# Yttrium Oxide Film for Protecting Quartz Glass Surface from Etching by Long-Term Exposure to Chlorine Trifluoride Gas at Room Temperature

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The anticorrosive property of yttrium oxide was evaluated using chlorine trifluoride gas. After the exposure to chlorine trifluoride gas at room temperature for the total time longer than 1000 minutes, the yttrium oxide film, formed on a quartz glass surface, did not show any etching behavior and surface morphology change, while the non-coated quartz glass showed a rough surface with the etching depth of nearly 0.1 mm. Because yttrium oxide had no chemical reaction with chlorine trifluoride gas at temperatures less than 300 °C, yttrium oxide film is expected to protect the quartz glass from etching by chlorine trifluoride gas at room temperature for a significantly long time.

Keywords: Yttrium oxide, chlorine trifluoride gas, coating film, quartz glass, etching

1. Introduction

Semiconductor processes use various reactive gases [1, 2]. For example, chemical vapor deposition (CVD) [1-5] consisting of film formation and reactor cleaning, uses highly reactive gases, such as hydrides, halides and organic metals at various temperatures and pressures. Specifically, significantly corrosive gases containing halogen atoms, such as hydrogen chloride and chlorine trifluoride, are used for the non-plasma cleaning of various parts in the CVD reactor. Because surfaces of the reactor parts are frequently exposed to these corrosive gases, they are very often coated with anticorrosive films. One of the anticorrosive films is yttrium oxide, which is widely used for protecting the quartz glass surface.

Quartz glass is one of the most important materials for the CVD reactor. The thinning and roughening of the quartz glass chamber due to the etching by the corrosive gases may reduce its entire mechanical strength and possibly cause a serious accident. In addition to this, imperfect fitting empirically occurs at the quartz glass flange, which is used at room temperature for tight connections with the metallic parts *via* a rubber gasket. This trouble is often caused by the significantly slow etching of the quartz glass surface by corrosive gases over a very long time. For avoiding such problems, the quartz glass surface should be coated with an anticorrosive material, such as the yttrium oxide ($Y_2O_3$) [6-9].

Recently, the CVD reactor cleaning process of a silicon carbide film [10-15] has been developed using chlorine trifluoride gas in order to reduce production cost of the silicon carbide power devices [3-5]. Because of the significant chemical stability of the silicon carbide, a strong

oxidant, such as chlorine trifluoride gas, was preferred for the silicon carbide CVD reactor cleaning. Such a highly reactive condition induces a significant etching of the reactor parts including the quartz glass. For achieving an industrially applicable cleaning process, the damage to the quartz glass by the chlorine trifluoride gas [16] should be suppressed. For this purpose, yttrium oxide film is expected to be useful. However, its anticorrosion ability to chlorine trifluoride gas has not been evaluated. Practically, the long-term exposure is important.

In this study, yttrium oxide was studied as a coating film material that stop etching by chlorine trifluoride gas. First, the occurrence of a chemical reaction between yttrium oxide and chlorine trifluoride gas was evaluated at various temperatures, using a powder form sample which was expected to have a high reaction rate due to the great surface area. Next, the capability of yttrium oxide film as the coating material of quartz glass surface was evaluated. After exposure to the chlorine trifluoride gas at room temperature for about 1000 minutes, the yttrium oxide coated and non-coated quartz glass surfaces were compared in detail, particularly focusing on the etching depth and the surface roughness.

## 2. Experimental procedure

In this study, the powder-form yttrium oxide was first used at various temperatures in order to obtain the entire view of the chemical reaction behaviour with chlorine trifluoride gas. Next, the yttrium oxide film coating the quartz glass surface was exposed to chlorine trifluoride gas at room temperature for a long time.

The etching reactor used in this study is shown in Fig. 1. A sample piece to be etched was placed in a quartz chamber. The sample piece was heated by infrared light emitted from six halogen lamps, placed outside the quartz chamber. The chlorine trifluoride gas often with a nitrogen carrier gas was supplied from gas cylinders via stainless steel tubes. The chlorine trifluoride gas etched the sample piece, such as the silicon carbide, for the etching study [17]. Simultaneously, the quartz glass chamber wall was etched following the chemical reactions [16] shown in Fig. 1. In order to evaluate the occurrence of chemical reactions between the yttrium oxide and the chlorine trifluoride gas, the yttrium oxide powder was contained in a square-shaped quartz glass tray and placed along with the silicon carbide plate at the sample piece position in the reactor.

The gas tube and the quartz chamber were connected using stainless steel flanges and quartz glass flanges at the gas inlet and at the gas exhaust. The stainless steel flange and the quartz glass flange were maintained at temperatures less than 30 $^{o}$C using flowing room air around them. Figure 2 shows a photograph of the quartz glass chamber shown in Fig. 1. The inlet and the exhaust had flanges made of flat-shaped transparent plates that had been mechanically polished. In order to evaluate the anticorrosion ability, the exhaust flange was coated with a yttrium oxide film, while the inlet flange was not coated. The yttrium oxide film was formed by the CVD method on the quartz glass flange surface (TOKITA CVD Systems Co., Ltd., Nagaoka, Japan).

The inlet flange was frequently opened and exposed to air when the sample piece was loaded and unloaded. In contrast, the exhaust flange was maintained closed, except of a few maintenance operations. The chlorine trifluoride gas arrived at the inlet flange had a high concentration that was

adjusted for the etching study. At the exhaust flange, the chlorine trifluoride gas concentration was lower than that at the inlet flange, due to consumption by the etching that occurred in the reactor. In order to account for the influence depending on the inlet and exhaust positions, the quartz chamber, both side flanges of which were not coated, was used as the reference.

Figure 3 shows the geometries of the stainless steel flange and the quartz glass flange. These two flanges were tightly connected to each other in order to avoid any gas leaks. Both of the flanges consisted of a flat plate and gas channel. The stainless steel flange has dual rubber gaskets (Kalrez, 4079, Du Pont, USA). The significantly small and thin space that existed between the inside and outside rubber gaskets was evacuated by a vacuum pump for maintaining no gas leakage. The space consisting of the stainless steel flange, the quartz glass flange and the inner rubber gasket was exposed to the chlorine trifluoride gas. Thus, the hatched region of the quartz flange in Fig. 3 (b) could undergo etching.

The exposure of the quartz glass flange to the chlorine trifluoride gas was performed along with the etching of the sample piece placed in the quartz chamber. The typical etching process is shown in Fig. 4. First, the sample piece was heated from room temperature in ambient nitrogen. After reaching the etching temperature, such as room temperature – 700 ºC, the chlorine trifluoride gas was introduced into the quartz chamber to etch the sample piece. After terminating the chlorine trifluoride gas flow, the sample piece was cooled to room temperature in ambient nitrogen. The time for supplying the chlorine trifluoride gas was recorded and evaluated. The chemical reaction

between the yttrium oxide powder and the chlorine trifluoride gas was evaluated following the process shown in Fig. 4.

After the exposure, the surface height of the flanges was evaluated using a non-contact three-dimensional NH-3SP surface profiler (Mitaka Koki Co., Ltd., Tokyo, Japan). The surface morphology and the surface roughness were measured by a VK-X250 laser microscope (Keyence Corp., Tokyo, Japan). The chemical condition was analyzed by X-ray photoelectron spectroscopy (Quantera SXM, ULVAC-PHI Corp., Tokyo, Japan).

## 3. Results and discussion

### 3.1 Reaction occurrence of yttrium oxide

For quickly evaluating the entire view of the chemical reaction between yttrium oxide and chlorine trifluoride, the yttrium oxide powder was used, because the small particles have a high surface area to make the chemical reactions fast. Figure 5 shows the weight change (%) of the yttrium oxide powder after exposure to the chlorine trifluoride gas at 100 % for 10 minutes at temperatures from room temperature to 600 $^{o}$C. The weight change at temperatures less than 300 $^{o}$C was near 0 %. At 500 $^{o}$C and 600 $^{o}$C, the weight increase in the powder was 18 % and 22 %, respectively. This indicated the occurrence of the change from yttrium oxide ($Y_2O_3$) to yttrium trifluoride ($YF_3$), the molecular weights of which were 225.8 and 145.9, respectively. When all of the yttrium oxide was changed to yttrium fluoride, the weight increased (145.9 x 2 / 225.8 =) 129%. The composition of the sample powder after the exposure to the chlorine trifluoride gas was

evaluated and shown in Fig. 6. Agreeing with the weight change behavior at 300 $^{o}$C, the fluorine content was significantly low; the oxygen content was maintained at the same value as that at room temperature. In contrast, after exposure to the chlorine trifluoride gas at 500 $^{o}$C and 600 $^{o}$C, the fluorine content increased from zero % to 41% and 65%, respectively. Consistently, the oxygen content decreased from 63% to 30% and 8% at 500 $^{o}$C and 600 $^{o}$C, respectively. This indicated the occurrence of the following chemical reaction.

$$2Y_2O_3 + 4ClF_3 \rightarrow 4YF_3 + 2Cl_2 + 3O_2 \quad (1)$$

3.2 Yttrium oxide film coating

The yttrium oxide film formed on the quartz glass was studied from the viewpoint of long term anti-corrosion. The yttrium oxide film thickness formed on the quartz glass flange is shown in Fig. 7. The upper-right and upper-left edges had the maximum thickness of 230 nm. The yttrium oxide film thickness at the bottom was thinner than that at the top. The minimum thickness was 150 nm at the center bottom position. The square at the center position corresponded to the gas channel. The region around the gas channel, as shown in Fig. 3, was exposed to the chlorine trifluoride gas.

The total exposure time to the chlorine trifluoride gas was 1012 minutes in this study. For most of the exposure time, the chlorine trifluoride gas concentration and the gas flow rate were 100 % and 50 sccm, respectively. A photograph of the quartz chamber after the 1012 minutes exposure is shown in Fig. 8. The overall view of the quartz chamber is shown in Fig. 8 (a). The right and left edges were the inlet and exhaust flanges, respectively. The center of the quartz chamber

body had a hazy appearance, which was caused by the etching of the inside surface of the quartz chamber by the chlorine trifluoride gas at the various etching temperatures, as shown in Fig. 4. Figs. 8 (b) and (c) show a close view of the inlet and exhaust flanges, respectively. The exhaust flange, yttrium-oxide coated, showed an appearance similar to that before the exposure, as that shown in Fig. 2 (c). In this figure, the outside edge lines of the quartz chamber body could be clearly recognized through the transparent flange. In contrast, the non-coated inlet flange showed a hazy appearance at the surface around the gas channel, obviously different from that shown in Fig. 2 (b) .

In order to evaluate the details of changes in the surface appearance shown in Fig. 8 (b), a closer view is shown in Fig. 9 (a); the typical outline is shown in Fig. 9 (b). In these figures, the center square hole is the gas channel. The region from the gas channel edge to its peripheral showed a hazy appearance caused by the etching.

The surface appearance and the surface roughness were evaluated and shown in Fig. 10. Figs. 10 A(I) and A(E) are the non-coated inlet flange and the yttrium oxide coated exhaust flange, respectively. Fig. 10 A(I) shows the many ambiguous shaped small patterns with dark and bright contrasts. The surface had the average roughness Ra of 0.85 – 1.7 μm and the Rz roughness of 11 - 23 μm. The rough surface morphology was considered to be produced due to the exposure to the chlorine trifluoride gas. In contrast, as shown in Fig. 10 A(E), the exhaust flange showed a flat surface having clearly shaped scratch-like lines, which were considered to be formed during the polishing process for finishing the quartz glass flange surface. The surface roughness was Ra of 0.13

– 0.32 μm and Rz of 1.2 – 3.8 μm, which were comparable to the typical values of original surface. These values were significantly lower that those of the inlet flange.

For further quantitative evaluation, the difference in the surface height was evaluated along the y axis in Fig. 3 (b). In Fig. 11 A, (I) shows the surface height of the inlet flange. In this figure, the two vertical walls at 0.5 and -0.5 mm indicated the gas channel. The position higher than 10 mm and lower than -10 mm had a surface height near zero mm. This region maintained the original surface, because of no exposure to chlorine trifluoride gas. In contrast, at the positions lower than 10 and higher than –10 mm, the height steeply decreased to -0.1 mm which showed the lowest valley. After indicating the bottom, the height again increased to about -0.03 mm. This figure showed that steep steps were formed on the non-coated inlet flange.

In contrast, as shown by (E) in Fig. 11A, the surface height of the yttrium oxide coated flange was totally flat, although only very shallow hills and valleys existed. Similar to (I) in Fig. 11 A, the steep walls near 5 and -5 mm was the gas channel. This figure showed that the yttrium oxide-coated quartz flange could maintain its initial surface profile even when the non-coated quartz flange produced significant steps.

As described in the Experimental procedure, the chlorine trifluoride gas concentration at the exhaust was lower than that at the inlet due to the gas consumption by the etching. For the reference, the quartz chamber, both sides of which were not coated, was used. The non-coated inlet and exhaust flanges were exposed to the chlorine trifluoride gas at room temperature for a long time

which produced the significant etched depth on the non-coated inlet flange compared to that shown by (I) in Fig. 11 A.

As shown by (I) in Fig. 11 B, the non-coated inlet flange of the reference quartz chamber showed a surface height profile similar to that shown by (I) in Fig. 11 A, particularly about the entire shape and positions showing steep valleys at the positions near ±10 mm and the sharp hills near ±5 mm. The depth near ±10 mm of (I) in Fig. 11 B was 0.09 – 0.1 mm, which was comparable to that shown by (I) in Fig. 11 A. Fig. 10 B(I) shows the typical surface morphology shown by (I) in Fig. 11 B. There were ambiguous dark and bright colors, which were quite similar to those in Fig. 10 A(I). Concerning the surface roughness, the Ra value was 1.5-1.7 μm and the Rz value was 15-20 μm. These values were similar to those in Fig. 10 A(I). Thus, the reference quartz chamber was expected to show the non-coated situation of the exhaust flanges in addition to that of the inlet flange.

Fig. 10 B(E) shows the surface morphology of the non-coated exhaust flange. The Ra and Rz values were 1.4-1.7 μm and 12-15 μm, respectively, which were comparable to those in Figs. 10 A(I) and 10 B(I). The non-coated exhaust flange surface showed ambiguous dark and bright patterns, even finer than in Figs. 10 A(I) and 10 B(I). The surface height profile is shown by (E) in Fig. 11 B. Its entire shape resembled those of (I) in Figs. 11 A and B, regarding the steep valleys and the sharp hills. The valley depth near ±10 mm and the sharp hills near ±5 mm were 0.03 mm and 0.015-0.02 mm, respectively. While these values were lower than those of the non-coated inlet flange, they

were significantly higher than those of the yttrium oxide coated exhaust flange shown by (E) in Fig. 11 A. Overall, the non-coated exhaust flange showed a moderate etching behavior similar to that of the non-coated inlet flange. This result concluded that the yttrium oxide coated flange showed a significant effect on stopping the etching by the chlorine trifluoride gas. This ability will help to improve the productivity of the CVD film by reducing the maintenance cost related to the reactor cleaning process.

## 4. Conclusions

The anticorrosive ability of yttrium oxide to chlorine trifluoride gas was evaluated. The yttrium oxide powder showed no change at temperatures lower than 300 $^{o}$C, while its weight and composition changed at higher than 500 $^{o}$C. The quartz glass surface was coated with a yttrium oxide thin film. The quartz surface was exposed to chlorine trifluoride gas at various concentrations from 1 to 100 % at room temperature for more than 1000 minutes. The non-coated quartz surface was etched and caused a nearly 0.1 mm deep step; the surface showed the average surface roughness $R_a$ of about 1.5 μm. In contrast, the yttrium oxide coated surface maintained a low surface roughness; the Ra value was 0.2 μm. Thus, yttrium oxide film is concluded to stop the etching during exposure to chlorine trifluoride gas for a long time at room temperature. This ability will reduce the maintenance cost of the CVD process, such as the reactor cleaning using the chlorine trifluoride gas.

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Figure captions

Figure 1 Reactor and chemical reactions used in this study

Figure 2 Quartz glass chamber before exposure to chlorine trifluoride gas. (a) overall view, (b) non-coated inlet flange and (c) $Y_2O_3$ coated exhaust flange.

Figure 3 Geometry of (a) stainless steel flange and (b) quartz flange. Hatched area was exposed to chlorine trifluoride gas.

Figure 4 Typical etching process using chlorine trifluoride gas

Figure 5 Weight change (%) of yttrium oxide power after exposure to chlorine trifluoride gas at 100 % for 10 minutes at temperatures from room temperature to 600 $^{o}$C.

Figure 6 Contents of yttrium, oxygen and fluorine after exposure of yttrium oxide power to chlorine trifluoride gas at 100 % for 10 minutes at temperatures from 300 $^{o}$C to 600 $^{o}$C.

Figure 7 Contour diagram of $Y_2O_3$ film thickness over the quartz flange. Measured by the ellipsometry (TOKITA CVD Systems).

Figure 8 Quartz process tube after 1012-minutes exposure to chlorine trifluoride gas. (a) overall view, (b) non-coated inlet flange and (c) $Y_2O_3$ coated exhaust flange.

Figure 9 Appearance of non-coated inlet flange after 1012-minutes exposure to chlorine trifluoride gas. (a): photograph and (b): geometry outline. Hazy area: caused by the chlorine trifluoride etching.

Figure 10 Morphology and roughness of quartz flange surface. A: $Y_2O_3$ coated quartz process tube, and B: non-coated process tube for reference. (I): inlet flange and (E) exhaust flange.

Figure 11 Surface height profile of quartz flange. A: $Y_2O_3$ coated quartz process tube, and B: non-coated process tube for reference. (I): inlet flange and (E) exhaust flange.

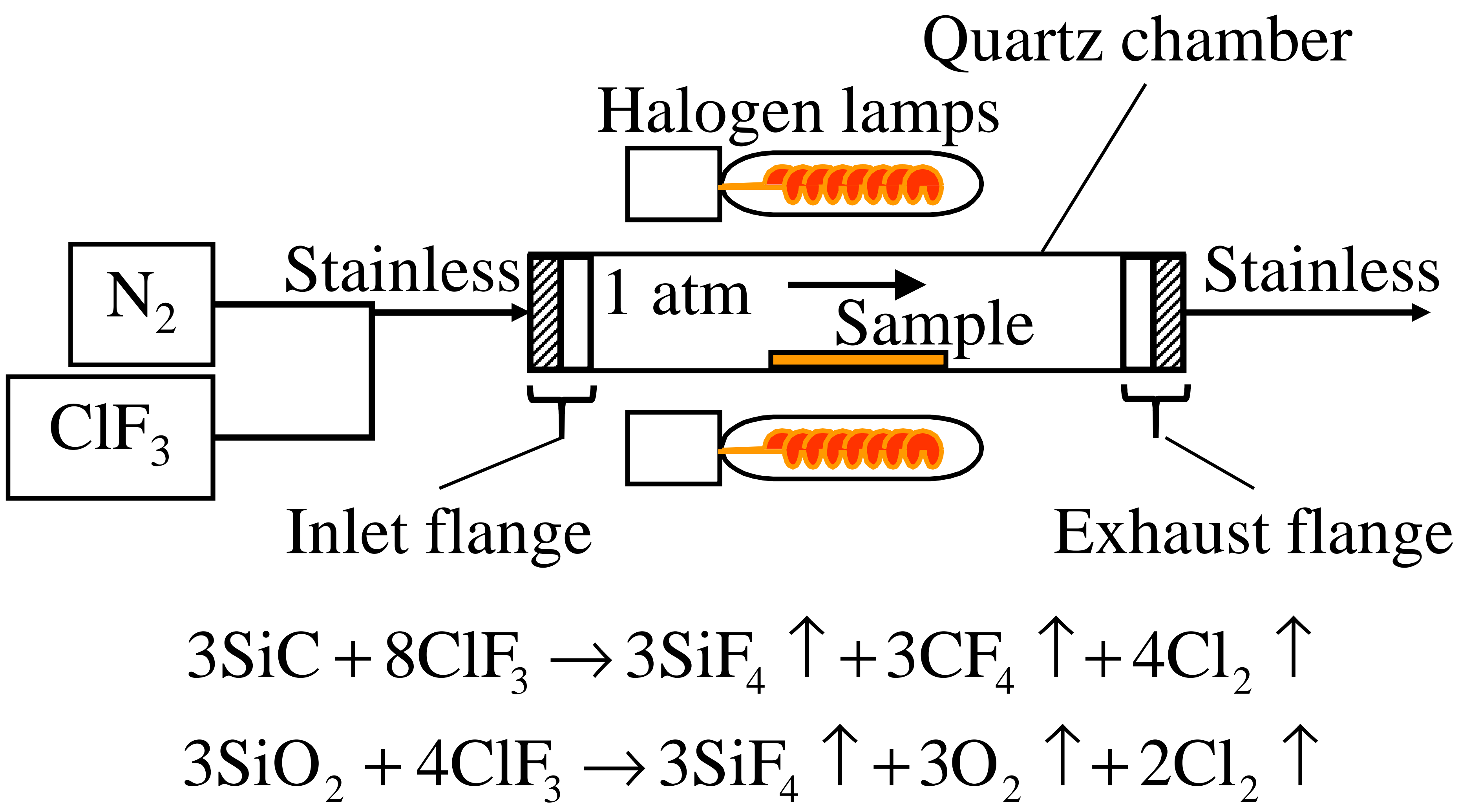



Fig. 1

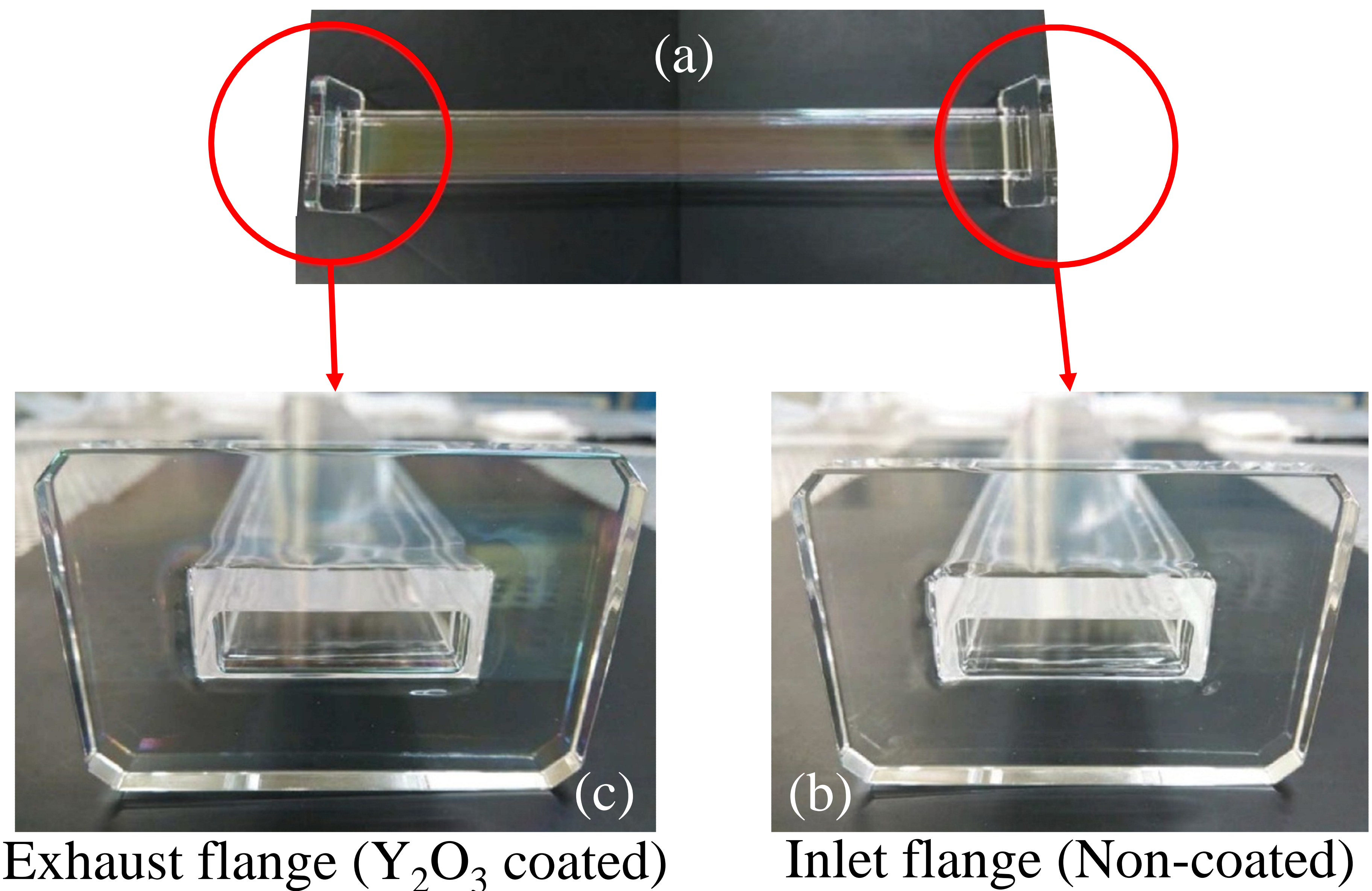
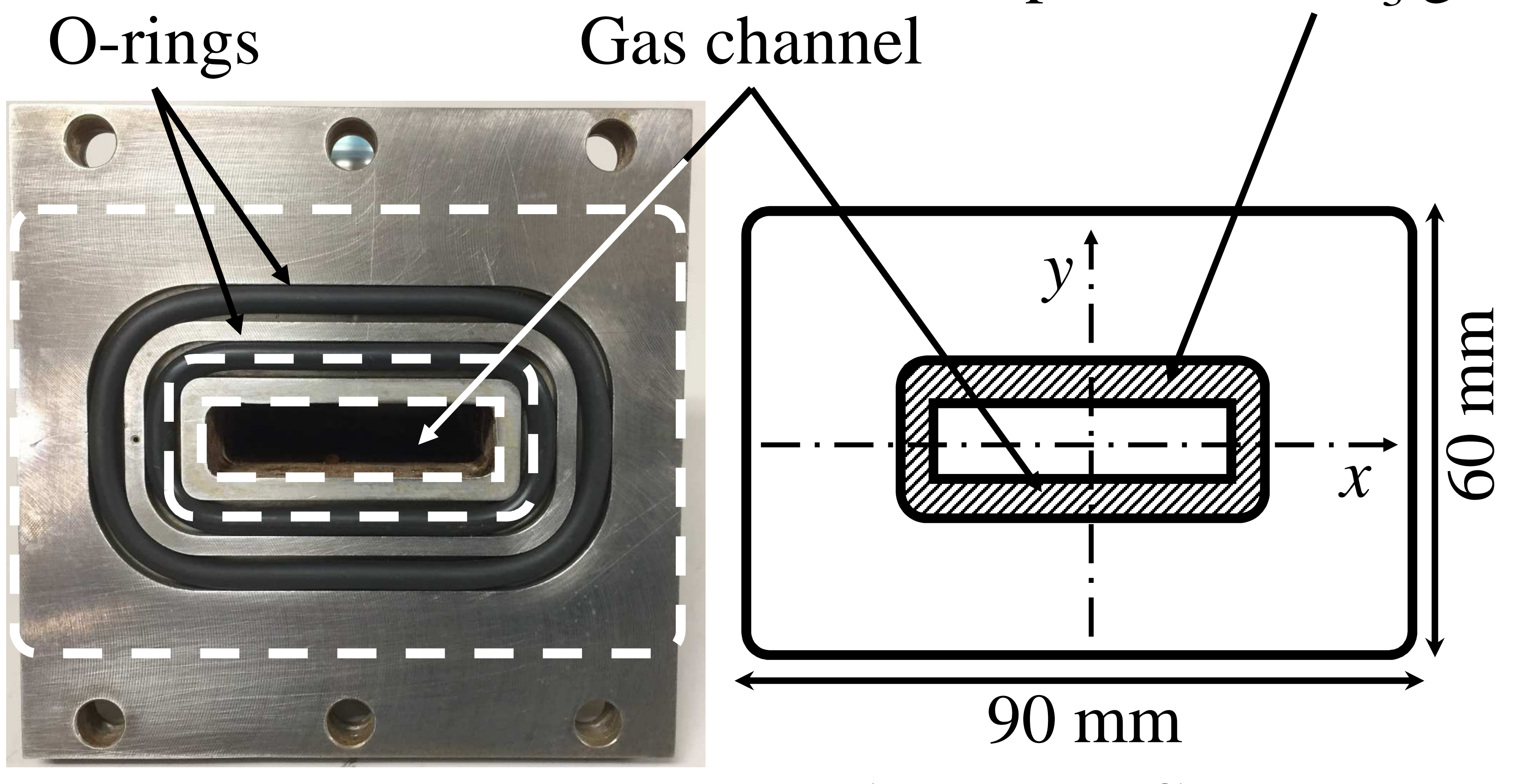



Fig. 2




(a) Stainless steel flange

(b) Quartz flange
Inlet: non-coated
Exhaust: $Y_2O_3$-coated

Fig. 3

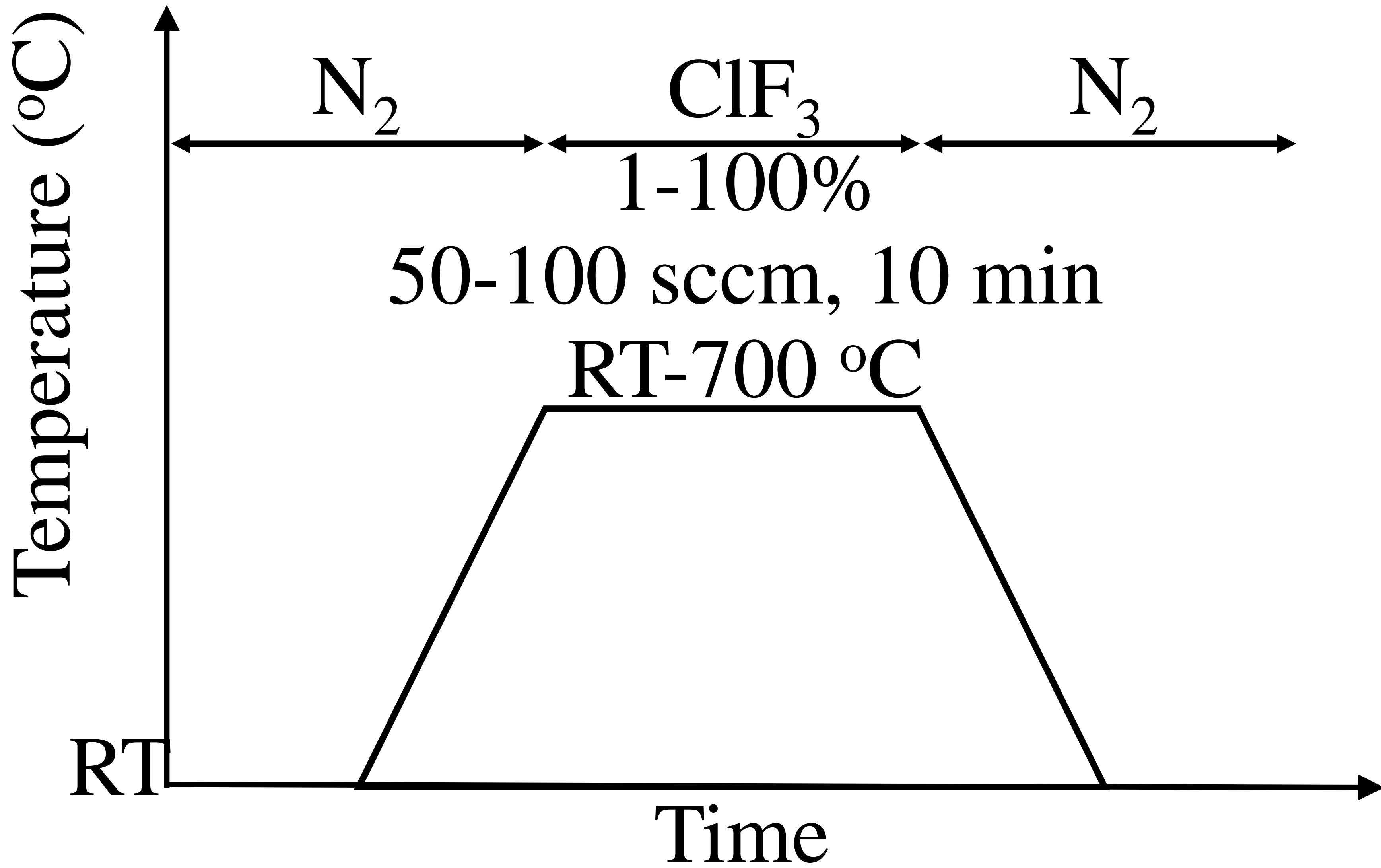



Fig. 4

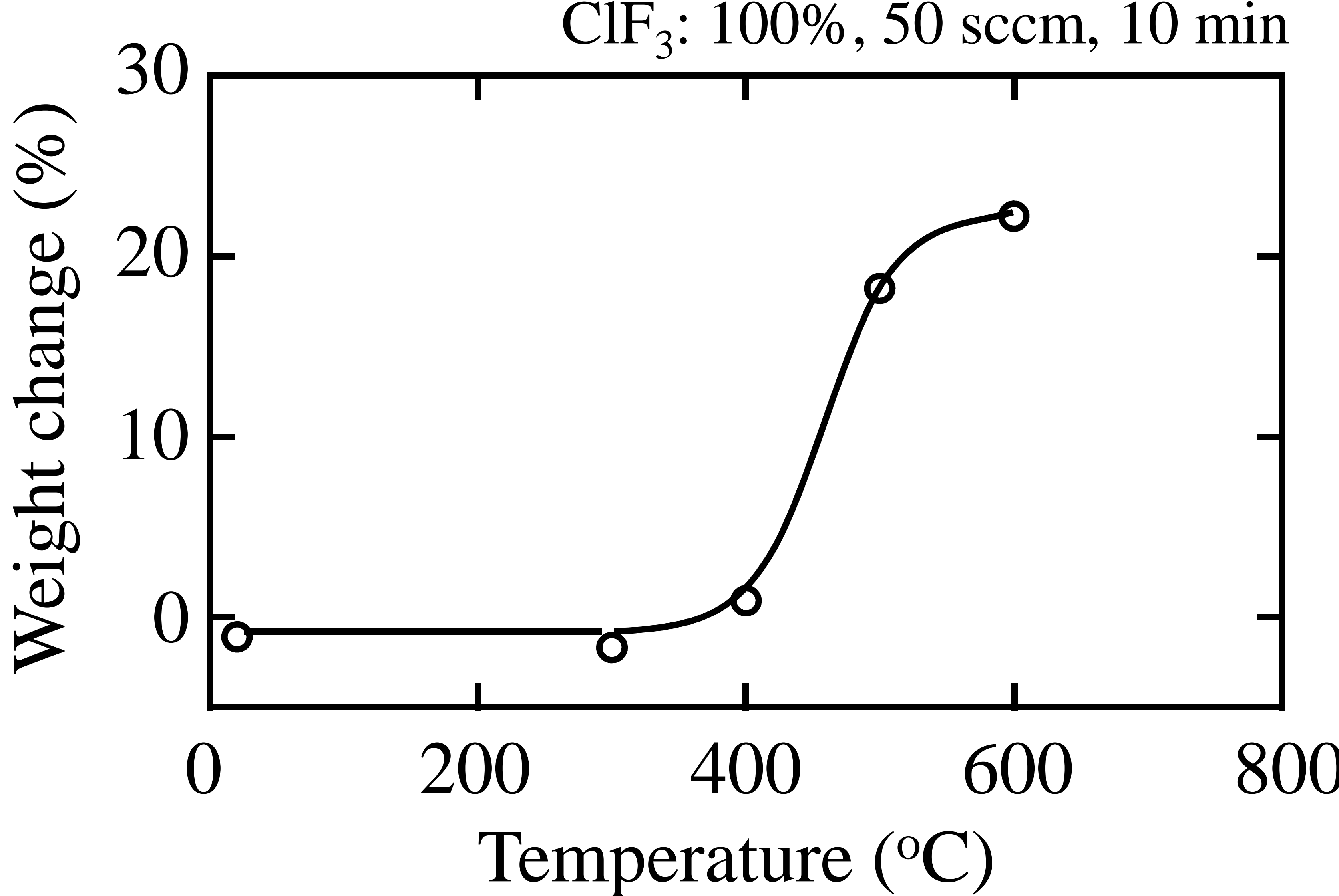



Fig. 5

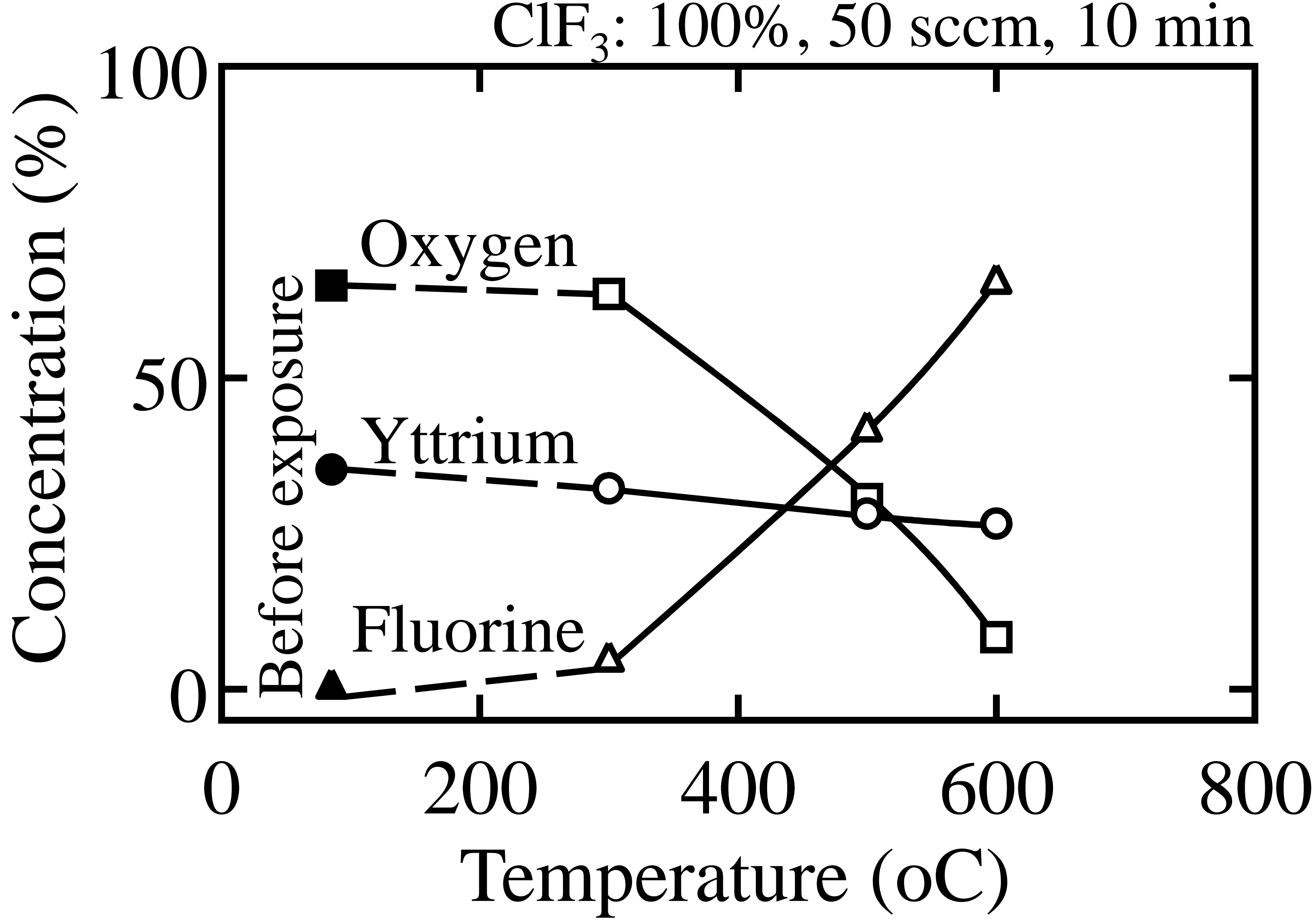



Fig. 6

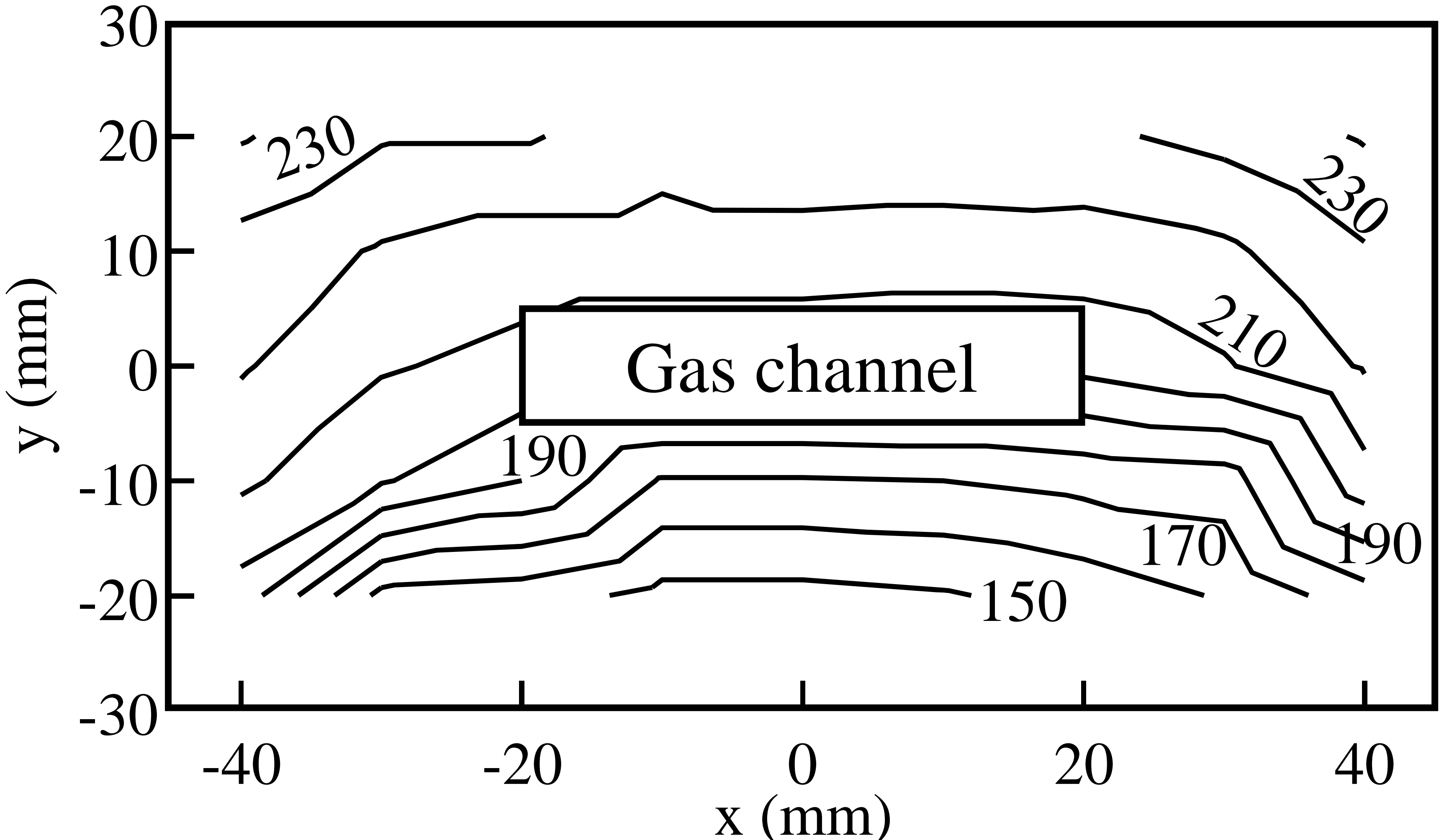



Fig. 7

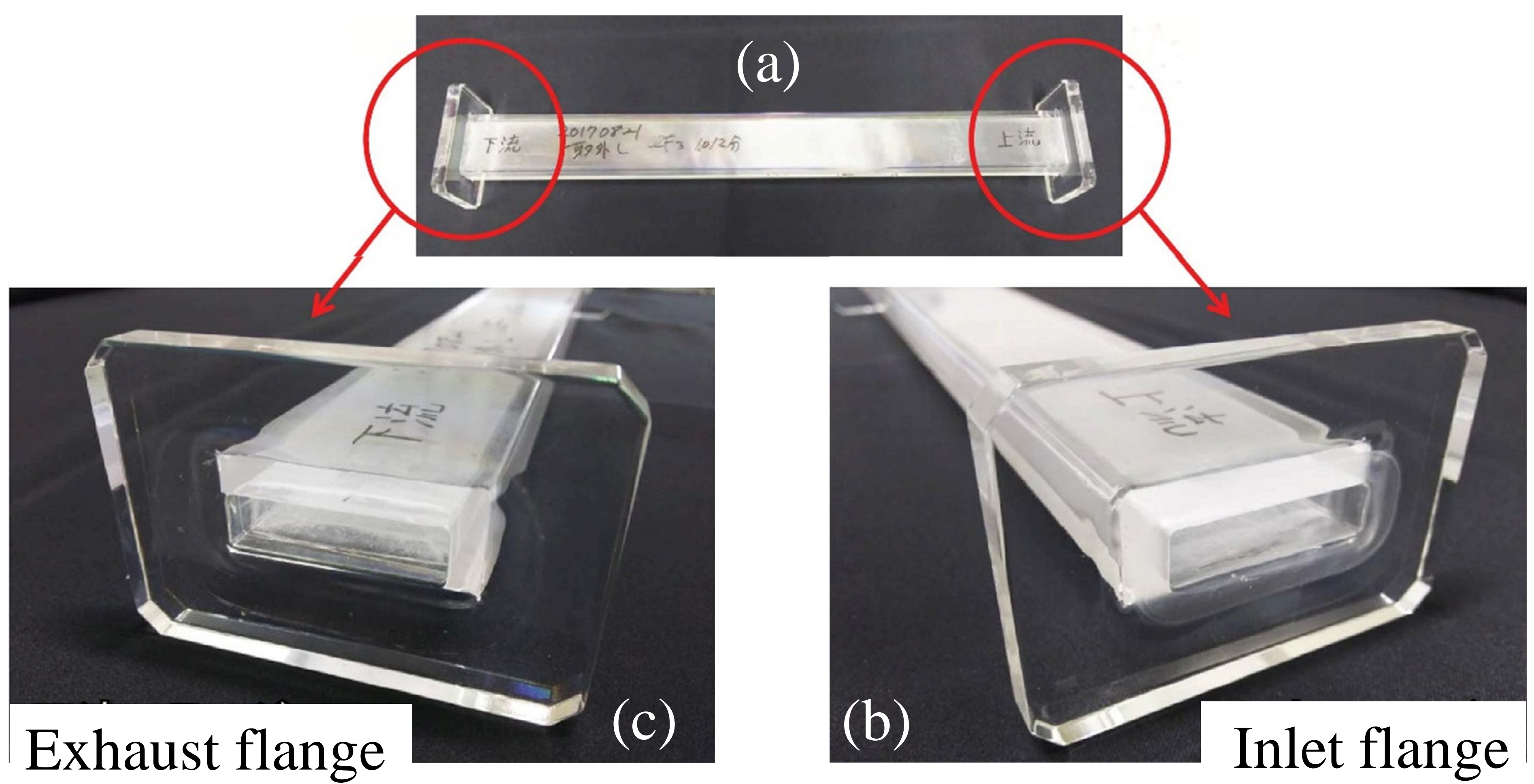



Fig. 8

(a) Photograph (Inlet flange, non-coated)

(b) Geometry outline

Inside line of rubber gasket

Area etched by $ClF_3$ gas

Quartz wall

Gas channel

Fig. 9

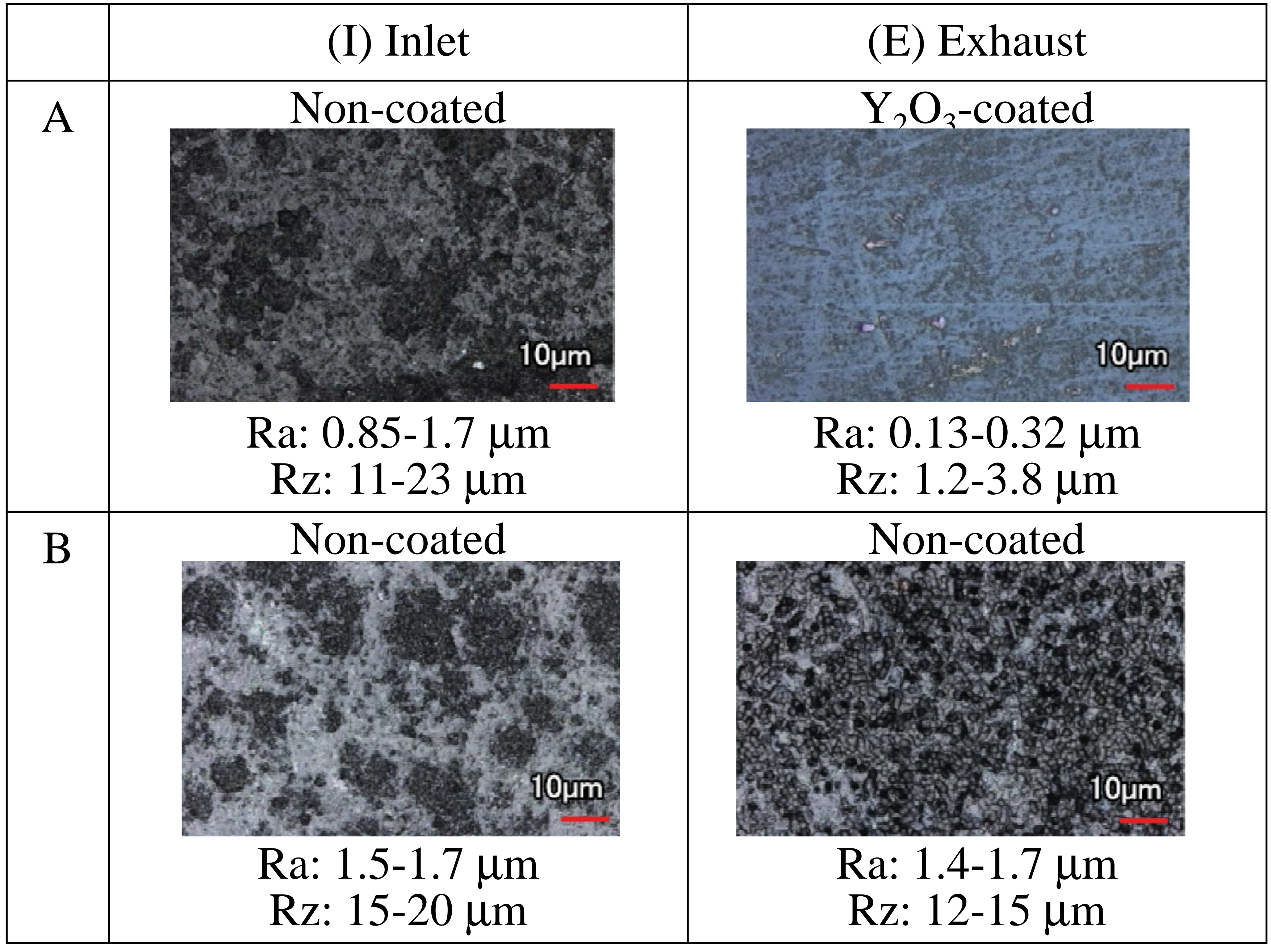



Fig. 10

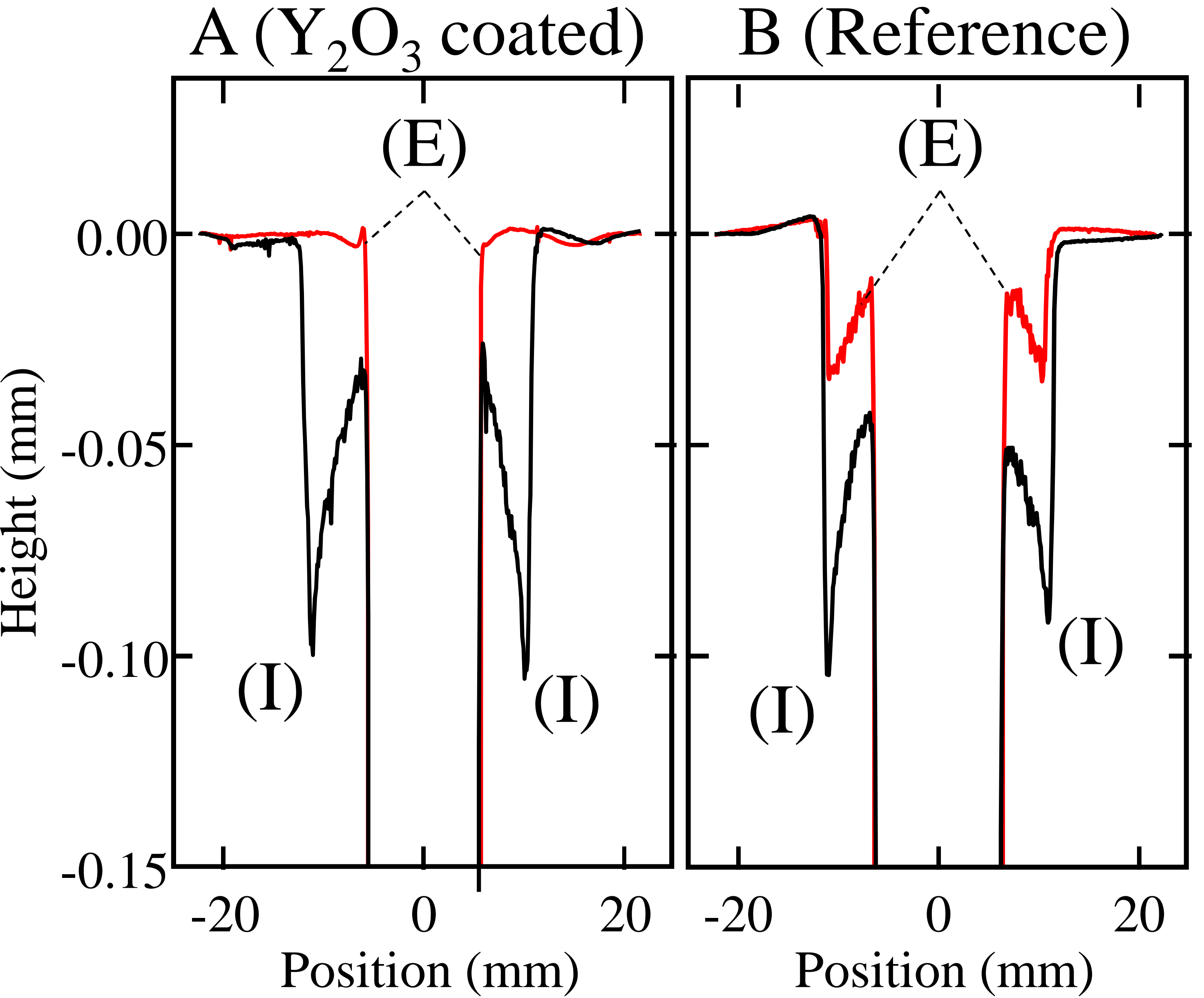



Fig. 11