 10-100% chlorine trifluoride gas.

2. Experimental

In order to etch polycrystalline β-SiC by chlorine trifluoride gas, the horizontal cold-wall reactor shown in Fig. 1 was used. This reactor consists of a gas supply system, a quartz chamber and infrared lamps. A 30mm width×50mm length×0.2mm thick polycrystalline β-SiC substrate manufactured using the chemical vapor deposition method (Admap Inc., Tokyo) is horizontally held on the bottom wall of the quartz chamber. This substrate is widely used in a thermal oxidation furnace for semiconductor silicon device manufacturing, because of its very high purity [3]. Because the grain boundary and the various crystal planes included in a polycrystalline material generally tend to be non-uniformly etched to produce a very coarse surface, the etching nature and performance, such as smoothing or roughening, can be easily and clearly studied.

The substrate is heated by infrared rays emitted from halogen lamps through the quartz chamber walls. The electric power provided to the infrared lamps is adjusted based on the temperatures previously measured in ambient nitrogen (without chlorine trifluoride gas).

The gas supply system has the function of introducing the chlorine trifluoride, nitrogen and hydrogen gases. Hydrogen gas is used in order to remove the silicon oxide film and the organic contamination on the substrate surface, the same as those on the silicon surface [4]. This reactor has a small cross section above the substrate in order to achieve a very high consumption efficiency of the chlorine trifluoride gas. The height and the width of the quartz chamber are compactly designed to be 10mm and 40mm, respectively, similar to our previous studies [4, 5].

The entire process shown in Fig. 2 was used in this study. This process mainly consisted of the following three steps:

(a) cleaning the substrate surface by baking at 1373K for 10min in ambient hydrogen,

(b) changing the gas from hydrogen to nitrogen, and

(c) etching the substrate surface by the chlorine trifluoride gas.

During step (a), hydrogen gas (>99.9999%, Sumitomo Seika Kogyo Co., Ltd., Tokyo) is introduced into the reactor at atmospheric pressure at a flow rate of 2 liter/min. Water vapor and the other impurities in the hydrogen gas are removed by passing it through a liquid nitrogen trap (77 K) at the entrance of the reactor. Next, in step (b), the quartz chamber and the substrate are cooled to room temperature. The hydrogen gas present in the quartz chamber is sufficiently purged with nitrogen gas in order to avoid an explosive reaction between the hydrogen gas and chlorine trifluoride gas. During step (c), the substrate is heated and adjusted to a temperature between 673K and 973 K. The substrate is then etched by the chlorine trifluoride gas (>99.9%, Kanto Denka Kogyo Co., Ltd., Tokyo) without further purification. Chlorine trifluoride gas is diluted using nitrogen gas to adjust its concentrations between 10-100%. The flow rate of the gas mixture is 0.2 liter/min,

The average etch rate of polycrystalline β-SiC by the chlorine trifluoride gas was evaluated by the decrease in the weight of the substrate. The etch period is adjusted in order to obtain a weight decrease greater than 0.01 g (2 μm) of the initial weight of the substrate. The measurement error of the etch rate obtained in this study is roughly estimated to be less than 1 μm/min.

In order to obtain the fundamental information of chemical reactions in the reactor based on the gaseous products, a part of the exhaust gas from the reactor was fed to the quadrupole mass spectra (QMS) analyzer (Microvision, Spectra International LLC), as shown in Fig. 1. For the measurement of the mass spectra, the ionization energy and current were set to 70 eV and 1.73

mA, respectively.

The surface morphology of the polycrystalline β-SiC substrate before and after the etching was observed using an optical microscope (VC4500-PC, OMRON Corp., Kyoto) and the laser microscope (VK-9500, Keyence, Tokyo). The latter was used in order to measure the root-mean-square (RMS) surface roughness, which scan area was 100 μm. The position of the RMS roughness measurement was fixed at the center position of each substrate, so that the measurement points have the same environment for the chemical reaction.

The etch rate and the change in the surface roughness after Step (a) were measured to be negligible.

3. Results and Discussion

3.1 Etch rate

The etch rate evaluation over a wide chlorine trifluoride gas concentration range was studied after the etch rate dependence on the flow rate was evaluated.

The etch rate of the polycrystalline β-SiC substrate surface using 100% chlorine trifluoride gas in the temperature range of 673 to 973K at atmospheric pressure is measured as an extension of our previous study [2]. Fig. 3 shows the etch rate of the polycrystalline β-SiC substrate surface at various chlorine trifluoride gas flow rates. The squares, circles and triangles show the etch rate at the chlorine trifluoride gas flow rate of 0.2, 0.1 and 0.05 liter/min, respectively. As shown in Fig. 3, the etch rate at the substrate temperature less than 673K is quite low; its value is less than 1 μm/min. However, with the increasing substrate temperature, the etch rate significantly increases particularly near 723 K. At the substrate temperature of 773 K, the etch rate at the flow rate of 0.2 liter/min becomes 20 μm/min; it remains constant at substrate temperatures greater than 773 K. The etch rate decreases with the flow rates. They are 10 and 5 μm/min at the flow rates of 0.1 and 0.05 liter/min, respectively. The trend in the flat etch rate at temperature greater than 773K is considered to be maintained for each chlorine trifluoride gas flow rate.

In order to evaluate the etch rate change with the chlorine trifluoride gas concentration, the etch rate of the polycrystalline β-SiC substrate surface using 10-100% chlorine trifluoride gas in ambient nitrogen is measured at the flow rate of 0.2 liter/min, atmospheric pressure and 673-973 K, as shown in Fig. 4. In this figure, the square, reverse triangle, circle, diamond, and triangle show the substrate temperatures of 673, 733, 773, 873 and 973 K, respectively. Being consistent with Fig. 3, the etch rate at the substrate temperature of 673K is very low. At this temperature, the etch rate at the chlorine trifluoride gas concentration of 50% is nearly a half that at 100 %.

The etch rates at 733 K are significantly higher that those at 673 K. Although the etch rate seems to be proportional to the chlorine trifluoride gas concentration, the etch rate at 100% is more than twice as that at 50%. Since the etch rate in this temperature range is very sensitive to the substrate temperature, a small deviation of the substrate temperature from the set value is considered to exist and influence the etch rate at 733 K.

At the substrate temperature of 773 K, the etch rate increases with the chlorine trifluoride gas concentration; it can be clearly recognized to be proportional to the chlorine trifluoride gas concentration. At 873 and 973 K, the etch rate at each chlorine trifluoride gas concentration appears to be the same as that at 773 K. Therefore, when the substrate temperature is higher than 773 K, the etch rate over a very wide chlorine trifluoride gas concentration range in this study is concluded not to be affected by the substrate temperature. This behavior is useful for obtaining an uniform etched depth, because a non-uniform distribution of the substrate temperature is allowed.

In order to quickly discuss the rate process of the etching in this study, the Arrhenius plot of the etch rate is shown in Fig. 5. In the 1/T range lower than 0.0013, the etch rate is nearly constant; the etch rate decreases with increasing 1/T. This behavior is considered to be the change in the rate process from the transport limited regime to the reaction limited regime, with increasing 1/T. The activation energy obtained near the 1/T of 0.0014 is 500 kJ/mol.

The mechanism to cause the temperature independent etch rate at higher temperatures in this study is considered to be the same as that for silicon etching [5] which is in the transport limited regime. The following mechanism of compensation is considered to be possible to achieve the temperature-independent etch rate in this study,

(i) the etch rate increase due to the increase in the diffusivity of chlorine trifluoride gas and the overall rate constant, and

(ii) the etch rate decrease due to the decrease in the chlorine trifluoride gas concentration by the gas volume expansion in the gas phase above the substrate, with the increasing substrate temperature.

The detail of these two transport factors has been discussed based on numerical calculation in our previous study [5], which showed that the rate process of the etching was in the transport limited regime; an appropriate reactor height was considered to enable the compensation between (i) and (ii). However, because the surface reaction rate is sufficiently small at the temperatures lower than 773K, the etching process is in the reaction limited regime; the etch rate increases with the substrate temperature.

Because the measured gaseous products using the QMS over the very wide chlorine trifluoride gas concentrations and temperatures in this study were chlorine, silicon tetrafluoride and carbon tetrafluoride, which were the same as those reported in our previous study [2], the significant increase in the etch rate near 723K is considered to be simply due to the increase in the rate constant following the Arrhenuis law, not due to any change in the chemical reaction.

3.2 Surface morphology and roughness

The surface morphology of the polycrystalline β-SiC substrate surface is studied using various chlorine trifluoride gas concentrations in addition to our previous report [2] which used only 100% chlorine trifluoride gas.

Fig. 6 shows photographs of the polycrystalline β-SiC substrate surface etched using a gas mixture of chlorine trifluoride and nitrogen at 673-873K for 15 min. The concentration and the flow rate of the gas mixture are 10-100% and 0.2 liter/min, respectively. Fig. 7 shows the RMS roughness of the polycrystalline β-SiC substrate surface etched by chlorine trifluoride gas at atmospheric pressure and 673-873K for 15 min. The triangle, diamond and circle show the RMS roughness at the chlorine trifluoride gas concentrations of 10, 50 and 100 %, respectively.

The photograph indicated by 'Before etch' in Fig. 6 shows the initial surface, which was finished by mechanical polishing. Only very narrow and shallow trenches remain, and their edge is vague.

First, the change in the surface morphology etched using the chlorine trifluoride gas concentration fixed at 10% was studied. The surface etched at 733K and 10% is recognized to have circular-shaped pits. Although the etch rate under this condition is very low, its surface shown in Fig. 6 has an etched depth of 15μm. This surface shows many circle-like pits, the edge of which is clearly observed. These are considered to be the grain boundary or some disordered region which can be etched at a slightly higher etch rate.

At 773K and 10 %, the shape of the circular-shaped pits is still clearly observed, similar to that at 733K and 10 %. The photograph at 873K and 10% shows pits smaller than those at 773K and 10%. Simultaneously, the conical shape of the pits still exists. This shows that the surface etched at the low concentration of 10% has a negligible role of smoothing the surface, but rather tends to roughen it. This trend is measured using the RMS roughness, shown by the triangles in Fig. 7. Although the RMS roughness before etching is nearly 0.5μm, it increases with the increasing substrate temperature at the chlorine trifluoride gas concentration of 10%.

Next, the change in the etched surface morphology is studied using Fig. 6 at the fixed chlorine trifluoride gas concentration of 50 %. The surface etched at 733K and 50% shows the clear edge shape of the pits. The surface etched at 773K and 50% still has a clear edge of the conical-shaped pits. Although some pits still have such this clearly observed edge shape, the rest of the surface has no clear edges. The surface morphology having clear and vague edges can also be simultaneously observed at 873K and 50%. Since semi-smoothed and clear pits coexist there, the RMS roughness, indicated by the diamonds in Fig. 7, still slightly increases with the substrate temperature.

For further study, the change in the surface morphology etched at 100% is evaluated using Fig. 6. The surface etched at 673K and 100% shows the clear edge of the pits. In contrast to this, the surface etched at 733K and 100% shows the slightly vague edge of the pits. For the surface etched at 773K and 100 %, the conical-shaped pits still remain, but are few. The edge of the conical-shaped pits cannot be recognized when the surface is etched at 873 K. Since this trend in smoothing the surface appears in the RMS roughness behavior, the RMS roughness at 100%, indicated using circles in Fig. 6, slightly decreases with the increasing substrate temperature.

The decrease in the surface roughness with increasing the etch depth has been reported using the chlorine trifluoride gas concentration of 100% in our previous paper [2]. The surface roughness decreased and maintained its minimum value, with increasing the etch depth.

From the view point of the effect of the etchant gas concentration at each temperature, the shape of the pits tends to become unclear with the increasing chlorine trifluoride gas concentration. Therefore, as the overall trend, the higher temperature and the higher chlorine trifluoride gas concentration is recognized to produce a smoother surface on the polycrystalline β-SiC.

From the results obtained in this study, it is concluded that the polycrystalline β-SiC etch rate can be adjusted using the combination of gas flow rate, chlorine trifluoride gas concentration and the substrate temperature, in order to obtain surfaces suitable for various purposes. This technique is expected to be used for various purposes, such as the dry cleaning of the SiC substrate surface instead of wet method, and the removal of the damaged layer formed during the chemical mechanical polishing using diamond slurry.

4. Conclusions

In order to study a dry etching method for high purity polycrystalline β-SiC material, the etch rate and the etched surface of a polycrystalline β-SiC were evaluated using the gas mixture of chlorine trifluoride and nitrogen in the concentration range of 10-100% at 673-973K and atmospheric pressure in a horizontal reactor. The etch rate immediately increases between the substrate temperatures of 673 and 773K over the entire chlorine trifluoride concentration range. Additionally, the etch rate above 773K does not depend on the substrate temperature in this study. The surface tends to be smooth at high temperature and high chlorine trifluoride gas concentration. The polycrystalline β-SiC etch rate can be adjusted using the combination of gas flow rate, the chlorine trifluoride gas concentration and the substrate temperature, in order to obtain surfaces suitable for various purposes.

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Figurecaptions

Fig. 1. Horizontal cold-wall reactor used for etching polycrystalline β-SiC in this study.

Fig. 2. Process for cleaning and etching the polycrystalline β-SiC surface.

Fig. 3. Etch rate of the polycrystalline β-SiC substrate surface by chlorine trifluoride gas (100%) at atmospheric pressure in the temperature range between 673 and 973 K. Square: 0.2 liter/min, circle: 0.1 liter/min, and triangle: 0.05 liter/min.

Fig. 4. Etch rate of the polycrystalline β-SiC substrate surface using chlorine trifluoride gas at 10-100%, 0.2 liter/min, atmospheric pressure, and 673-973K. Square: 673 K, reverse triangle: 733K, circle: 773K, diamond: 873 K, and triangle:973K.

Fig. 5. Arrhenius plot of etch rate of the polycrystalline β-SiC substrate surface using chlorine trifluoride gas at 100 % in the temperature range between 673 and 973 K. Square: 0.2 liter/min, and circle: 0.1 liter/min.

Fig. 6. Photograph of the polycrystalline β-SiC substrate surface etched using chlorine trifluoride gas at atmospheric pressure for 15min at 673-873 K, 10-100% and 0.2 liter/min.

Fig. 7. RMS roughness of the polycrystalline β-SiC substrate surface etched by chlorine trifluoride gas at atmospheric pressure and 673-873K for 15min. Triangle: 10 %, diamond: 50 %, and circle: 100%.

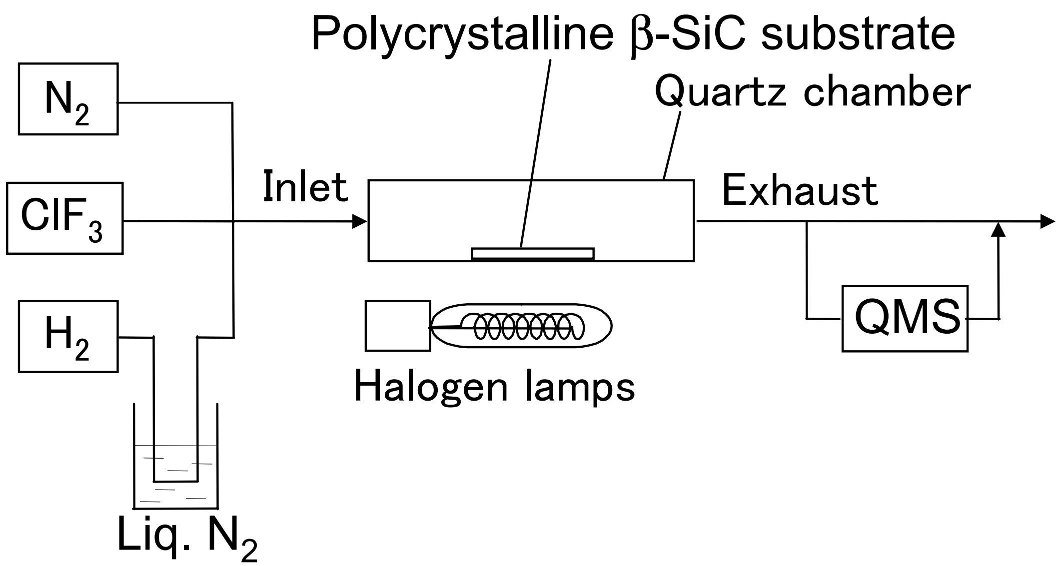
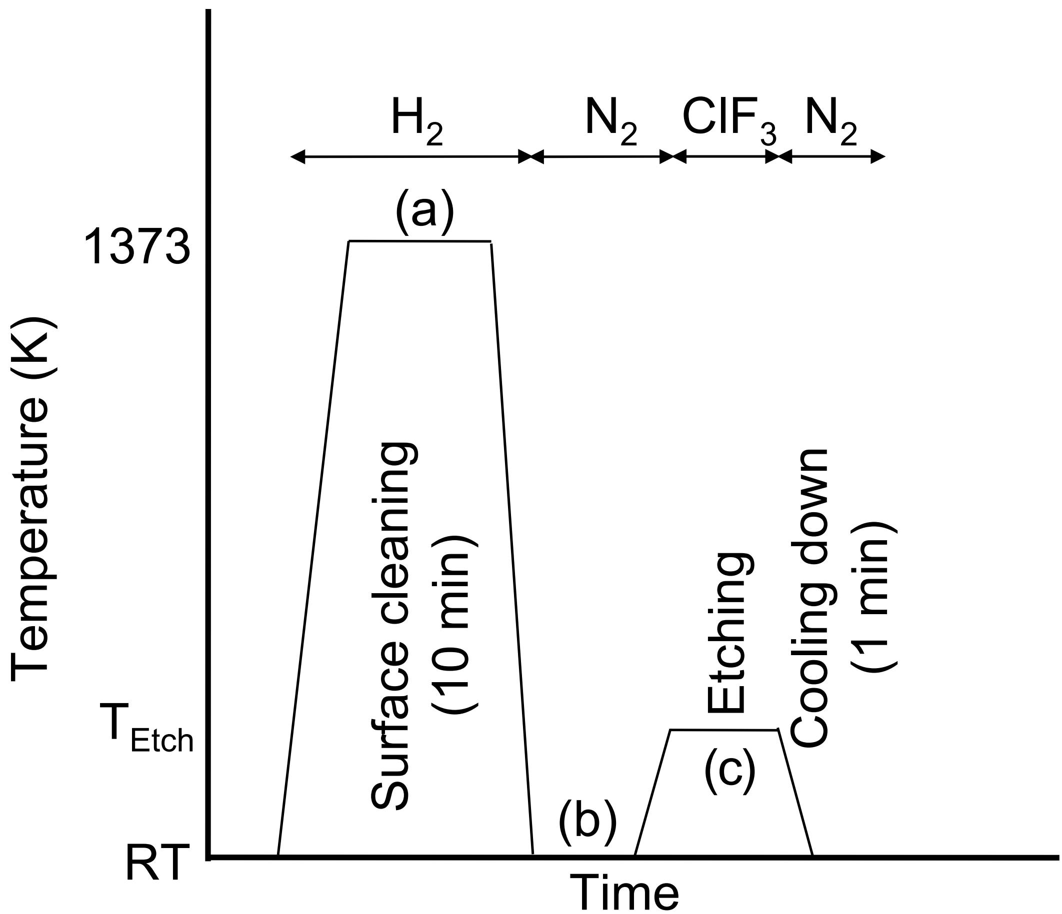
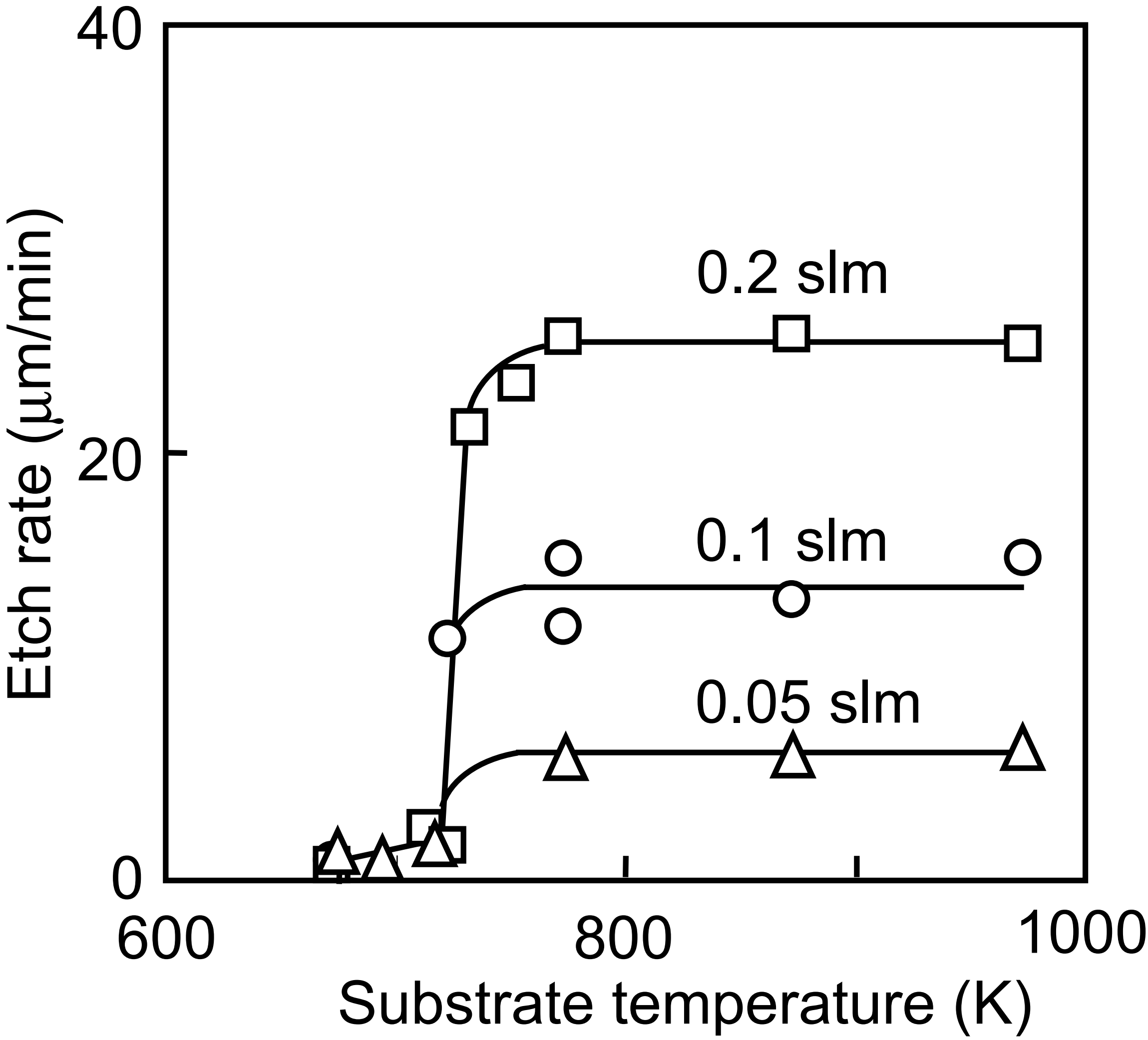

Polycrystalline β-SiC substrate
Quartz chamber
N2
ClF3
H2
Inlet
Exhaust
QMS
Halogen lamps
Liq. N2

Fig. 1



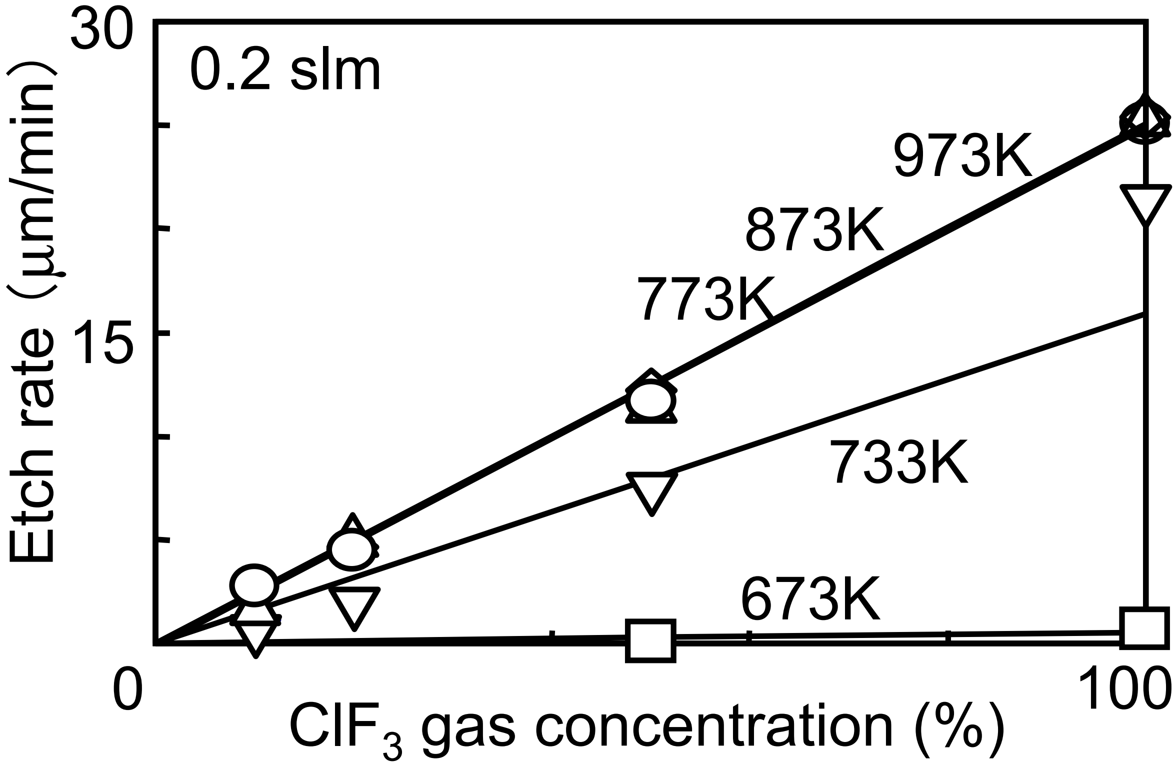
H2
N2
ClF3
N2
(a)
1373
Temperature (K)
Surface cleaning
(10 min)
Etching
Cooling down
(1 min)
T_Etch
(c)
(b)
RT
Time

Fig. 2



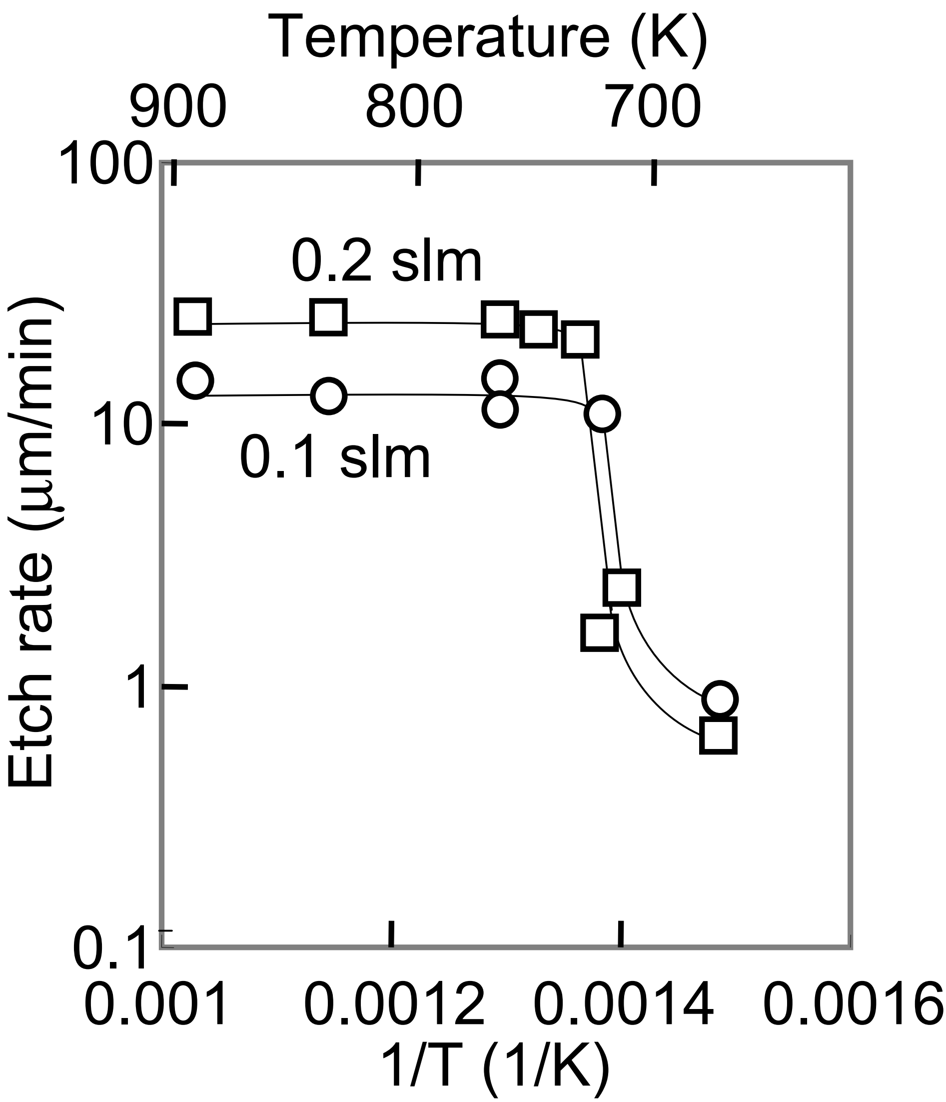
40
20
0
600
800
1000
Etch rate (μm/min)
Substrate temperature (K)
0.2 slm
0.1 slm
0.05 slm

Fig. 3



Etch rate (μm/min)
30
15
0
0.2 slm
973K
873K
773K
733K
673K
100
ClF3 gas concentration (%)

Fig. 4



Temperature (K)
900
800
700
100
10
1
0.1
0.2 slm
0.1 slm
Etch rate (μm/min)
0.001
0.0012
0.0014
0.0016
1/T (1/K)

Fig. 5

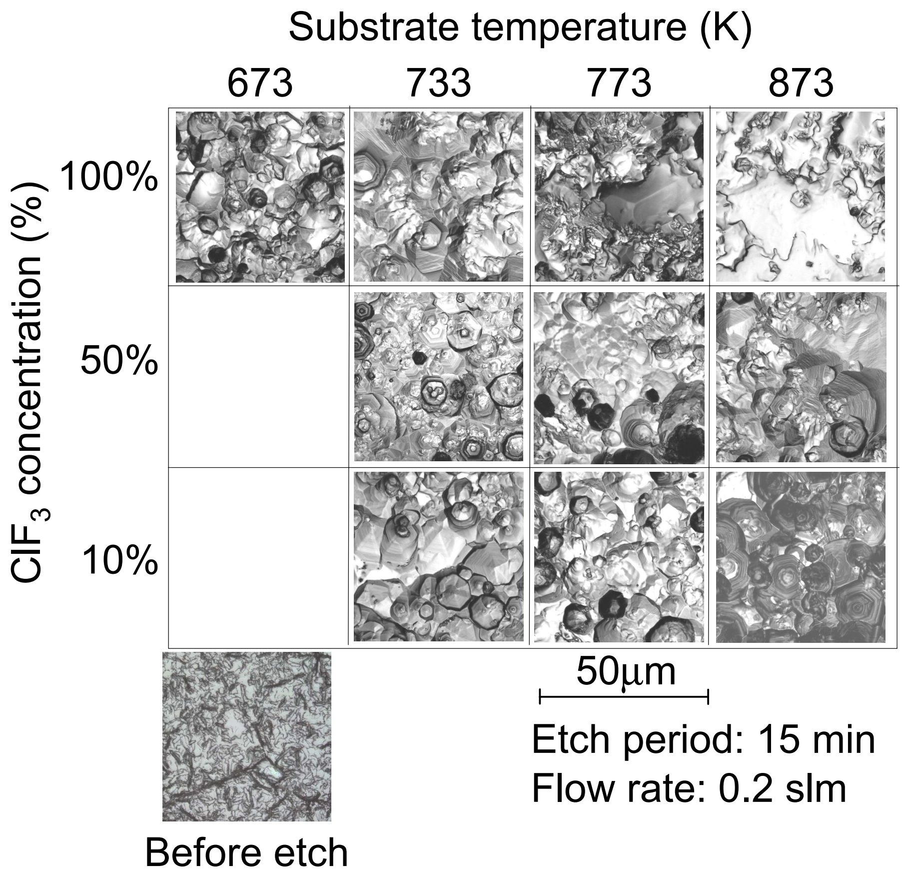
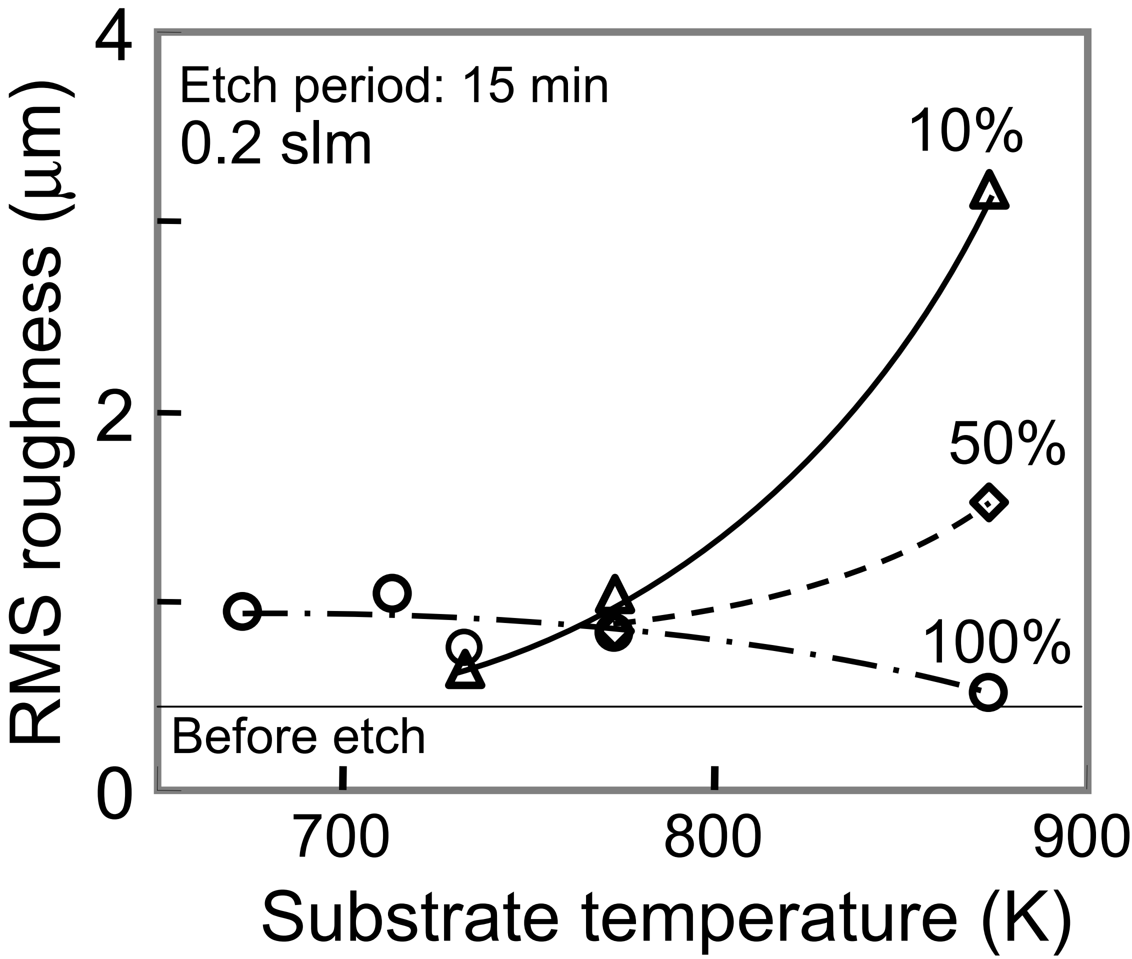

Substrate temperature (K)
673
733
773
873
ClF3 concentration (%)
100%
50%
10%
50μm
Etch period: 15 min
Flow rate: 0.2 slm
Before etch

Fig. 6



4
2
0
RMS roughness (μm)
Etch period: 15 min
0.2 slm
10%
50%
100%
Before etch
700
800
900
Substrate temperature (K)

Fig. 7