

Deposition and Etching Behaviour of Boron Trichloride Gas at Silicon Surface

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The deposition and etching at a silicon surface by boron trichloride gas were overviewed in a wide temperature range using a chemical vapour deposition reactor. At temperatures lower than 800 °C, while the silicon surface was covered with boron, the formed film thickness was ignorable. At 900 °C, the boron deposition rate increased to 0.25 $\mu\text{m min}^{-1}$. In the temperature range between 900 and 1000 °C, the boron film formation was considerable. In contrast, at 1100 °C, the silicon surface was etched at 0.36 $\mu\text{m min}^{-1}$. At temperatures higher than 1050 °C, while the etching occurred along with producing chlorosilanes, the silicon surface after the etching was still covered with boron. The boron deposition and the silicon etching might simultaneously occur at high temperatures by the boron trichloride gas. By adjusting the surface temperature to 800 °C, the boron and silicon co-deposition was possible using the gas mixture of dichlorosilane and boron trichloride.

A1. Doping; A1. Etching; A1. Surface processes; A3. Chemical vapor deposition processes; B1.

Elemental solid; B2. Semiconductor silicon

1. Introduction

Semiconductor manufacturing processes [1-4] use various gases, particularly for chemical vapour deposition (CVD) and dry etching. One of the very important elements is boron. It is not only used as a p-type dopant [5] for semiconductor silicon, but also expected as film materials for various advanced devices, such as solar cells [6], micromachines [7], photo detectors [8-10] and microelectronic devices [11]. For these purposes, the CVD and the ion implantation [1, 3-6] currently use a diborane gas. However, because a diborane gas is significantly toxic and flammable, significantly careful operations are indispensable.

In contrast, a boron trichloride gas [2] is expected to be a safe boron source for fabricating various advanced devices, because it is non-flammable and less toxic [2]. Thus, a boron trichloride gas was used for forming boron doped silicon films by a plasma enhanced CVD [6]. However, a boron trichloride gas is currently used as a useful etchant [1, 12]. The opposite applications, such as deposition and etching, may indicate that the chemical behaviour of boron trichloride gas is complicated. While the boron trichloride gas for various processes has been studied by many researchers [6-18], most of the studies have been limited to each process. In order to understand the complicated chemical nature of boron trichloride gas, the entire chemical behaviour containing deposition and etching should be overviewed. The obtained information will help designing safe and multi-purpose processes using only a boron trichloride gas.

In this study, the overall chemical behaviour of boron trichloride gas was thus studied at the silicon surface over a wide temperature range. First, the deposition and etching rate at a

silicon surface were studied at various temperatures by evaluating gas phase species and surface chemical conditions. Next, the boron and silicon co-deposition was shown to be possible by boron trichloride and dichlorosilane gases by choosing the low temperature range.

2. Experimental procedure

The horizontal cold wall reactor used in this study is shown in Fig. 1 (a). A (100) silicon wafer (30 x 30 x 0.72 mm) was placed in a quartz chamber which had the height and width of 10 and 40 mm, respectively. The wafer was heated by the infrared light through the transparent quartz chamber coming from six halogen lamps set at the outside of quartz chamber. The thermal condition was a cold wall. The boron trichloride and dichlorosilane gases were introduced at the flow rate of 100 and 0-20 sccm, respectively, along with the hydrogen gas typically at 1000 sccm from the inlet at atmospheric pressure.

A quadrupole mass spectra (QMS) analyzer and a quartz crystal microbalance (QCM) were used for the real-time measurement of chemical species in the gas phase and of the byproduct deposition at the exhaust, respectively. The QMS and QCM were installed at the position where the exhaust gases were sufficiently cooled to room temperature.

The QCM is a simple, small and low-cost sensor. The QCM frequency is sensitively decreased mainly by (i) an arrival of heavy and viscous gases and (ii) an occurrence of deposition, at the QCM surface [21]. The former is significantly quick, the latter is rather slow. In the report applying the QCM to exhaust gas evaluation for the Minimal CVD system [22], the gas property change and the byproduct deposition at the exhaust of reactor were shown to be

related to the silicon film deposition occurred in the reactor. The detection limit of QCM used in this study was 0.5 ng cm^{-2} , which was significantly lower than the silicon monolayer of 60 ng cm^{-2} .

Figure 1 (b) shows the typical evaluation process in ambient hydrogen at atmospheric pressure. First, the silicon wafer was heated to $1150 \text{ }^{\circ}\text{C}$ for 10 minutes in order to obtain a clean silicon surface by removing the existing native oxide and organic contamination. The boron trichloride gas was introduced from the inlet for 20 minutes to the silicon wafers at the temperatures of 600, 700, 800, 900, 1000, 1050 and $1100 \text{ }^{\circ}\text{C}$, individually. For performing the silicon and boron co-deposition, the dichlorosilane gas was simultaneously introduced along with the boron trichloride gas. After terminating the boron trichloride gas and dichlorosilane gas, the silicon wafer was cooled to room temperature in the ambient hydrogen.

The changes in the thickness and the weight of the silicon wafer were measured in order to evaluate the deposition rate and the etching rate. The obtained deposition rate and etching rate were the average value over the wafer surface, assuming that the changing rate during the exposure to boron trichloride gas was constant. The chemical condition of silicon surface was *ex situ* evaluated by an X-ray photoelectron spectroscopy (XPS) (Quantera SXM, ULVAC-PHI Corp., Tokyo, Japan). A secondary ion mass spectrometry (SIMS, CAMECA IMS-6f, France) was used for measuring the boron concentration in the obtained film. The SIMS measurement was performed at the Foundation of Promotion of Material Science and Technology of Japan (Tokyo).

3. Results and discussion

3.1 Deposition and etching

Figure 2 shows the thickness change rate ($\mu\text{m min}^{-1}$) of the silicon wafer after the exposure to the boron trichloride gas at the concentration of 20 % at various temperatures. In this figure, the positive and negative values were the boron deposition rate and the silicon etching rate, respectively. At the temperatures between 600 and 800 °C, the thickness change rate was negligible. This result showed that both the deposition and etching were very slow. At temperatures higher than 800 °C, the wafer thickness was shown to increase. The deposition rate was $0.25 \mu\text{m min}^{-1}$ at 900 °C. In contrast, with the increasing wafer temperature from 900 to 1100 °C, the thickness change rate decreased. At 1000 °C, the deposition rate decreased to $0.15 \mu\text{m min}^{-1}$. At 1050 °C, the thickness change rate again became nearly zero $\mu\text{m min}^{-1}$ and rather a negative value. At 1100 °C, the wafer thickness change rate further decreased to a clearly negative value. The etching rate was about $0.36 \mu\text{m min}^{-1}$ at 1100 °C. The overall trend is expressed by the solid line in Fig. 2.

Overall, with the increasing temperature from 600 to 1100 °C, the surface chemical process changed from a negligible thickness change to a deposition, then finally to an etching. The detail was real time evaluated using the QMS and QCM.

3.2 Gas phase species

In order to clarify the chemical process causing both the deposition and etching by the boron trichloride gas, the gas phase species were evaluated using the QMS. Figure 3 shows the mass spectra of the gaseous species taken from the exhaust of reactor during the boron film deposition at 1000 °C. In this figure, the partial pressure of various gaseous species was normalized using that of hydrogen, which had the highest partial pressure. This figure shows the existence of boron trichloride near 115 a.m.u. The peaks near 80, 45 and 10 were assigned to BCl_2^+ , BCl^+ , and B^+ , respectively. Because they were observed even at room temperature, they were considered to be the fragments of boron trichloride. The chlorine and hydrogen chloride, in the range between 35 and 38, were assigned to both the byproduct of boron film formation and the fragment of boron trichloride. From Fig. 3, the boron trichloride gas was assumed to form the boron film due to its decomposition by the hydrogen gas based on equation (1).

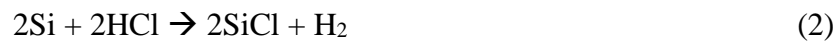


In Fig. 3, the major gaseous species were assigned to those supplied from the inlet, except for the hydrogen chloride.

The gaseous chemical species were next evaluated during the silicon wafer etching at $0.36 \mu\text{m min}^{-1}$ and 1100 °C, as shown in Fig. 4. The gas concentration was the same as that for the deposition at 1000 °C. Similar to Fig. 3, the partial pressures of BCl_3^+ , BCl_2^+ , BCl^+ , B^+ and Cl^+ were observed at 115, 80, 45, 10 and 35, respectively. These were assigned to the boron trichloride and its fragments, similar to Fig. 3. The obvious differences from Fig. 3 were the

existence of chlorosilanes, such as SiCl_4^+ , SiCl_3^+ , SiCl_2^+ and SiCl^+ at 168, 133, 98 and 63, respectively. Additionally, the chlorosilane peaks disappeared with the boron chloride peaks immediately after terminating the boron trichloride gas. The four chlorosilanes were the same as those typically observed for the silicon wafer etching by the hydrogen chloride gas at high temperatures near 1100 °C [19].

Based on the observed behaviour, the chlorosilanes were considered to be produced following equations (2) – (5) due to the etching by the hydrogen chloride gas, which was produced by equation (1) from the boron trichloride gas.



The SiCl_2 , SiHCl_3 and SiCl_4 are gaseous species. In the gas phase, the SiCl_2 is known to form $(\text{SiCl}_2)_n$ which often causes an oily silane [20] in an exhaust tube. Because the $(\text{SiCl}_2)_n$ formation was quite slow, such a slow process could be evaluated by a highly sensitive measurement, such as the QCM.

The QCM frequency behaviour was thus measured in this study. Figure 5 shows the QCM frequency change at 1100 °C after the boron trichloride gas introduction at zero seconds.

The QCM frequency quickly shifted down to the 4000 Hz lower value because of the increase in the product of the gas density and the gas viscosity [21].

In Fig. 5, after the quick frequency decrease, a continuous and gradual frequency decrease occurred. Because the QCM frequency decrease was proportional to the weight increase at the QCM sensor surface, the gradual QCM frequency decrease was assigned to the $(\text{SiCl}_2)_n$ deposition.

When the $(\text{SiCl}_2)_n$ deposition rate increased at the high temperatures, the downward shift of the QCM frequency was expected to be enhanced even from the initial stage of the boron trichloride gas introduction. The $(\text{SiCl}_2)_n$ deposition on the QCM surface immediately after the boron trichloride introduction was evaluated in Fig. 6. Because the QCM frequency shift at the temperatures between 800 °C and 900 °C did not show any significant difference, it was simply due to the gas property change, not containing the byproduct deposition. Thus, the etching rate by the hydrogen chloride gas was considered to be negligible, even though the boron deposition clearly occurred at 900 °C. With the increasing temperature from 900 °C to 1100 °C, the thickness change rate decreased from positive to negative, that is, from the deposition to the etching, respectively. Corresponding to this trend, the QCM frequency shift was enhanced. The large frequency shift at 1100 °C in Fig. 6 was considered to show the increase in the $(\text{SiCl}_2)_n$ deposition at the QCM surface even during the initial stage. This behaviour was consistent with that of the QMS measurement at 1100 °C shown in Fig. 4.

3.3 Surface chemical condition

The chemical condition of silicon wafer surface after the exposure to the boron trichloride gas was then evaluated by XPS. Figures 7 (a) and (b) show the chemical condition of boron 1s and silicon 2p orbitals, respectively, at the silicon wafer surface which was exposed to the boron trichloride gas at 800 °C. While silicon peaks appeared at the surface, as shown in Fig. 7 (b), Fig. 7 (a) simultaneously and clearly showed the existence of boron [23, 24] at the silicon wafer surface. This indicated that the boron film could be formed at the silicon surface even though significantly thin at 800 °C, at which temperature the deposition rate was negligible, as shown in Fig. 2.

The surface being exposed to boron trichloride gas at 900 and 1000 °C showed the existence and non-existence of boron and silicon, respectively, by the XPS. Thus, in the temperature range between 900 and 1000 °C, the boron film was considered to be formed at the silicon surface.

Next, Figure 8 shows the boron 1s spectra of the silicon surface after being exposed to the boron trichloride gas at 1100 °C, at which temperature the etching rate was $0.36 \mu\text{m min}^{-1}$. The bonding energy of boron became 191 eV which was assigned to boron bonded with oxygen [24] which was caused due to the oxidation. This figure clearly showed that the boron atoms remained after the significant etching. This result showed that the boron deposition and the silicon etching simultaneously occurred at the surface. At the high temperatures, the etching by the byproduct of hydrogen chloride gas became faster than the deposition by the boron trichloride gas, while both of the processes were accelerated.

In the last part of this section, the surface process is studied in detail, from the viewpoint of an amount of hydrogen chloride gas. First, the chemical reaction in equation (1) is assumed to occur only at the surface. By forming a solid boron film of n mol, a hydrogen chloride gas of $3n$ mol is produced and emitted to the gas phase. Simultaneously, the hydrogen chloride gas is expected to etch the silicon wafer surface, following equations (2) – (5). Additionally, the boron film formed at the surface is considered to be etched, following equation (6).



In order to perfectly etch off the formed boron film of n mol, the hydrogen chloride gas of more than $3n$ mol must be supplied to the surface. However, because some part of the hydrogen chloride gas produced by equation (1) is already transported away in the gas phase, an amount of the hydrogen chloride gas still remained around the surface is less than $3n$ mol. Thus, when equation (1) occurs only at the surface, some part of the boron film could remain. This behaviour agrees with that at the temperatures lower than 1000 °C in Fig. 2.

At the temperatures higher than 1000 °C, the thermal decomposition of boron trichloride, in equation (1), is expected to additionally occur in the gas phase. While the produced boron may be transported away in the gas phase in a form of small particles, the hydrogen chloride gas can arrive at the wafer surface. Assuming the gas phase reaction rate follows the Arrhenius law, the hydrogen chloride gas produced in the gas phase exponentially increases and etches the surface with those produced by the surface reaction. Thus, the wafer surface is significantly etched; the

etching rate increases with the increasing temperature higher than 1050 °C, as shown in Fig. 2.

However, because the rate of boron film formation in equation (1) also increases due to the high temperature, the boron film formation and the surface etching simultaneously occur. The surface consequently has boron atoms after being exposed to the boron trichloride gas at high temperatures, as shown in Fig. 8.

Overall, the change rate behaviour shown in Fig. 2 is explained by the surface reaction and the gas phase thermal decomposition of boron trichloride gas.

3.4 Co-deposition of boron and silicon

From Figs. 2 and 7, the boron trichloride gas is expected to have a slow deposition rate at the temperatures lower than 800 °C. Such a slow rate was expected to be useful for the boron doping of the silicon film deposition. The film was thus formed using the dichlorosilane gas and boron trichloride gas at the flow rate of 20 sccm and 100 sccm, respectively, at 800 °C for 20 minutes. The 20- μ m-thick film was obtained on the silicon surface. Figures 9 and 10 showed the XPS *ex-situ* measured for the chemical condition of silicon and boron, respectively, at the obtained film surface. The boron at 191 eV indicated that the film surface contained boron oxide [24]. Because the silicon and boron were clearly observed, the co-deposition of boron and silicon was considered to be successfully performed at the silicon wafer surface. The average boron concentration in the obtained film was nearly 50%, as measured by SIMS. Such a high concentration is considered to be possible from the phase diagram [25].

3.5 Chemical reaction process by boron trichloride

The results obtained in this study showed that the boron trichloride gas could produce the boron film and etch the silicon surface depending on the silicon surface temperature.

Additionally, the dichlorosilane gas mixed with the boron trichloride gas could produce the boron-silicon mixture film. The overall chemical behaviour of boron trichloride gas is schematically shown in Fig. 11.

The boron trichloride gas is decomposed to form the boron film and the hydrogen chloride gas at the low and high temperatures. At the high temperatures, because the amount of hydrogen chloride increases due to the thermal decomposition in the gas phase, the silicon surface etching becomes active and fast. Thus, the boron deposition rate tends to decrease with the increasing etching rate. Finally, the deposition was switched to the etching. Such a surface process change appeared with the increase in the partial pressure of the chlorosilanes on the QMS and the increase in the deposition of $(\text{SiCl}_2)_n$ on the QCM surface. The boron trichloride decomposition with the reversible reactions of silicon and hydrogen chloride was concluded to exist at the silicon surface.

Choosing the temperature for adjusting the reversible reactions, the silicon film can be produced using the gas mixture of dichlorosilane and boron trichloride without using the significantly toxic and burnable gas, such as diborane.

The quality of the obtained film should be evaluated in future, because this process may become practical and industrial for producing semiconductor materials.

4. Conclusions

The deposition and etching behaviour by the boron trichloride gas were studied at the silicon surface and at various temperatures in a chemical vapour deposition reactor. At the temperatures lower than 800 °C, the silicon surface was covered with a significantly thin boron layer but the boron film formation rate was very low. In the temperature range between 900 – 1000 °C, the boron film formation at the silicon surface was observed. The boron deposition rate at 900 °C was $0.25 \mu\text{m min}^{-1}$. At the temperatures higher than 1050 °C, while the silicon surface was still covered with the boron atoms after the exposure to the boron trichloride gas, it was significantly etched to produce chlorosilanes because of the high amount of hydrogen chloride, which was the byproduct of the boron trichloride decomposition. Taking into account the reversible reactions of the deposition and the etching, the gas mixture of dichlorosilane and boron trichloride could perform the boron and silicon co-deposition in the low temperature range.

Acknowledgment

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Figure captions

Figure 1 (a) Horizontal cold wall reactor and (b) process used in this study.

Figure 2 Wafer thickness change rate due to deposition and etching caused by boron trichloride gas on silicon surface at various temperatures.

Figure 3 Quadrupole mass spectra of exhaust gas during boron film deposition at 1000 °C.

Figure 4 Quadrupole mass spectra of exhaust gas during silicon etching at 1100 °C.

Figure 5 QCM frequency change versus time after introducing boron trichloride gas at 1100 °C.

Figure 6 QCM frequency shift immediately after introducing boron trichloride gas at various temperatures.

Figure 7 Chemical condition of (a) boron 1s orbital and (b) silicon 2p orbital after exposed to boron trichloride gas at 800 °C.

Figure 8 Chemical condition of boron 1s orbital after exposed to boron trichloride gas at 1100 °C.

Figure 9 Chemical condition of boron 1s orbital after exposed to boron trichloride gas and dichlorosilane gas at 800 °C.

Figure 10 Chemical condition of silicon 2p orbital after exposed to boron trichloride gas and dichlorosilane gas at 800 °C.

Figure 11 Schematic of chemical reactions of boron trichloride and dichlorosilane at silicon surface.

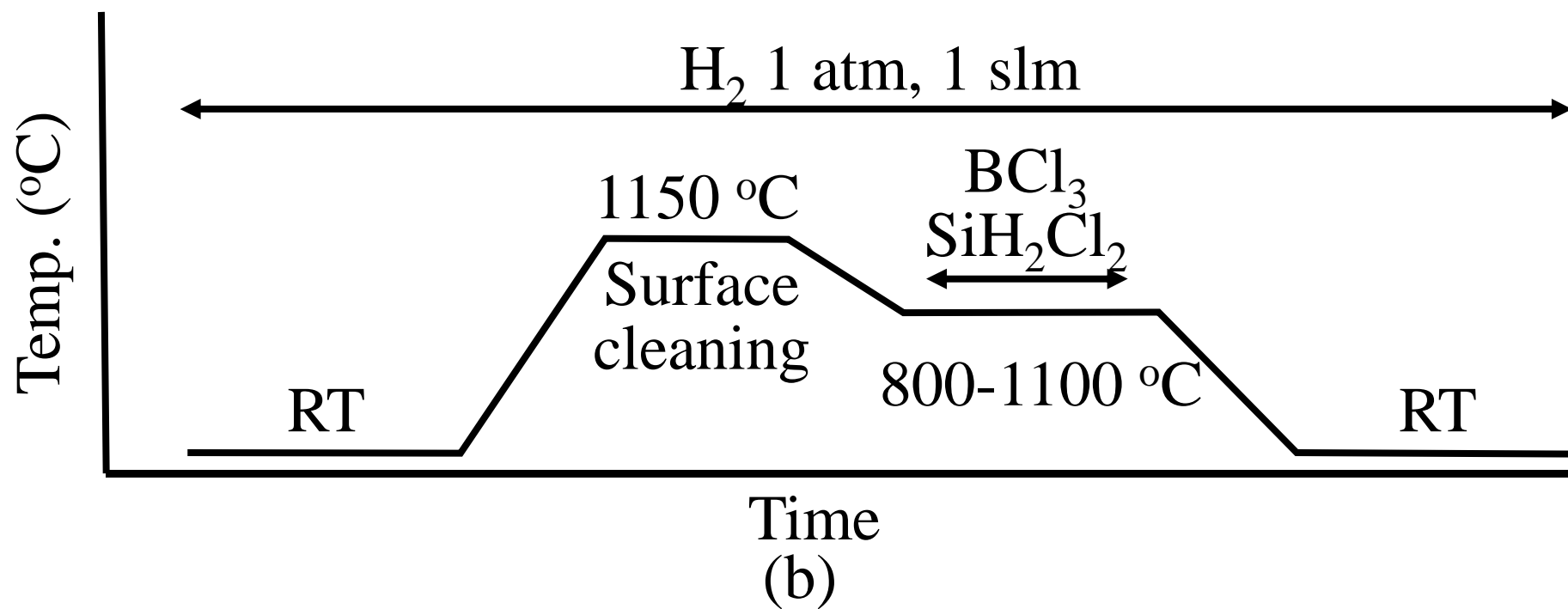
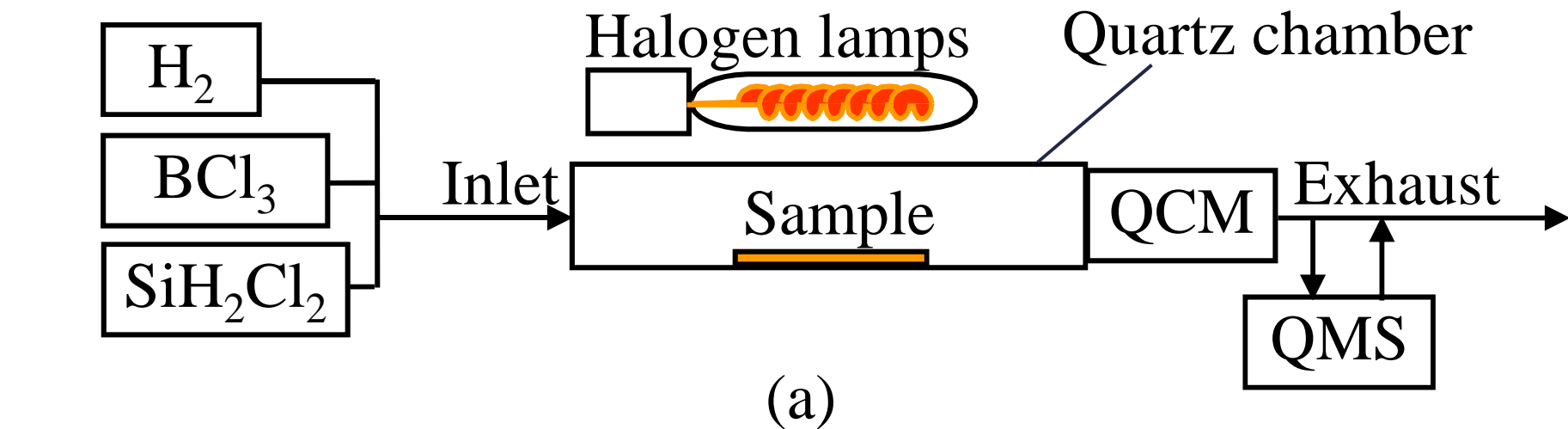


Fig. 1

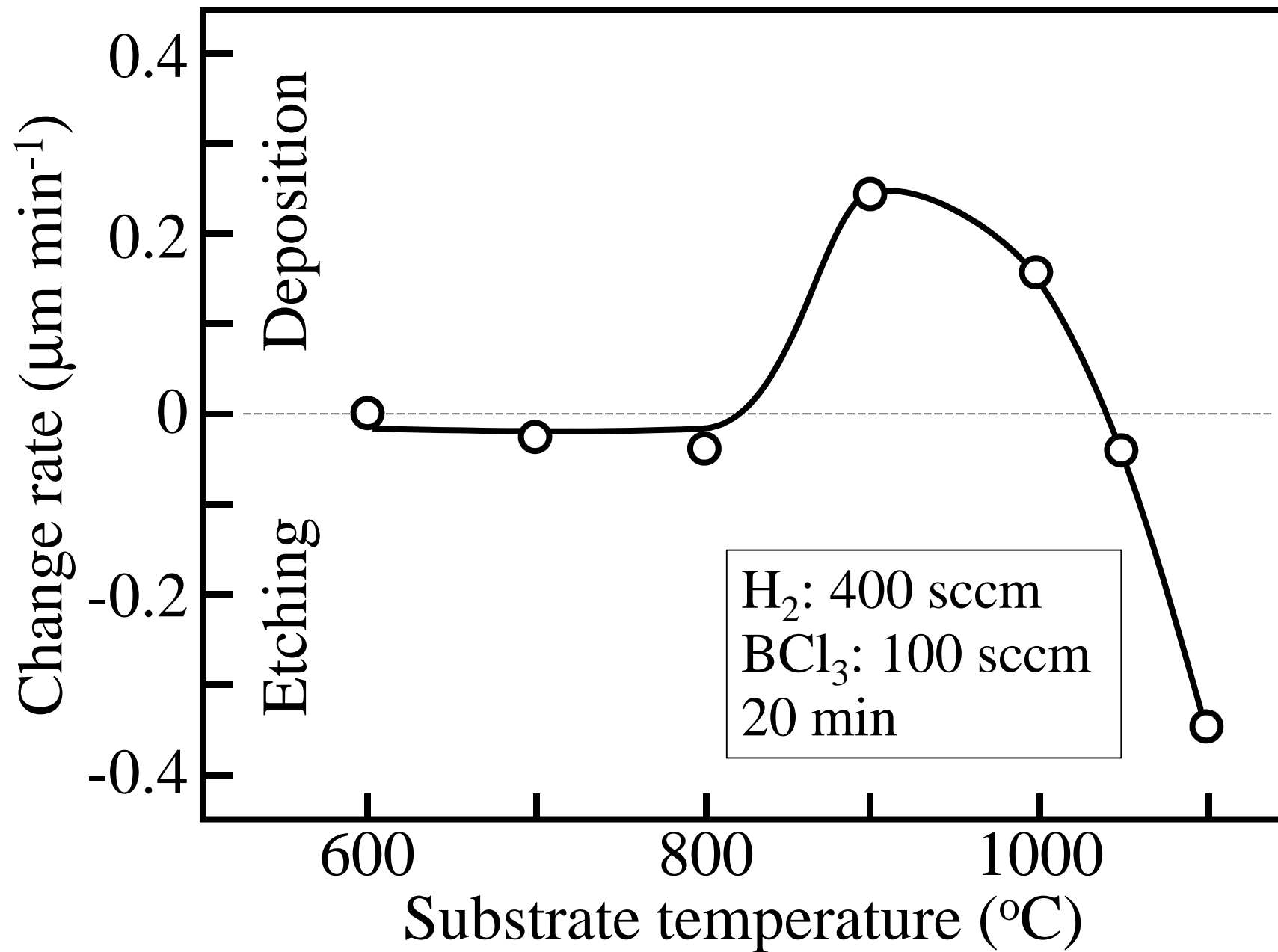


Fig. 2

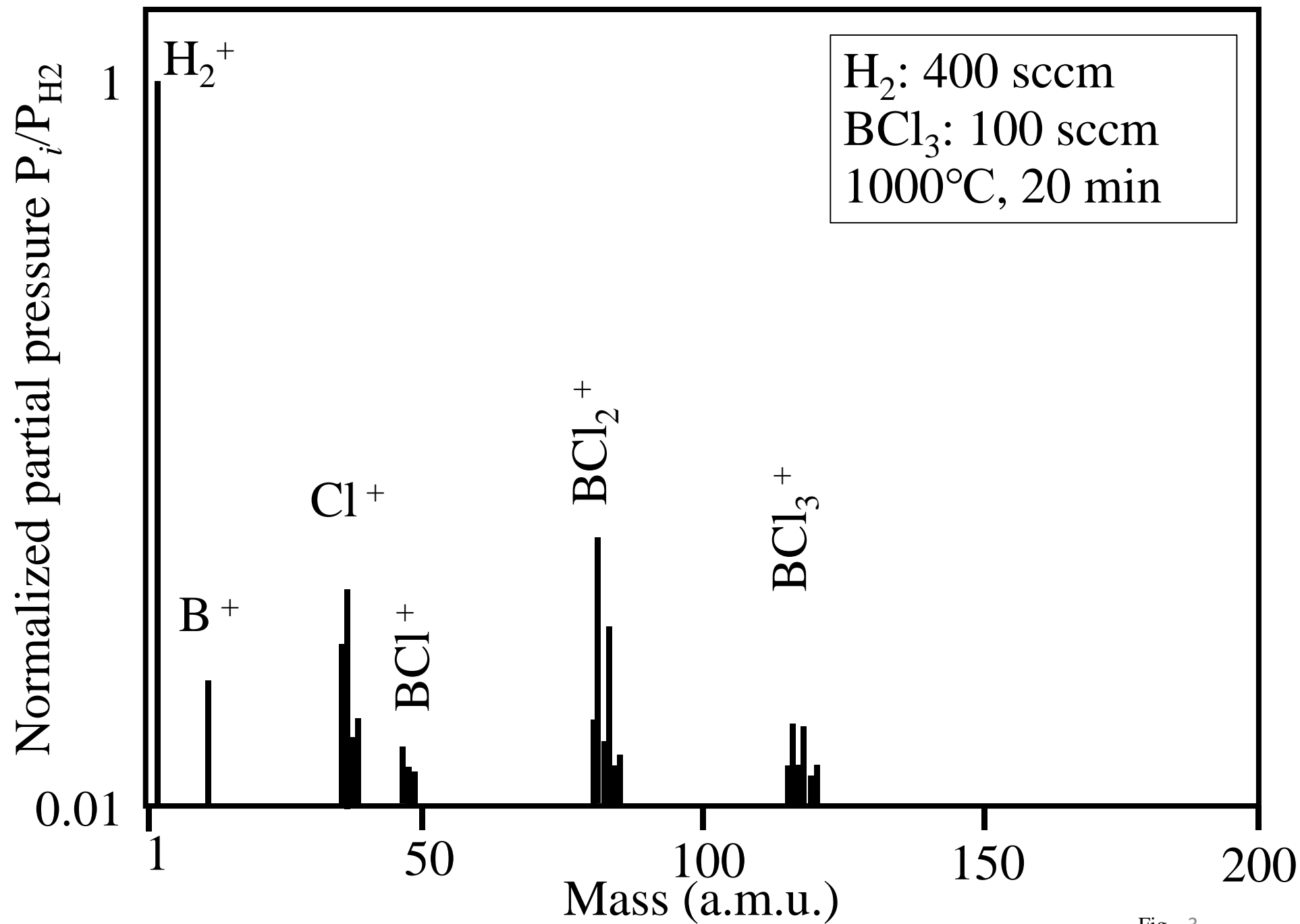


Fig. 3

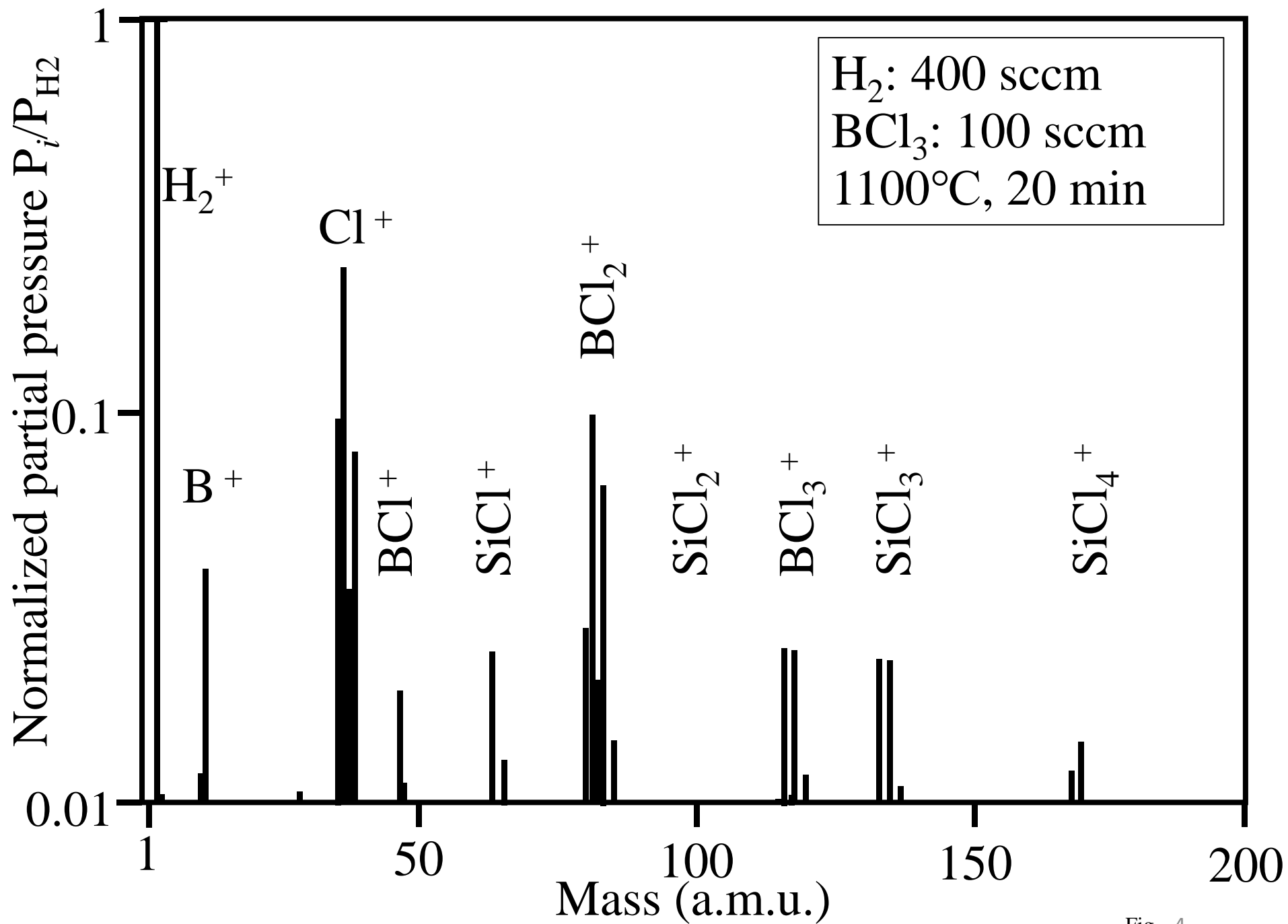


Fig. 4

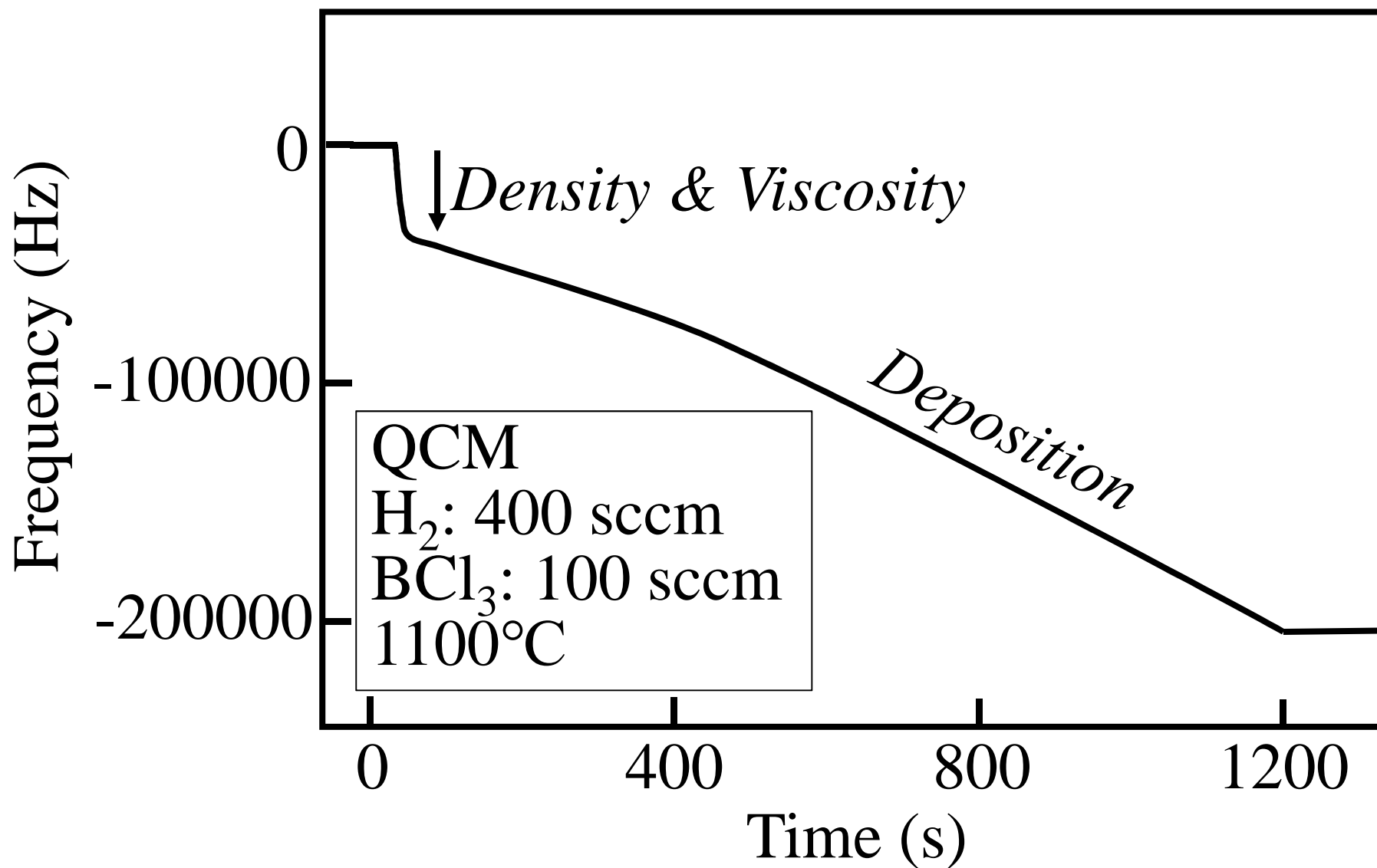


Fig. 5

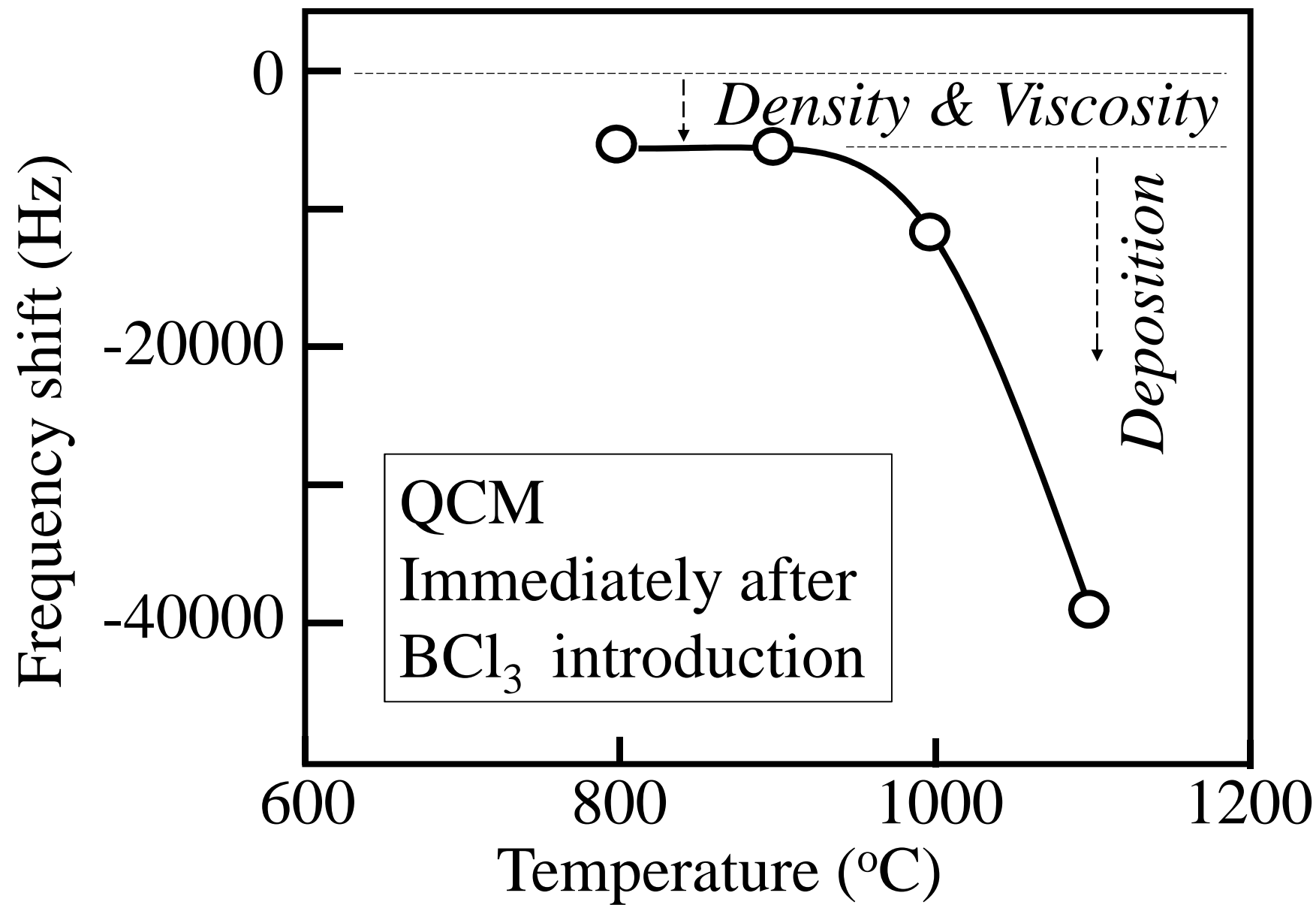


Fig. 6

H_2 : 400 sccm, BCl_3 : 100 sccm, 800 °C, 20 min

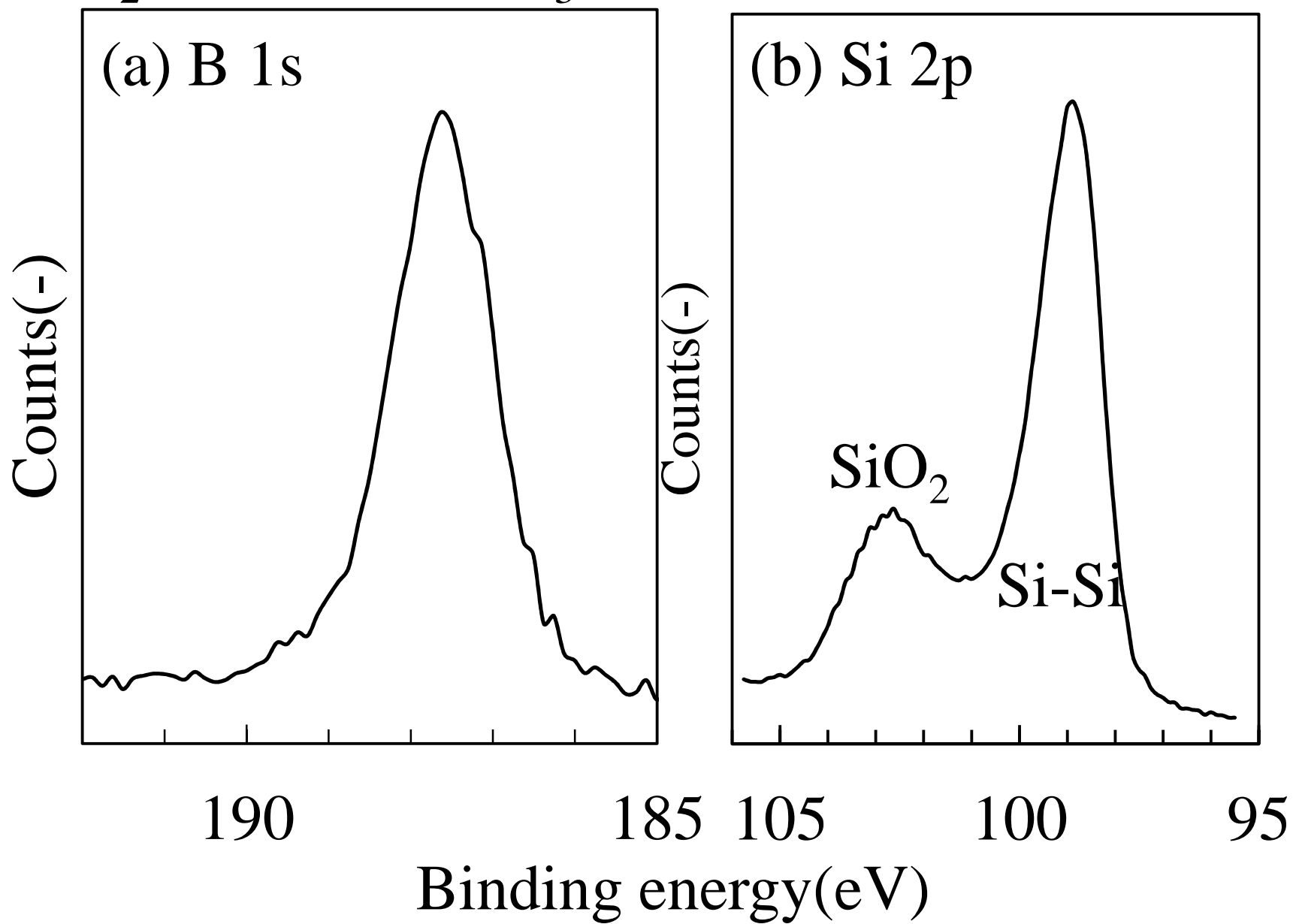


Fig. 7

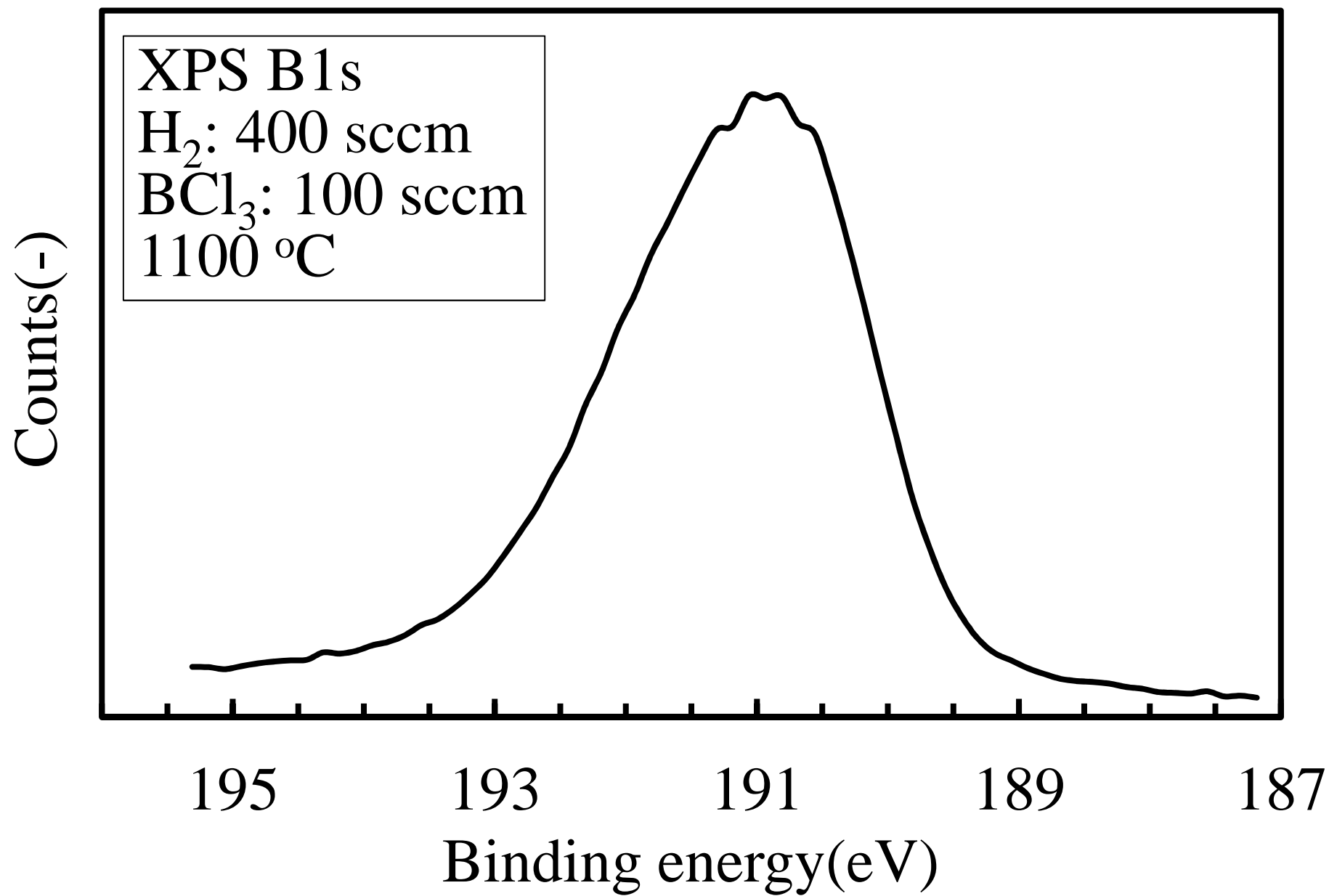


Fig. 8

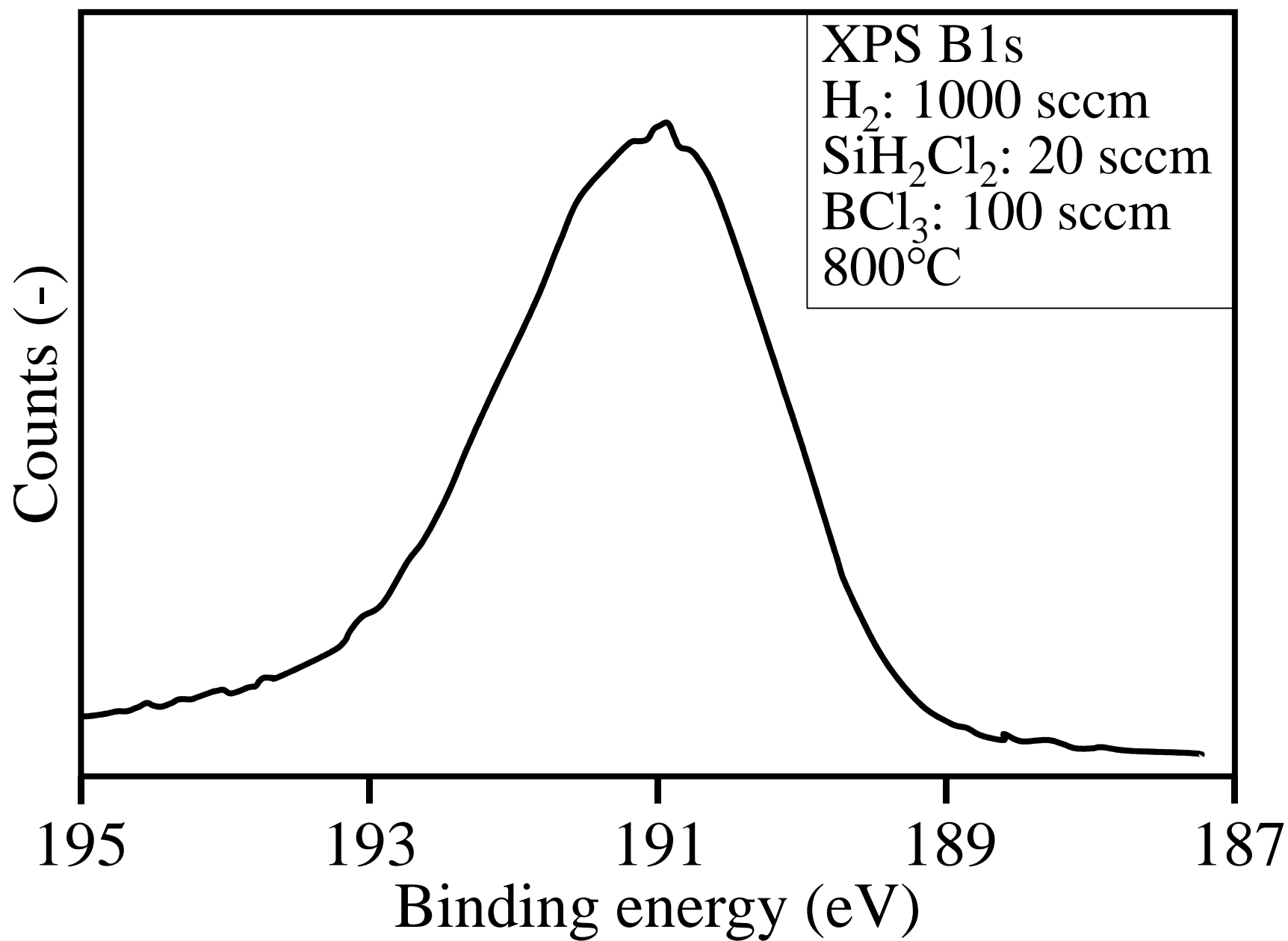


Fig. 9

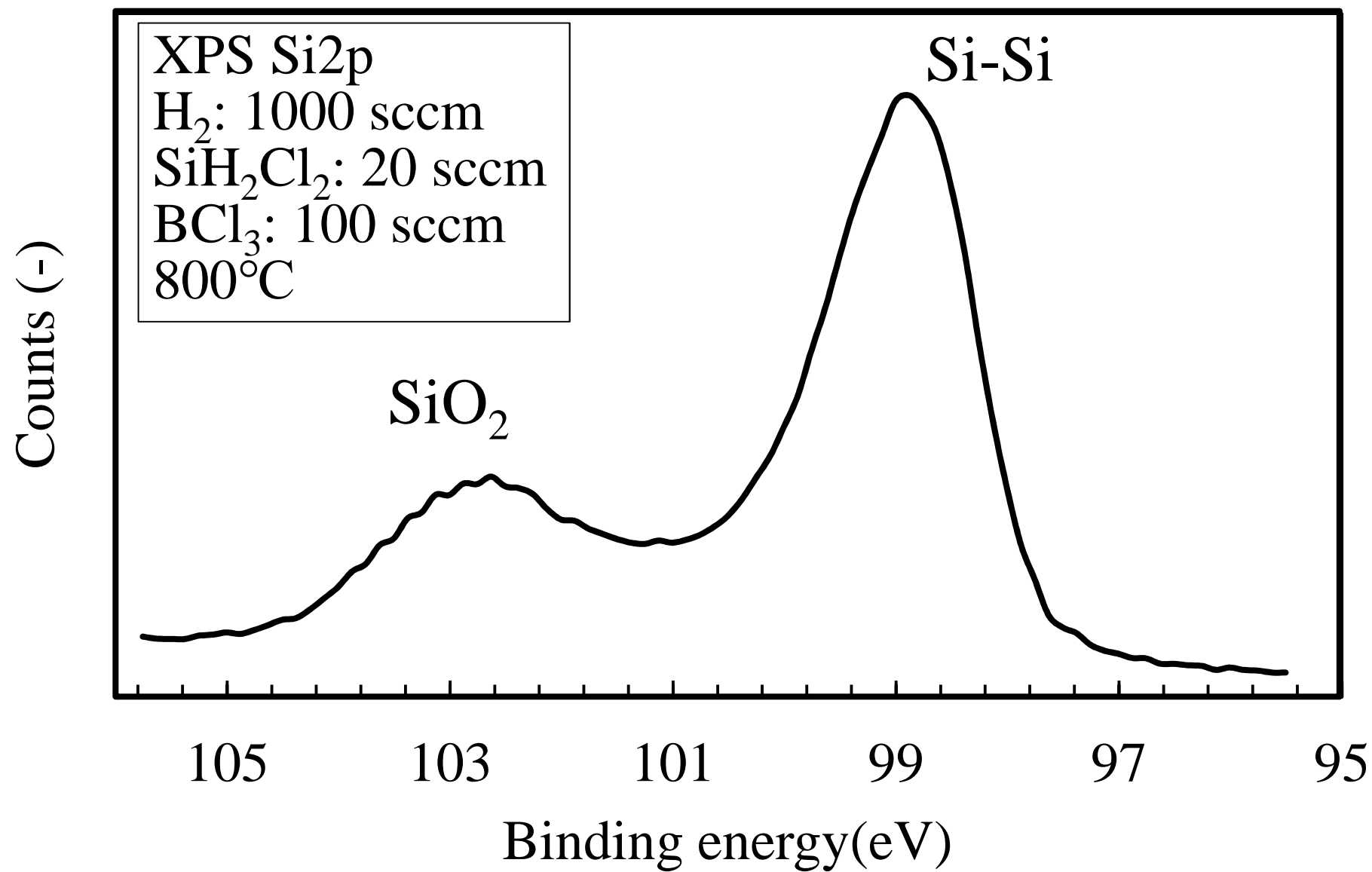


Fig. 10

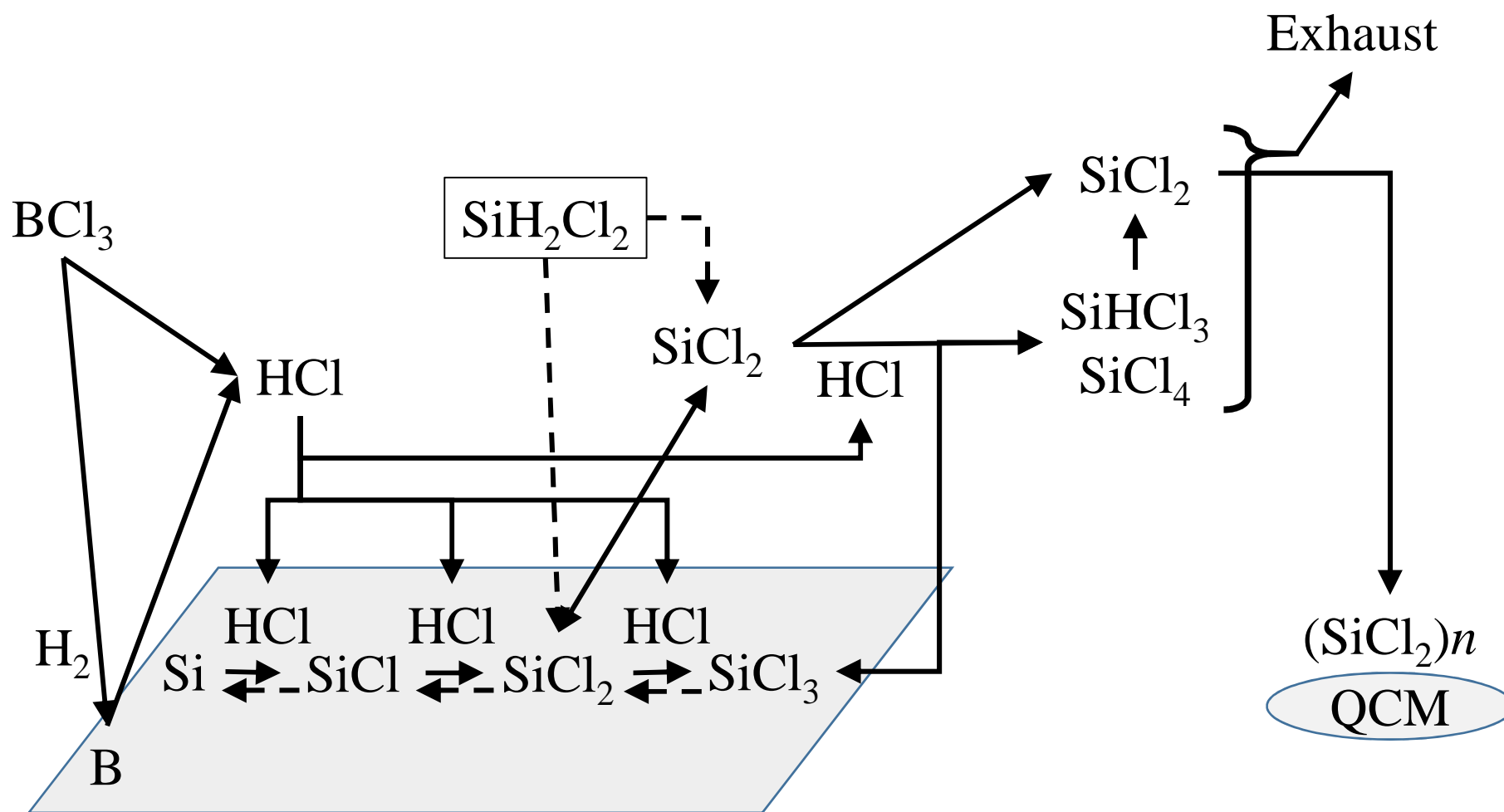


Fig. 11