In order to develop the in situ cleaning process using chlorine trifluoride gas for a silicon carbide epitaxial reactor, the etching conditions and process were studied for removing the silicon carbide film formed on the susceptor. The formed silicon carbide film consisted of stacked layers of a polycrystalline 4H-like silicon carbide film, a polycrystalline 3C-silicon carbide film and a silicon-rich silicon carbide film. The average etching rate of the formed film was about four times higher than the silicon carbide coating film of the carbon susceptor. By adjusting the etching temperature to less than 330 °C, the formed silicon carbide films could be removed without significant damage to the susceptor.

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In Situ Cleaning Process of Silicon Carbide Epitaxial Reactor

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Power electronic devices necessary for the current and future industries have been developed using 4H-silicon carbide (SiC) epitaxial wafers,1,2 which were produced by means of the chemical vapor deposition (CVD) method. Generally, in most chemical vapor deposition processes, the film deposition on the substrate surface simultaneously produces an unnecessary film deposition around the substrate. When the amount of such the unnecessary formed films are increased, the formed films emit particles that cause various and serious surface defects in the epitaxial film.3,4 Thus, they must be removed by means of the reactor cleaning technique for the thermal and plasma-enhanced CVD reactor.3,4

Various non-plasma reactors for silicon, gallium arsenide and gallium nitride have an in situ cleaning technique5–7 using appropriate etchant gases, such as hydrogen chloride. In contrast, silicon carbide materials are recognized to be significantly stable8 and are able to be etched only by a few highly reactive reagents, such as chlorine trifluoride gas.9,10,11 Thus, the in situ cleaning process using the chlorine trifluoride gas has been studied.11,12

In our previous study12 as the first report on the silicon carbide epitaxial reactor in situ cleaning technique, chlorine trifluoride gas could remove the particle-type deposition present on the susceptor, the surface of which is coated by a silicon carbide coating film. The particles could be detached at temperatures less than 290 °C while maintaining the silicon carbide coating film on the carbon susceptor. For future studies, the in situ cleaning process should be applied to more frequent forms, that is, the film-shaped deposition.

In this study, the chemical reaction conditions using chlorine trifluoride gas were studied in detail for developing a silicon carbide epitaxial reactor in situ cleaning process applicable for the formed silicon carbide film. Similar to a previous study,12 the key issue to realize a successful cleaning process is to find the practical process window for removing the unnecessary silicon carbide films while minimizing the damage to the susceptor. This study shows that the in situ cleaning is possible by taking into account the difference in the etching rate and the color appearance between the various types of silicon carbide materials.

Experimental

Figure 1 shows the reactor used in this study. Small carbon plates, having 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 silicon carbide coating film (Toyo Tanso Co., Ltd., Tokyo, Japan) the same as that for the industrial CVD reactor. The silicon carbide films were formed on the susceptor surface following the 4H-silicon carbide epitaxial growth process13 so that the 30–50 μm-thick 4H-silicon carbide epitaxial film was formed on the 4H-silicon carbide substrate surface.

For performing the etching, the susceptor having 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 2 shows the typical process used in this study. First, the susceptor was heated in ambient nitrogen to the required temperatures for etching. Next, it was exposed to the chlorine trifluoride gas (> 99.9%, Kanto Denka Kogyo Co., Ltd., Tokyo) at 100% and 50–100 sccm without the nitrogen gas. After exchanging the ambient gas from chlorine trifluoride to nitrogen for terminating the etching, the susceptor was cooled to room temperature. A set of steps, consisting of heating, exposing and cooling, were repeated while adjusting the susceptor temperature. 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 with measuring the weight. For performing the cleaning process, careful operations with the appropriate equipment16,17 are necessary, because chlorine trifluoride is a dangerous and toxic gas.8

Because the shape and contact condition of the silicon carbide films may influence the results of the chemical reaction, the interface...
between the silicon carbide films and the susceptor surface was evaluated using an SEM (JSM-7000F, JEOL Ltd., Japan). Additionally, the surface morphology and the thickness of the silicon carbide coating film on the susceptor were evaluated. The cross-sectional SEM photographs were taken at the Foundation of Promotion of Material Science and Technology of Japan (Tokyo).

Results and Discussion

**Formed film.**—First, the thickness and the contact conditions of the formed silicon carbide film were evaluated. Figure 3 shows the cross-sectional SEM image of the susceptor sample. At the bottom of this figure, the letter c indicates the susceptor main body made of a porous carbon. The letter b indicates the silicon carbide coating film having the thickness of about 60 μm. This film was produced for coating the carbon surface at a high temperature in a corrosive environment. The layer indicated by letter a was the formed silicon carbide film by the 4H-silicon carbide epitaxial film growth process. This layer has a slightly darker contrast than the silicon carbide coating film. Its thickness was about 30 μm. Very thin voids or slits were observed in this layer. The interface between layers a and b had neither voids nor cracks. The formed silicon carbide film was continuously and tightly combined with the silicon carbide coating film surface.

Next, the average etching rate of the formed silicon carbide film and the silicon carbide coating film produced on the carbon susceptor surface was evaluated. The etching was performed by the chlorine trifluoride gas at the concentration of 100%, flow rate of 50 sccm, atmospheric pressure, and temperature of 320 °C. The etching rate was evaluated by means of the weight decrease before and after the etching. Accounting for the non-uniformity of the formed film, the etching rate obtained in this study is the average value over the susceptor surface.

The average etching rate of the formed silicon carbide film was 0.79 μm min⁻¹, while that of the silicon carbide coating film was 0.18 μm min⁻¹. The etching rate of the formed film was about four times greater than that of the susceptor coating film. This indicates that the in situ cleaning is possible when the etching period is carefully adjusted accounting for the film thickness and its surface condition.

**Etching and surface appearance change.**—The susceptor surface having the formed silicon carbide film was etched using the chlorine trifluoride gas. Figure 4a-(i) shows the entire image of the susceptor sample surface. There was a gray colored region near the left bottom edge, as indicated by the letter B. The rest region, indicated by the letter A, has a slightly yellow color. Figure 4a-(ii) shows the SEM image of the susceptor surface in region B, particularly at the position indicated by the arrow. The surface was densely covered with very small grains or platelets having the dimension near 10–20 μm.

This surface was etched by the chlorine trifluoride gas at 290 °C for 120 min. The surface appearance was changed as indicated by Fig. 4a-(i) to Fig. 4b-(i). An elliptical shaped yellow region appeared at the center of region B, as indicated by the letter C. The outside edge shape and position of region B did not change. The color of region A changed from slightly yellow to dark yellow. As shown in Fig. 4b-(ii), region C, indicated by the arrow, showed an entirely flat surface containing pits.

After an additional etching at 300 °C for 60 min, the entire image changed as shown in Fig. 4c-(i). The center of region C again turned to dark gray, indicated by the letter D. The color, shape and position for the outside edge of regions B and C were still the same as those shown in Fig. 4b-(i). The color of region A seemed to have not changed from Fig. 4b-(i). Figure 4c-(ii) shows the magnified image of region C in Fig. 4c-(i). In this figure, the etching was shown to cause many small flakes or fragments from the layer present in Fig. 4b-(ii). The flakes still remained. The surface, to which the bottoms of flakes were attached, seemed to have a flat shape.

Further etching was performed at 310 °C for 120 min. As shown in Fig. 4d-(i), The shape and position of regions A and B remained the same as those in Fig. 4c-(i). The outside border of region D expanded, while region C became narrow. The appearance of region D seemed to be similar to region B. Region D was observed in detail as shown in Fig. 4d-(ii). The surface was entirely flat but with shallow hills.

The silicon carbide layers formed on the susceptor were determined based on the appearance changes caused by the etching. Because the top layer, which covered the entire susceptor surface could be quickly etched off by the etching at 290 °C, this layer might consist of silicon-rich silicon carbide. Because the silicon etch rate by chlorine trifluoride gas is quite high, the etching rate is expected to increase with the increasing silicon content. Next, region C is considered to be 3C-silicon carbide, because the color yellow is characteristic of 3C-silicon carbide. The 4H-like silicon carbide deposition was also expected to be formed on the silicon carbide coating film of the carbon.
susceptor, because the epitaxial growth condition was finely adjusted for producing the 4H-silicon carbide film.

Based on these assignments, the layers of the formed silicon carbide, particularly those at the positions indicated by arrows in Figs. 4a-(i), 4b-(i), 4c-(i) and 4d-(i) were determined as shown in Figs. 4a-(iii), 4b-(iii), 4c-(iii) and 4d-(iii), respectively. The first formed layer was the polycrystalline 4H-like silicon carbide film. Next, the polycrystalline 3C-silicon carbide film was formed. Finally, the silicon-rich silicon carbide film covered the entire surface. By the etching at 290°C, the silicon-rich layer was quickly etched off, thus the 3C-silicon carbide film surface appeared as the top layer, as shown in Fig. 4b-(iii). This figure also shows that the grain boundaries in the 3C-silicon carbide layer were etched to form pits. By further etching, the grains of the 3C-silicon carbide film were removed, but a part of them still remained, as shown in Fig. 4c-(iii). Simultaneously, the surface of the 4H-like silicon carbide film under the 3C-silicon carbide film began to be etched. In Figure 4d-(iii), the silicon carbide film showed a slightly rough surface. The cross section of regions A, B and C on the susceptor after finishing the etching shown in Fig. 4d was observed as shown in Fig. 5. In this figure, (a) is the layer structure before the etching, (b) is the cross sectional SEM image, and (c) is the layer structure after the etching.

Before etching, region C was considered to have three layers on the silicon carbide coating film, as shown in Figs. 5a-(C). After the etching, as shown in Fig. 5b-(C), a needle-shaped residue having a yellow color remained on the silicon carbide coating film. The remaining silicon carbide seemed to have no obvious interface. Taking into account these results, these needles might be a part of the poly 3C-silicon carbide film directly deposited on the silicon carbide coating film. In this region, the 4H-like silicon carbide film was significantly thin or not present.

In Figure 5b-(B), two layers could be recognized in the film on the porous carbon. The upper layer might correspond to the 4H-like silicon carbide film; the lower layer was the silicon carbide coating film. Because this region does not show a yellow appearance during the repetition of etching in Fig. 4, the 3C-silicon carbide film did not exist or the film thickness might be so thin to be very quickly etched off. Although the top surface was not flat, its hills and valleys were shallow. Because the surface had neither steep nor needle-like shapes, this surface might not be the origin for emitting particles.

Figure 5. Cross sectional SEM images and the film conditions. (b): cross sectional SEM image after the etching shown in Figure 4d. (a) and (c): the possible film conditions before and after etching, respectively. (A), (B) and (C) are the positions of the susceptor surface showing various appearance changes.

Figure 6. Surface appearance changes caused at the various temperatures and times. (a): surface before etching. (b-1) and (b-2): after the etching at 340°C for 60 min and extended 150 min, respectively. (c-1): after the etching at 320°C for 60 min, and (c-2): after extended etching at 330 for 150 min.

Etching temperature.—The highest temperature for maintaining the silicon carbide coating film was evaluated. Figure 6 shows the surface appearance changes caused at the various temperatures and time periods. The susceptor initially had a gray colored and slightly specular surface, as shown in Fig. 6a. At 340°C, the susceptor having the formed silicon carbide film was etched for 60 min. As shown in Fig. 6b-1, the entire gray colored surface was split to two regions, such as gray-colored and yellow-colored ones. This kind of change was similar to that seen in Fig. 4a to Fig. 4b. The yellow-colored narrow region along the edges of the susceptor showed that the formed silicon carbide still entirely remained. In the yellow-colored large triangle-like region in the left bottom side, the formed silicon carbide film might remain thick.

The susceptor was further etched at the same temperature, 340°C, for 150 min. Its surface is shown in Fig. 6b-2. Because the yellow-colored narrow region along the susceptor edges became quite thin, the etching was shown to have advanced. Compared to Fig. 6b-1, the yellow-colored region had expanded from the left bottom to the upper position of the susceptor. This color change might not be similar to that seen in Fig. 4a to Figs. 4b and 4c, because the black-colored region appeared at the left bottom position of the susceptor, accompanied by a very clear shape and border. This black surface had an appearance obviously different from the original susceptor surface, but had a porous-like appearance. Thus, this region was concluded to be the bare surface of the porous carbon, which was produced due to the peeling of the silicon carbide coating film during the etching. Thus, the color of the left bottom region of the susceptor in Fig. 6b-2 should be recognized to be slightly different from that in Fig. 6b-1. This slight
color difference, yellow and light yellow, might indicate an important result, that is, the condition immediately before caused peeling of the silicon carbide coating film. The temperature of 340 °C was concluded to be too high to prevent damage to the silicon carbide coating film due to the etching.

Next, a lower temperature, such as 320 °C, was evaluated. After 60 min, the surface was changed from dark gray, as shown in Fig. 6a, to yellow, as shown in Fig. 6c-1. The formed silicon carbide film at three edges, i.e., top, right, and left, was perfectly removed; the surface from the bottom to the near the top showed a yellow color. Because this surface did not have the light yellow color, like Fig. 6b-2, further etching was performed at the higher temperature of 330 °C for 150 min. As shown in Fig. 6c-2, the susceptor surface had a significantly slight yellow color, indicating that most of the formed silicon carbide film was removed. Simultaneously, there was no peeling of the coating film. Based on this result, 330 °C could be the highest possible temperature for avoiding peeling.

Cleaning process.— Figure 7 shows the possible susceptor cleaning process applicable for the film-type deposition. After finishing the 4H-silicon carbide epitaxial growth, the total thickness of the formed film was estimated in order to determine the necessary etching time period. The etching is performed for a time shorter than the estimated etching period, for example, 50–80% of the required minutes. After the etching, the surface of the susceptor is observed by visual inspection. When the amount of the formed silicon carbide film remained is recognized to be significant, further etching is required. After repeating the cleaning operation, termination of the cleaning is carefully determined based on the appearance color of the susceptor.

Although the needle-like shaped residue, like that shown in Fig. 4c, should be removed, additional etching might cause the fatal risk of peeling, like the black region shown in Fig. 6b-2. When the needle-like residue exists at a position far from the wafer position and when it has no possible mechanical contact with any wafer handling device, perfect removal should not be pursued. Because the needle-like residue is tightly attached at the susceptor surface and is not easily detached, such a residue will not have a chance to become the origin of the surface defects of the epitaxial film.

For applying the cleaning process to the epitaxial reactor, the fluorine contamination due to the chlorine trifluoride gas should be taken care. When the carbon susceptor cleaned by the chlorine trifluoride gas was placed near the 4H-silicon carbide substrate during the epitaxial growth, there was fortunately no significant contamination to the epitaxial film. However, further evaluation is necessary.

Conclusions

In order to develop an in situ cleaning process using chlorine trifluoride gas for a silicon carbide epitaxial reactor, the etching conditions and process for removing the formed silicon carbide film were studied. Based on the changes in the surface appearance that occurred during the etching, the formed silicon carbide film was shown to consist of multiple stacked films, such as a polycrystalline 4H-like silicon carbide film, polycrystalline 3C-silicon carbide film and silicon-rich silicon carbide film. Taking into account the etching rate difference between the formed silicon carbide film and the silicon carbide coating film of the carbon susceptor, the formed silicon carbide films could be removed at temperatures less than 330 °C, while the silicon carbide coating film suffered from acceptable damage. Based on the results, a possible in situ reactor cleaning process was designed.

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