Repetition of In Situ Cleaning Using Chlorine Trifluoride Gas for Silicon Carbide Epitaxial Reactor

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In order to develop a practical in situ cleaning method applicable for a silicon carbide epitaxial reactor, the silicon carbide film formation and the cleaning using chlorine trifluoride gas were repeated three times on the susceptor. The 40-μm-thick silicon carbide film was removed by the optimized condition consisting of the susceptor temperature, the chlorine trifluoride gas concentration and its flow rate of 530 °C, 100% and 50 sccm, respectively, at atmospheric pressure for 120–180 min. The susceptor coating film having a round-shaped morphology had an allowable surface damage after the three repetitions of the film formation and cleaning.

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4H-silicon carbide (SiC) epitaxial wafers12 are currently produced by the chemical vapor deposition (CVD) method in order to develop and produce various electronic power devices. The epitaxial layers are used due to fewer crystalline defects than that of the substrate produced by the Modified-Lely Method. For further improving the silicon carbide epitaxial layer quality along with reducing the production costs, one of the key technologies to be developed is the reactor cleaning method,3–7 which is for removing the unnecessary films formed around the substrate.

Silicon carbide has a significantly stable chemical nature which makes the silicon carbide reactor cleaning very difficult. Thus, the current silicon carbide CVD process has no reactor cleaning method, different from the other CVD processes, such as those for silicon, gallium arsenide and gallium nitride, having very useful one. Fortunately, the authors found that chlorine trifluoride gas was an excellent candidate for the reactor cleaning,5–7 because chlorine trifluoride gas can significantly etch off many kinds of materials including silicon carbide. For this purpose, the challenging point is the way to reduce the damage to the susceptor surface to less than an allowable level.5–7

The authors have studied the chemical reactions of silicon carbide with chlorine trifluoride gas5–15 in order to find the possible conditions for the in situ cleaning.3–7 In these studies, two kinds of depositions, such as the particle-type and film-type, could be removed by the chlorine trifluoride gas at temperatures lower than 330 °C for a long period, such as one-two hours, with an allowable damage to the susceptor coating film. In order to further show the capability for achieving a practical in situ cleaning process, the following three issues should be studied by the production-like process consisting of the repetition of the film formation and the in situ cleaning.

1. Removing deposition: The deposition on the susceptor is removed by every cleaning.
2. Susceptor damage: The susceptor surface suffers an allowable damage after every cleaning.
3. Deposition: The deposition formed on the susceptor after the cleaning is similar to the previous one.

The susceptor coating materials are expected to be evaluated by 2. Unfortunately, this type of study has not been performed, although it significantly advances the silicon carbide epitaxial reactor cleaning technique.

In this study, the chemical reaction conditions using chlorine trifluoride gas were further studied in detail in order to develop a practical process of the silicon carbide epitaxial reactor in situ cleaning. For this purpose, the silicon carbide film deposition and the cleaning were repeated on the susceptor surface, for the first time, along with carefully evaluating the surface damage to the susceptor.

Experimental

Figure 1 shows the reactor used in this study. Small carbon plates with the dimensions of 3 cm × 3 cm were used as the susceptor. The susceptors used in this study were made of high purity carbon, the surface of which was covered with a coating film (Toyo Tanso Co., Ltd., Tokyo, Japan) the same as that used in the industrial CVD reactor. The silicon carbide films were formed on the susceptor surface following the 4H-silicon carbide epitaxial growth process11 so that the 40-μm-thick 4H-silicon carbide epitaxial film was formed on the 4H-silicon carbide substrate surface. The gas flow rate of hydrogen, monosilane, propane was typically 5 slm, 20 sccm and 4 sccm, respectively. The susceptor temperature and the pressure were 1630 °C and 200 Torr, respectively.

For performing the etching, the susceptor with the silicon carbide films was inserted into the horizontal reactor,12 as shown in Fig. 1. This reactor consisted of a gas supply system, a quartz chamber and six infrared lamps. The gas supply system introduces the chlorine trifluoride gas and nitrogen gas. This reactor has a small cross section in order to achieve a high consumption efficiency of the chlorine trifluoride gas. The height and the width of the quartz chamber were 10 mm and 40 mm, respectively. The susceptor was heated by infrared rays emitted from halogen lamps through the quartz chamber walls. The electric power to the six infrared lamps was adjusted based on the temperatures previously measured in ambient nitrogen.

![Figure 1. Reactor for etching silicon carbide film using chlorine trifluoride gas.](image-url)
Figure 2. Process for etching silicon carbide film using chlorine trifluoride gas.

Figure 2 shows the cleaning process used in this study. First, the susceptor was heated in ambient nitrogen to 330°C for the etching. Next, it was exposed to the chlorine trifluoride gas (>99.9%, Kanto Denka Kogyo Co., Ltd., Tokyo) at 100% and 50 sccm without the nitrogen gas. After exchanging the ambient gas from the chlorine trifluoride to nitrogen for terminating the etching, the susceptor was cooled to room temperature. The temperature for cleaning was fixed at 330°C, because the susceptor coating film would be damaged at 340°C, based on our previous study.7 A set of processes, consisting of the 40-μm-thick film deposition and the cleaning at 330°C, were repeated while evaluating the susceptor surface condition. For performing the cleaning process, careful operations with the appropriate equipment16,17 are necessary, because chlorine trifluoride is a dangerous and toxic gas.8

Before and after exposure to the chlorine trifluoride gas, the susceptor surface was evaluated using a scanning electron microscope (SEM) (VE-8800, Keyence, Tokyo) and optical microscope along with measuring the weight.

Results and Discussion

The susceptors used in this study were classified into two types, Types A and B, which were the same as those used in our previous studies for the film type deposition7 and the particle type deposition,5,6 respectively. Figure 3 shows the surface appearance of the Types A and B by the optical microscope and their magnified image by SEM. Both susceptors similarly showed a gray-colored appearance. Based on the SEM, Type A showed a surface consisting of many small polycrystalline platelets. In contrast, Type B had round-shaped hills and valleys. Before using these susceptors, the etching rates of the Types A and B by the chlorine trifluoride gas were measured. The etching rates of the Types A and B were 0.18 μm/min at 324°C and 0.03 μm/min at 330°C, respectively. The etching rate of the Type B was lower than that of the Type A.

The silicon carbide film was formed on the Types A and B susceptors. Figure 4a shows the surface of the Type A after the 40-μm-thick silicon carbide film deposition; Fig. 4b shows that after cleaning by the chlorine trifluoride gas at 100% and 330°C for 120 min. As shown in Fig. 4a, the susceptor surface was entirely covered with gray films having a slightly yellow color. After the cleaning, most of the susceptor surface had a dark gray color which indicated that the susceptor coating film surface appeared. The yellow-colored region existed at the right bottom edge. This showed that a part of the silicon carbide film remained in this region. Figure 4c shows the magnified image of the surface at the center position of Fig. 4b. This figure shows that there were random-shaped small hills and valleys obviously different from the surface shown in Fig. 3b. The crystalline-like clear-shaped edges of the platelets, shown in Fig. 3b, disappeared by the etching and became a shallow wavy surface.

Figure 5a shows the Type B surface after the 40 μm-thick silicon carbide film deposition, while Fig. 5b shows that after cleaning by the
chlorine trifluoride gas at 100% and 330°C for 180 min. As shown in Fig. 5a, the susceptor surface was entirely covered with the gray films along with a slightly yellow color, similar to that in Fig. 4a. After the cleaning, the entire susceptor surface showed a dark gray color which indicated that the susceptor coating film surface was present. Unlike that in Fig. 4, there was no yellow-colored region. This showed that the silicon carbide film did not remain over the entire surface. Figure 5c shows a magnified image of the surface at the center position of Fig. 5a. This figure shows that there were still round-shaped hills and valleys obviously similar to the surface morphology shown in Fig. 3d. This verified that the Type B had significantly less damage than the Type A.

Next, the film formation and the cleaning were repeated. Figure 6 shows the surface of the Type A susceptor during the process. Figure 6a shows the surface before the silicon carbide film deposition. Figure 6b shows that the surface after the silicon carbide film deposition. This surface was covered with a gray-colored film. The top right region had a dark gray color along with some slight yellow coloring. After the first in situ cleaning by the chlorine trifluoride gas at 100% and 330°C for 120 min, the gray-colored region, Region I, existed in the top left region, the periphery of which was surrounded by the dark gray region, as shown in Fig. 6c. Additionally, at the bottom edge, there was a gray region, Region II, the border of which was traced by the slightly dark-gray-colored region.

After the second film deposition, the thick yellow lines were observed in the top left region, Region I, and at the bottom region, Region II, as shown in Fig. 6d, the positions and shapes of which were similar to those in Fig. 6c. The yellow-colored lines, showing the periphery of Regions I and II, might indicate the polycrystalline 3C-silicon carbide. The shapes of Regions I and II did not change after the second in situ cleaning. The dark color at the inside and the light color at the periphery of Region I in Fig. 6d changed to a light yellow color and gray color, respectively, in Fig. 6e. Region II still had a yellow-colored line tracing in its border. The polycrystalline 3C-silicon carbide might remain along the periphery of Region II.

The third deposition was performed, as shown in Fig. 6f. The center of Region I showed a yellow color. The region around it was dark gray with a slight yellow color. The border of Region II became vague except for its right edge. This surface was in situ cleaned, as shown in Fig. 6g. There was a black region having a nonregular shaped clear edge at the center position of Region I. This position corresponded to the light-yellow region in Fig. 6e. Taking into account its black color appearance, the surface coating film was determined to have peeled off; the bare susceptor surface consisting of high purity carbon appeared. In contrast, the shape of Region II became more vague than that in Fig. 6e; its shape remained only in the right bottom region. Thus, Region II was recognized to be successfully cleaned by three in situ cleanings. Overall, it is concluded that the in situ cleaning of the Type A could be repeated only less than twice.

Next, the in situ cleaning of the Type B susceptor was evaluated. Figure 7a shows the original surface of the Type B. The 40-μm-thick silicon carbide film was formed on its surface, as shown in Fig. 7b. There was a square-shaped dark region, which was prepared due to the small device used for fixing the susceptor in the epitaxial reactor. From Fig. 7b, the Type B surface was entirely covered with a slightly yellow-colored film, which might indicate the polycrystalline 3C-silicon carbide film. The Type B after the first deposition was in situ cleaned by the chlorine trifluoride gas at 100% and 330°C for 120 min. Figure 7c shows the Type B surface after the first cleaning. It has an entirely gray color with no appearance of any damage.

The second deposition was performed, as shown in Fig. 7d. The Type B surface had an entirely uniform gray color along with a slightly yellow color. This surface was exposed to the chlorine trifluoride gas, as the second cleaning. Figure 7e shows the Type B surface after the cleaning. The center region had a gray color, similar to Fig. 7a. The bottom region showed a color darker than that in the center region. The narrow region along the top edge showed a light gray color which might indicate that the silicon carbide film remained.

Figure 7f shows the surface after the third deposition. The top edge region still had a light gray color different from the other region. Except for this, the surface was uniformly covered with the silicon carbide film. The third in situ cleaning was performed to obtain the surface, as shown in Fig. 7g. Similar to Fig. 7e, the top edge region had a light gray color indicating some remaining silicon carbide film. However, the present silicon carbide film over the entire surface could be removed without any recognizable damage, based on

![Figure 6](image-url)
the uniform gray color which was the same as that shown in Fig. 7a. Thus, from the results of Figs. 7a–7g, the three repetitions of the silicon carbide film deposition and the in situ cleaning were successfully completed.

From this study, by choosing the coating film, the number of repetitions of the silicon carbide film formation and cleaning using chlorine trifluoride gas is possible. In order to reduce the cleaning period from two hours to less than one hour, the cleaning temperature should be increased to higher than 400 °C. For this purpose, suitable materials for the coating film should be developed. Candidates are expected to be pyrolytic carbon, silicon nitride, and materials having a strong chemical bonding with melting and boiling points higher than 1500 °C. Material parameters which lessen the damage should be scientifically evaluated in further studies.

Conclusions

The practical in situ cleaning condition applicable to the susceptor in a silicon carbide epitaxial reactor was obtained based on the three repetitions of the 40-μm-thick silicon carbide film formation and the in situ cleaning using chlorine trifluoride gas. The silicon carbide film was removed at the susceptor temperature of 330 °C, the chlorine trifluoride gas concentration and flow rate of 100% and 50 sccm, respectively, at atmospheric pressure for 120–180 min. Allowable surface damage appeared at the susceptor coating film having a round-shaped appearance.

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