Exposure of Tantalum Carbide, Silicon Nitride and Aluminum Nitride to Chlorine Trifluoride Gas

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Manufacturing processes of semiconductor materials and devices utilize various chemical reactions caused by various reactive compounds,1,2 such as hydrides, halides and organic metals, at various temperatures and pressures. The highly corrosive gases not only perform the targeted processes, such as etching, but also frequently and simultaneously corrode and deteriorate the surface of co-existing materials, such as carbon and quartz. The weak material surfaces are covered with robust coating films, made of tantalum carbide, silicon nitride, aluminum nitride and yttrium oxide.3–5

One of the industrially-used highly-reactive etchants is chlorine trifluoride gas,6–13 which is used for the reactor cleaning6–11 and the silicon carbide wafer etching.13 The chlorine trifluoride gas can quickly etch silicon, silicon carbide and tungsten oxide.14 However, because the various parts in the reactor often suffer from corrosion, they should be coated with anticorrosive materials. For this purpose, yttrium oxide has been evaluated in a previous study.15 The other widely used coating materials, such as tantalum carbide,16 silicon nitride,17,18 and aluminum nitride,19 should also be evaluated.

In this study, tantalum carbide, silicon nitride and aluminum nitride were thus exposed to the chlorine trifluoride gas at various temperatures. First, powder-formed materials were used so that the chemical reaction could be active due to the high surface areas. Next, plate-shaped samples of the anticorrosive materials were exposed to the chlorine trifluoride gas in order to observe changes in their thickness and surface morphology.

Experimental

The etching reactor shown in Fig. 1 was used in this study. The sample to be etched was placed in a quartz chamber. Infrared light was emitted from halogen lamps to heat the sample pieces. The chlorine trifluoride gas and nitrogen gas were supplied from gas cylinders via stainless steel tubes. The chlorine trifluoride gas and nitrogen gas were supplied from gas cylinders via stainless steel tubes. The chlorine trifluoride gas at the concentration of 20–100% in ambient nitrogen was supplied to the sample pieces at atmospheric pressure in order to achieve a highly-corrosive condition.

Figure 2 shows the process for exposing the samples to the chlorine trifluoride gas. After heating the samples in ambient nitrogen at the flow rate of 1000 sccm, the chlorine trifluoride gas at 100% and at the flow rate of 50 sccm was introduced in place of the nitrogen gas. The sample temperature was between room temperature, 25°C, and 900°C. After 10 minutes, the chlorine trifluoride gas was replaced with nitrogen gas, then the samples were cooled to room temperature.

In this study, tantalum carbide (m. p. 3880°C, b.p. 4780°C), silicon nitride (m. p. 1900°C) and aluminum nitride (m. p. 3000°C) were evaluated. The powder-formed samples were first used at various temperatures for quickly obtaining any occurrence of chemical reactions with the chlorine trifluoride gas. Next, the plate-formed samples were used in order to observe changes in their thickness and surface morphology.

The powders of tantalum carbide (Wako Pure Chemical Corp., Tokyo, diameter: 1–3 μm), silicon nitride (The National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan, Accreditation substance. The particle diameter was about 0.5 mm.) and aluminum nitride (Nilaco Corp., Tokyo, diameter: 2 μm) were contained in a square-shaped quartz glass tray and placed along with the silicon carbide plate in the reactor. The sample powder after the etching was carefully transported to a different tray for the weight measurement, because the quartz tray could simultaneously etched by the chlorine trifluoride gas at high temperatures.12 The aluminum nitride plate (30 × 30 × 1 mm, TOMOE Engineering Co., Ltd., Tokyo), made by sintering without using any binders, was also exposed to the chlorine trifluoride gas.

The plate surface was observed by scanning electron microscopy, SEM (VK-X250 laser microscope, Keyence Corp., Tokyo, Japan and SU8240, Hitachi High-Technologies Corp., Tokyo Japan.). The chemical condition was analyzed by X-ray photoelectron spectroscopy (Quantera SXM, ULVAC-PHI Corp., Tokyo, Japan). The depth profiles of the fluorine and aluminum concentrations were measured using secondary ion mass spectrometry, SIMS (IMS-7i, CAMECA, Genevilliers Cedex - France). The SIMS measurement and the related observation by SEM were performed at the Foundation of Promotion of Material Science and Technology of Japan (Tokyo).

The following chemical reactions were expected to occur by the chlorine trifluoride gas, taking into account the reactions with various materials:14

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6\text{TaC} + 18\text{ClF}_3 \rightarrow 6\text{TaF}_5 + 6\text{CF}_4 + 5\text{Cl}_2. \quad [1]
\]

Figure 1. Reactor used in this study for exposing samples to the chlorine trifluoride gas.

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In these reactions, the etching products are tantalum pentafluoride (white, m. p. 95.1°C, b. p. 225.0°C) and aluminum trifluoride (white, m. p. 2250°C (200 MPa), sublimation 1276°C). Because tantalum fluoride and silicon fluoride can vaporize at low temperatures, low temperature etching is expected to occur. In contrast, because aluminum fluoride has a high sublimation point, the aluminum compounds are expected to be anticorrosive at the high temperatures even undergoing fluorination.

Results and Discussion

**Tantalum carbide.**—Figure 3a is a photograph of the tantalum carbide before its exposure to the chlorine trifluoride gas. The tantalum carbide powder had 1–3 μm diameters and a black color. The powder diameter at the room temperature could be seen through the quartz chamber wall, as shown in Fig. 3b1. In this photograph taken at seven minutes after initiating the exposure to the chlorine trifluoride gas, a small region flashes a red color. Additionally, a small flare could be observed. This indicated that a significantly high temperature region was caused by the endothermic chemical reaction during its exposure to the chlorine trifluoride gas. Figure 3b2 shows the tantalum carbide powder along with the presence of etching products after exposure. The numerical values below the photograph in Fig. 3 are the weight changes caused by the exposure. The materials in the center region showing a black appearance were the remaining tantalum carbide. In the left-top and left bottom regions, there were grains showing a white color, which indicated that the etching product was tantalum pentafluoride (TaF₅). The by-product was not analyzed, because it unfortunately seemed to be chemically unstable. The temperatures might be increased versus those higher than the melting point (95.1°C) which could melt and aggregate the tantalum pentafluoride to produce the large-sized grains of nearly a few millimeters in diameter. The chemical reaction of tantalum carbide with the chlorine trifluoride gas was concluded to be significant at room temperature.

When the temperature was higher than the boiling point of the tantalum pentafluoride, 229.2°C, the tantalum pentafluoride was expected to be effectively transported away. Thus, the tantalum carbide powder was exposed at 200°C and 300°C to the chlorine trifluoride gas. Figs. 3c and 3d show photographs of the powder after its exposure to the chlorine trifluoride gas. At both 200 and 300°C, more than 90% of the tantalum carbide powder was shown to be removed without any remaining tantalum pentafluoride. The tantalum carbide powder was aggregated after the exposure, because the melt of the by-product might exist to help the tantalum carbide particle aggregation immediately before the vaporization.

Overall, the tantalum carbide easily and significantly reacted with the chlorine trifluoride gas even at room temperature. In order to effectively remove the etching by-product, the tantalum carbide should be heated at temperatures higher than the boiling point of the tantalum pentafluoride (b. p. 229.2°C).

**Silicon nitride.**—Figure 4 shows the appearance of the silicon nitride powder before and after its exposure to the chlorine trifluoride gas at (a) room temperature, (b) 250°C and (c) 300°C. The numerical values below the photographs are the weight change caused by the exposure. As shown in Fig. 4a, a slight weight decrease, ~9%, occurred at room temperature. Next, at 250 and 300°C, as shown in Figs. 4c and 4d, the silicon nitride powder were perfectly etched and removed. Thus, the silicon nitride could react with the chlorine trifluoride gas near room temperature. With the help of moderate heating, silicon nitride is expected to be perfectly removed and produced volatile byproducts without leaving any residue.

**Aluminum nitride.**—The aluminum nitride powder was exposed to the chlorine trifluoride gas at various temperatures from 300°C to 800°C, as shown in Fig. 5. Figure 5a shows the initial appearance without any exposure. The sample initially had a gray color. At 300°C and 500°C, the appearance of the powder was the same as the initial one, as shown in Figs. 5b and 5c, respectively. At 550°C, a part of the sample powder showed a white color, as shown in Fig. 5d. After

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\begin{align*}
\text{Si}_3\text{N}_4 + 4\text{ClF}_3 & \rightarrow 3\text{SiF}_4 + 2\text{N}_2 + 2\text{Cl}_2. \\
2\text{AlN} + 2\text{ClF}_3 & \rightarrow 2\text{AlF}_3 + \text{N}_2 + \text{Cl}_2.
\end{align*}
\]
Figure 5. Appearance of aluminum nitride powder before and after exposure to the chlorine trifluoride gas at (a) 300°C, (b) 500°C, (c) 550°C, (d) 600°C, (e) 700°C and (g) 800°C.

exposure in the temperature range between 600°C and 800°C, the powder had a white appearance.

The aluminum nitride simultaneously showed a weight increase as shown in Fig. 6. At temperatures below 500°C, the weight of the powder samples did not show a significant change. At 550°C, the powder weight showed a nearly 50% increase. At temperatures higher than 600°C, the powder weight became 60–98% greater than the initial ones. At 600°C, a powder weight increase was observed when the chlorine trifluoride gas concentration was higher than 50%.

Such a weight change might show the occurrence of a chemical reaction between the aluminum nitride powder and the chlorine trifluoride gas, as shown in Equation 3. The composition of the powder was evaluated by XPS, as shown in Fig. 7. Before any exposure, the sample powder had aluminum and nitrogen at the atomic percent of about 60 and 30%, respectively, along with a small amount of oxygen at less than 10%. After its exposure at 500°C, while the aluminum concentration was similar to that before the exposure, those of nitrogen and fluorine showed about a 10% decrease and increase, respectively. At 550°C, the fluorine concentration increased to nearly 40% and the nitrogen decreased to less than 10%. At 600°C, the concentrations of aluminum and nitrogen decreased and became nearly 0% and 30%, respectively, while the fluorine concentration significantly increased to 75%. This indicated that most of the aluminum nitride powder was changed into aluminum fluoride powder. Because the molecular weight of aluminum fluoride, 84, is twice higher than that of aluminum nitride, 41, the increase in the sample weight shown in Fig. 6 coincided with the change in the composition shown in Fig. 7.

Next, the aluminum nitride plate was exposed to the chlorine trifluoride gas at various temperatures. The change in the composition was measured as shown in Fig. 8. With the increasing temperature, the aluminum and nitrogen concentrations moderately decreased, while the fluorine concentration increased from about 0% to nearly 30%. Because the surface area of the plate-shaped samples was generally lower than that of the powder-formed ones, the composition change in the aluminum plate was lower than that of the aluminum powder.

Because the density of aluminum nitride, 3.26 g/cm³, is greater than that of aluminum fluoride, 3.07 g/cm³, the thickness of the aluminum nitride plate should increase by the fluorination. Figure 9 shows the change in the aluminum plate thickness by exposure to the chlorine trifluoride gas for 10 minutes. The thickness slightly increased with the increasing temperature. At 800 and 900°C, the thickness increased by less than 2 μm.

The surface morphology of the aluminum nitride plate was evaluated as shown in Fig. 10. Figure 10a shows that the surface before the exposure had shallow hills and valleys which might correspond to the aluminum nitride grains. While the surface morphology did not show a considerable change after the exposure at 475°C, the shallow surface texture showing the grains seemed to become unclear at 550°C. At 600°C and 900°C, the surface similarly showed a smooth appearance. This surface morphology change was considered to be due to the volume expansion by the difference in the density. In Fig. 10, the weight increase was quite low.
At high temperatures, fluorine atoms are considered to deeply diffuse into the aluminum nitride. Figure 11 shows the depth profile of the fluorine and aluminum atoms after the exposure to the chlorine trifluoride gas at 900°C for 10 minutes. Near the surface at less than 5 μm, the fluorine concentration was greater than $10^{21}$ atoms cm$^{-3}$, while the aluminum concentration was low. At the 10-μm depth, the fluorine concentration was $10^{20}$ atoms cm$^{-3}$. Thus, a significantly fluorinated layer was formed from the surface to a 10-μm depth. In addition, a low fluorine concentration layer existed to about a 50-μm depth. The fluorine atoms were shown to reach a deep position. Such a thick layer was expected to cause the volume expansion.

In this study, the aluminum nitride plate maintained its surface morphology near 500°C; however, it became rather smooth at temperatures higher than 600°C. The aluminum nitride is expected to be a practically useful anticorrosive coating material for the etching process using chlorine trifluoride gas, particularly at temperatures higher than 500°C which show a significantly high etching rate of the silicon carbide. While the aluminum nitride is expected to be a good coating material, the anticorrosion material should be chosen taking into account the temperature and the chlorine trifluoride gas concentration of the process.

Conclusions

The anticorrosive nature of frequently-used coating materials, such as tantalum carbide, silicon nitride and aluminum nitride, were studied by exposing them to chlorine trifluoride gas at the concentration of 100%, at atmospheric pressure and at temperatures from room temperature to 900°C. The tantalum carbide powder underwent a quick and significant exothermic chemical reaction without any heating. The silicon nitride powder was etched to produce volatile products at temperatures higher than 250°C. Chlorine trifluoride gas may rapidly etch off the tantalum carbide and silicon nitride at moderately high temperatures without leaving any residue.

The aluminum nitride powder and plate showed a slight increase in weight at temperatures higher than 500°C due to the fluorination. The aluminum nitride plate simultaneously showed a moderate thickness increase along with smoothing the surface. While undergoing fluorination, the aluminum nitride was expected to be useful as an anticorrosive coating film to the chlorine fluoride gas.

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