Quick Cleaning Process for Silicon Carbide Chemical Vapor Deposition Reactor

Kohei Shiboda, a Keisuke Kurashima, a Hitoshi Habuka,a,⁎⁎ Hideki Ito, b Shin-ichi Mitani, b and Yoshinao Takahashi c

a Yokohama National University, Hodogaya, Yokohama 240-8501, Japan
b NuFlare Technology, Inc., Yokohama 235-8522, Japan
c Kanto Denka Kogyo Co., Ltd., Tokyo 101-0003, Japan

A quick cleaning process was developed for a silicon carbide chemical vapor deposition reactor. For this purpose, the stability of the susceptor coating film made of pyrolytic carbon was evaluated by means of exposing it to 100% chlorine trifluoride gas for 10 min at various temperatures. The original surface morphology of the pyrolytic carbon film was maintained under 480 °C. The fluorine atoms incorporated into the pyrolytic carbon film were removed by annealing at 900 °C either in ambient hydrogen or in ambient nitrogen. Finally, the 30-μm thick silicon carbide film formed on the pyrolytic carbon was successfully cleaned by the chlorine trifluoride gas either at 400 °C for 30 min or at 460 °C for 15 min and by additional annealing in ambient nitrogen at 900 °C.

Chemical vapor deposition (CVD)1–5 is one of the most frequently used techniques for producing advanced materials. It consists of two processes, such as film deposition and cleaning. The cleaning process is necessary for removing the unnecessary film formed on the susceptor and various reactor parts other than the substrate, because such films very often emit small particles. In order to maintain a clean condition for the deposition, a cleaning process has been implemented in the CVD for producing various materials, except for silicon carbide.

The semiconductor silicon carbide (SiC) film is produced by means of the CVD process.3–5 For realizing high efficiency power devices, silicon carbide has suitable properties,6 such as a wide bandgap, high electron mobility, high thermal conduction, and high chemical and mechanical stabilities. However, these significant chemical and mechanical stabilities often cause practical problems, particularly for the CVD reactor cleaning. Currently, the silicon carbide CVD reactor cleaning process using chlorine trifluoride (ClF3) gas was 1000 sccm and 50 sccm, respectively.

Typically, the flow rates of the nitrogen gas and chlorine trifluoride gas were 100% and 50 sccm, respectively.

The entire process used in this study is shown in Fig. 2. In ambient nitrogen, the sample piece was heated to a temperature, such as 430–490 °C, for exposure to the chlorine trifluoride gas. The chlorine trifluoride gas was introduced into the reactor at the flow rate of 50 sccm for 10 min. After terminating the chlorine trifluoride gas, the sample piece was cooled to room temperature in ambient nitrogen.

Figure 1 shows the etching reactor for exposing the sample to the chlorine trifluoride gas. The sample piece was a high-purity carbon plate, the surface of which was coated with a pyrolytic carbon film (Toyo Tanso, Tokyo). The sample was placed at the bottom of the quartz chamber and heated by an infrared light coming from halogen lamps through the quartz chamber wall. Nitrogen gas and chlorine trifluoride gas were introduced from the inlet at atmospheric pressure. Typically, the flow rates of the nitrogen gas and chlorine trifluoride gas were 1000 sccm and 50 sccm, respectively.

For performing the silicon carbide film formation, a high speed rotation vertical flow epitaxial reactor, the EPIREVO S6 reactor (NuFlare Technologies), was used. The 30-μm-thick silicon carbide film was formed on the sample piece using trichlorosilane gas near 1500 °C. After being taken out from the reactor, the sample piece was inserted into the etching reactor, shown in Fig. 1, for cleaning. The cleaning temperature and the cleaning time were 400–480 °C and 15–30 min, respectively. The chlorine trifluoride gas concentration and its gas flow rate were 100% and 50 sccm, respectively. After the etching, the sample piece was annealed in ambient nitrogen at 900 °C for removing the remaining fluorine atoms.12

Experimental

For this purpose, the authors have developed the in situ silicon carbide CVD reactor cleaning process using chlorine trifluoride (ClF3) gas.8–12 Previous studies8–10 have shown that the chlorine trifluoride gas could remove the various types of silicon carbide films formed on the silicon-carbide-coated carbon susceptor in spite of operating for a significantly long time, such as 1–2 hours. This very long time was unfortunately necessary, because the cleaning temperature must be kept low for suppressing any etching damage to the susceptor coating film made of silicon carbide. However, recently and fortunately, the pyrolytic carbon film has been found to have a very low etching rate for the chlorine trifluoride gas.12 Thus, the combination of the chlorine trifluoride gas and the pyrolytic carbon coating film should be studied in detail for achieving a quick cleaning process which is applicable for industrial production.

As an extension of our previous study,12 this study evaluated the temperature range in which the chlorine trifluoride gas did not cause serious damage to the pyrolytic carbon film. Next, the incorporation and the out-diffusion of fluorine atoms from the pyrolytic carbon film were studied based on a chemical analysis. Finally, the silicon carbide film formed on the pyrolytic carbon film was quickly removed using the chlorine trifluoride gas.

Figure 1. Etching reactor used in this study.

N2

Halogen lamps

sample (3 x 3 cm)

Inlet

Exhaust

Quartz chamber

3SiC + 8ClF3 → 3SiF6 + 3CF4 + 4Cl2

ClF3; 100%, 1 atm, 50 sccm

⁎⁎ Electrochemical Society Member.
⁎⁎⁎ E-mail: habuka-hitoshi-ng@ynu.ac.jp

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Figure 1. Etching reactor used in this study.
Figure 2. Etching process used in this study.

The surface morphology of the sample piece was evaluated by scanning electron microscopy (VE-8800, Keyence, Tokyo). The chemical condition, particularly, the fluorine concentration, was analyzed by X-ray photoelectron spectroscopy (Quantera SXM, ULVAC- PHI Corp., Tokyo, Japan).

Results and Discussion

Pyrolytic carbon film.—Figure 4 shows the pyrolytic carbon film surface before and after exposure to a 100% chlorine trifluoride gas at the flow rate of 50 sccm for 10 min. Before the exposure, the pyrolytic carbon film had a dark gray appearance, as shown in Fig. 4.1.a. Fig. 4.2.a shows that the surface was filled with pebble-like grains, based on the SEM observations. After exposure to the chlorine trifluoride gas at 430 °C, the surface appearance and the surface morphology, shown in Figs. 4.1.b and 4.2.b, respectively, were the same as those before the exposure. At 430 °C, the change in the pyrolytic carbon film surface was negligible. At 440 °C, the chlorine trifluoride gas changed the total color of the pyrolytic carbon surface from a dark to slightly blueish color, as shown in Fig. 4.1.c, while the surface morphology shown in Fig. 4.2.c remained the same as those shown in Fig. 4.2.a. The color change caused by the chlorine trifluoride gas was obvious at temperatures higher than 480 °C, as shown in Fig. 4.1.d. The pyrolytic carbon surface showed various colors from blue to green and violet. Even though the color changed, as shown in Fig. 4.1.d, the SEM image, shown in Fig. 4.2.d, was still the same as that before the exposure as shown in Fig. 4.2.a. The trend showed that the surface change became significant with the increasing temperature due to the exposure to the chlorine trifluoride gas. Finally, after exposure at 490 °C for 10 min, the pyrolytic carbon film surface was peeled to produce the rainbow-colored thin films, as shown in Fig. 4.1.e. In order to quickly evaluate the damaged situation of the pyrolytic carbon film, the fragile rainbow-like-colored film was mechanically removed; the exposed surface was observed by the SEM as shown in Fig. 4.2.e. This figure showed that the remaining surface was similar to that before exposure to the chlorine trifluoride gas as shown in Fig. 4.2.a. Thus, the chlorine trifluoride gas caused a significant damage, but the damage was limited only to the region near the pyrolytic carbon film surface. The layer immediately below the damaged layer had grains and a surface morphology similar to those before the exposure.

In order to study the change in the pyrolytic carbon film due to the exposure to the chlorine trifluoride gas, the chemical condition, particularly, the contents in the pyrolytic carbon film, was evaluated by XPS as shown in Fig. 5. Before exposure to the chlorine trifluoride gas, the peak near 284 eV was clearly detected as shown in Fig. 5a. After the exposure at 430 °C, the peak near 284 eV became weak, as shown in Figs. 5b and 4.2.b, respectively, were the same as those shown in Fig. 4.1.c. The color change caused by the chlorine trifluoride gas was obvious at temperatures higher than 480 °C, as shown in Fig. 4.1.d. The pyrolytic carbon surface showed various colors from blue to green and violet. Even though the color changed, as shown in Fig. 4.1.d, the SEM image, shown in Fig. 4.2.d, was still the same as that before the exposure as shown in Fig. 4.2.a. The trend showed that the surface change became significant with the increasing temperature due to the exposure to the chlorine trifluoride gas. Finally, after exposure at 490 °C for 10 min, the pyrolytic carbon film surface was peeled to produce the rainbow-colored thin films, as shown in Fig. 4.1.e. In order to quickly evaluate the damaged situation of the pyrolytic carbon film, the fragile rainbow-like-colored film was mechanically removed; the exposed surface was observed by the SEM as shown in Fig. 4.2.e. This figure showed that the remaining surface was similar to that before exposure to the chlorine trifluoride gas as shown in Fig. 4.2.a. Thus, the chlorine trifluoride gas caused a significant damage, but the damage was limited only to the region near the pyrolytic carbon film surface. The layer immediately below the damaged layer had grains and a surface morphology similar to those before the exposure.

Figure 3. Entire SiC CVD process consisting of film formation, susceptor cleaning and annealing.

|   | a. Before | b. 430°C | c. 440°C | d. 480°C | e. 490°C |
|---|---|---|---|---|---|
| 1. | Entire view | 3 cm | | | |
| 2. | SEM Image | 30 μm | | | |
| 3. | C (%) | 98 | 56 | 60 | 50 |
| 4. | F (%) | 0 | 40 | 37 | 49 |
| 5. | Thickness (nm) | 0 | 60 | 200 | 500 |

CIF$_3$ at 100%, 50 sccm for 10 min

Figure 4. Surface morphology and composition of pyrolytic carbon film after exposure to chlorine trifluoride gas.
After the exposure at 480°C, the film thickness was evaluated to about 200 nm as listed in Fig. 4.4.c. Near 200 nm, although it was low near the surface. The fluorinated layer at 440°C was evaluated to about 60 nm as listed in Fig. 4.4.b. After exposure to the chlorine trifluoride gas, the carbon and fluorine contents were 98% and 2%, respectively, at the surface. The carbon and fluorine contents after the exposure at 480°C did not show any significant change from those at 430°C and 440°C. The change in the pyrolytic carbon film was determined to be due to the fluorine incorporation. However, because the carbon and fluorine contents at the surface did not show any dependence on the concentration, it was concluded that the fluorine incorporation was increased with the increasing temperature.

Next, the carbon and fluorine concentration profiles along the depth from the surface were measured as shown in Fig. 6. Figure 6a is the carbon and fluorine concentration profiles in the pyrolytic carbon film after exposure to the chlorine trifluoride gas at 100°C and at 430°C for 10 min. The fluorescence concentration, which was high at the surface, decreased with the increasing depth. Simultaneously, the reverse behavior of the carbon concentration was observed, that is, an increase in the carbon concentration with the increasing depth. Both of the profiles became flat at depths greater than 100 nm. Based on these behaviors shown in Fig. 6a, the thickness of the fluorinated layer was evaluated to about 60 nm as listed in Fig. 4.4.b. After exposure to the 100% chlorine trifluoride gas at 440°C for 10 min, the fluorine atoms were distributed from the surface to the depth of 200 nm as shown in Fig. 6b. Similar to Fig. 6a, the carbon concentration became 100% near 200 nm, although it was low near the surface. The fluorinated film thickness was evaluated to about 200 nm as listed in Fig. 4.4.c. After exposure at 480°C, the fluorescence concentration profile spread from the surface to a depth of 500 nm as shown in Fig. 6c and listed in Fig. 4.4.d. At the surface, both the fluorine and carbon concentrations were about 50% as listed in Fig. 4.3.d. From 100 to 400 nm deep, the fluoride and carbon concentrations were constant at 30% and 70%, respectively. From 400 to 500 nm deep, the fluorine and carbon concentrations decreased to 0% and increased to 100%, respectively. Based on these behaviors, with the increasing temperature for exposing the pyrolytic carbon film to the 100% chlorine trifluoride gas for 10 min, the fluorinated layer became thick. Thus, the pyrolytic carbon film exposed at 490°C was considered to contain the incorporated fluorine atoms at a very high concentration from the surface to a significantly deep position. The fluorinated layer was formed and detached from the non-fluorinated region of the pyrolytic carbon film. With the increasing repetition of the cleaning, the fluorine atoms are predicted to have accumulated in the pyrolytic carbon film, which finally cause peeling. Thus, the fluorine accumulation should be reduced by means of any technique, such as an annealing for out-diffusion, in order to avoid serious damage like that shown in Fig. 4.1.d. In order to produce the out-diffusion of the fluorine atoms, the pyrolytic carbon film fluorinated at 480°C was annealed at 900°C for 10 min either in ambient hydrogen or in ambient nitrogen. The carbon and fluorine contents were measured by XPS. Figures 7a and 7b show the carbon and fluorine concentration profiles in the pyrolytic carbon film after annealing in ambient hydrogen and in ambient nitrogen, respectively. In both figures, the concentration of fluorine atoms, which was incorporated in the film as in Fig. 6c, became 0%; the carbon concentration increased to 100% after the annealing in both ambient hydrogen and in ambient nitrogen. Because the carbon content was nearly 100% in the entire film from the surface to a depth position, the fluorine atoms were shown to be perfectly out-diffused. Thus, the high temperature annealing is considered to be an easy and practical way for removing the fluorine atoms after exposure to the chlorine trifluoride gas.

**Deposition and cleaning.—** Based on the behavior of the surface morphology and chemical condition, the entire CVD process accompanying the cleaning is designed as shown in Fig. 3. The silicon carbide film formed at the susceptor surface at temperatures higher than 1500°C is exposed to the chlorine trifluoride gas at temperatures lower than 480°C for removing the silicon carbide film. The fluorine atoms incorporated during the exposure to the chlorine trifluoride gas were removed by means of any technique, such as an annealing for out-diffusion, in order to avoid serious damage like that shown in Fig. 4.1.d. In order to produce the out-diffusion of the fluorine atoms, the pyrolytic carbon film fluorinated at 480°C was annealed at 900°C for 10 min either in ambient hydrogen or in ambient nitrogen. The carbon and fluorine contents were measured by XPS. Figures 7a and 7b show the carbon and fluorine concentration profiles in the pyrolytic carbon film after annealing in ambient hydrogen and in ambient nitrogen, respectively. In both figures, the concentration of fluorine atoms, which was incorporated in the film as in Fig. 6c, became 0%; the carbon concentration increased to 100% after the annealing in both ambient hydrogen and in ambient nitrogen. Because the carbon content was nearly 100% in the entire film from the surface to a depth position, the fluorine atoms were shown to be perfectly out-diffused. Thus, the high temperature annealing is considered to be an easy and practical way for removing the fluorine atoms after exposure to the chlorine trifluoride gas.

![Figure 5](image5.png) Chemical condition of pyrolytic carbon film surface (a) before and after exposure to chlorine trifluoride gas at (b) 430°C, (c) 440°C and (d) 480°C for 10 min.

![Figure 6](image6.png) Carbon and fluorine concentration depth profile from the surface after exposure to chlorine trifluoride gas at (a) 430°C, (b) 440°C and (c) 480°C for 10 min.

![Figure 7](image7.png) Carbon and fluorine concentration depth profile from the surface after exposure to chlorine trifluoride gas at 480°C for 10 min and additional annealing for 10 min in (a) ambient hydrogen and (b) ambient nitrogen.
are removed by annealing at temperatures higher than 900°C either in ambient nitrogen or in ambient hydrogen.

In order to verify the silicon carbide CVD reactor cleaning process, the silicon carbide film deposition and cleaning were performed. By using the EPIREVO S6 reactor, a 30-μm thick silicon carbide film was formed on the pyrolytic carbon film at about 1500°C. Figure 8 shows the chemical condition of the obtained silicon carbide film evaluated by the XPS. The peaks near 100 and 99 eV were assigned to the peaks of Si-C and Si-Si, respectively. This figure shows that most of the film contained Si-C bonds. The content of the film was silicon and carbon at 50% and 49%, respectively. Thus, the obtained film was determined to be silicon carbide.

The surface of the obtained film is shown in Fig. 9b. The appearance and the morphology of the obtained film surface were obviously different from the original ones as shown in Fig. 9a. The thin pebble-like grains, as shown in Fig. 9a, were fully covered with the obtained silicon carbide film having significantly small hills and valleys as shown in Fig. 9b.

The two sample pieces were individually cleaned at the temperatures of 400°C and 460°C for exposure to the chlorine trifluoride gas. One was exposed at 400°C for 30 min and the other was at 460°C for 15 min as shown in Figs. 10a1 and 10a2, respectively. Figures 10a1 and 10a2 show that the silicon carbide film was perfectly removed as determined by a visual inspection. Because the higher temperature induced more fluorination, the color change in Fig. 10a2 was more as determined by a visual inspection. Because the higher temperature and 10a2 show that the silicon carbide film was perfectly removed. Figures 10a1 and 10a2 show that the silicon carbide film was perfectly removed by means of annealing at temperatures higher than 900°C either in ambient nitrogen or in ambient hydrogen.

Next, the combination of chlorine trifluoride gas and the other coating materials, such as tantalum carbide (TaC), silicon carbide and stainless steel, should be discussed. By our preliminary experiments, tantalum carbide was unfortunately and significantly decomposed by chlorine trifluoride gas even at temperatures lower than 300°C. The chemical reactions are considered to occur for producing the gaseous byproducts, TaF5 and CF4. Thus, the tantalum carbide material is not applicable for the process using the chlorine trifluoride gas.

The high quality silicon carbide coating film is industrially produced by the finely-tuned process. Although the coating film made of silicon carbide is simultaneously etched by the chlorine trifluoride gas, the parasitically formed silicon carbide film was more easily removed than the silicon carbide coating film, as reported in our previous study.13

Any reactor has the stainless steel parts which are located at the low temperature positions far from the hot susceptor, and are cooled by the air and water flow. Thus, the parasitic depositions have the significantly different qualities from those formed on the high temperature surface; the cleaning technique developed in this study is considered to be not applicable. For cleaning such the deposition, abrasive operations might be convenient.

Conclusions

In order to develop a practical quick reactor cleaning process for the silicon carbide CVD, the pyrolytic carbon film was chosen as the coating material for the carbon susceptor surface. The pyrolytic carbon film produced no serious damage at temperatures lower than 480°C by the 100% chlorine trifluoride gas for 10 min. The fluorine atoms incorporated into the film surface were perfectly removed by means of annealing in the ambient hydrogen and in the ambient nitrogen. The 30 μm-thick SiC film formed on the pyrolytic carbon film was removed by the chlorine trifluoride gas either at 400°C for 30 min

Figure 8. Chemical bonding state of the formed 30-μm thick silicon carbide film on the pyrolytic carbon film.

Figure 9. Surface morphology of 30-μm thick silicon carbide film formed on the pyrolytic carbon film. (a) before and (b) after the silicon carbide deposition.

Figure 10. Pyrolytic carbon film surface after cleaning at 400°C and 460°C and annealing.
or at 460 °C for 15 min. The annealing process at 900 °C was added after the exposure to the chlorine trifluoride gas. Finally, the cleaning process was shown to be possible within 25–40 minutes. The process developed in this study will provide a quick and practical reactor cleaning method for the silicon carbide CVD.

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