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Anticorrosive Behavior of SiC$_2$N$_2$O$_2$ Film Formed by Non-Heat Assistance Plasma-Enhanced Chemical Vapor Deposition Using Monomethylsilane, Nitrogen and Argon Gases

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A SiC$_2$N$_2$O$_2$ film was formed on an aluminum substrate without any heating assistance using monomethylsilane, nitrogen and argon gases at 10–30 Pa by the parallel plate plasma-enhanced chemical vapor deposition method. The obtained film did not have any considerable pinhole and crack, based on the evaluation using a concentrated hydrogen chloride aqueous solution. The anticorrosive behavior of the obtained film was studied by means of chlorine trifluoride gas etching at the concentration of 100% at atmospheric pressure and at various temperatures. The etching rate increased with the increasing temperature and with the increasing nitrogen concentration in the film. The increase in the nitrogen concentration in the film enhanced the fluorine diffusion through the film during the etching. The anticorrosive behavior was determined to be adjustable by the nitrogen concentration contained in the film.

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Various electronic tools and devices are used in industry and daily life, often under various chemical conditions, such as a humid and harsh environment. For achieving the anticorrosive conditions, silicon carbide (SiC), silicon nitride (SiN), silicon dioxide (SiO$_2$) and SiC$_2$N$_2$O$_2$ films are very useful as anticorrosive coating films. The SiC$_2$N$_2$O$_2$ film is useful for various purposes, such as low dielectric constant films, diffusion barrier, copper capping layer and etch stop.5–8 Because the advanced electronic devices often consist of various materials having a low melting point,9 the anticorrosive films should be produced at low temperatures, such as room temperature. Thus, as a new formation process, the plasma-enhanced chemical vapor deposition (PECVD) without any heating assistance has been developed and used for the SiC$_2$N$_2$O$_2$ film formation on various substrate materials, in the previous studies.9–11 Some of the substrate materials were shown to influence the formation rate and the contents of the film.

For further development, the issue to be studied is the anticorrosive behavior of the SiC$_2$N$_2$O$_2$ film obtained by this technique. For this purpose, chlorine trifluoride gas was used, because it can quickly etch off significantly stable materials, such as single-crystalline silicon carbide at the typical rate of 5 μm min$^{-1}$. In this study using the PECVD technique without any heating assistance, the SiC$_2$N$_2$O$_2$ film was formed on an aluminum substrate surface. First, the non existence of pinhole and crack in the obtained film was confirmed by means of the etching by a concentrated hydrogen chloride aqueous solution. Next, the obtained film was exposed to the chlorine trifluoride gas in order to evaluate the etching rate and the fluorine diffusion in the film.

Experimental

Figure 1(a) schematically shows the parallel plate PECVD reactor (Soft Plasma Etcher-SE, Meiwafosis Co., Ltd, Tokyo, Japan.) used in this study. This is the same reactor as that used in previous studies.10,11 The PECVD reactor has 80-mm-diameter upper and lower electrodes for the glow discharge. Fluorocarbon rings are attached along the periphery of the electrodes. The chamber, made of acrylic resin, maintains the height of 62 mm between the electrodes.

Aluminum plates were used as the substrate. Because an aluminum surface is quickly covered with the anti-corrosive film consisting of aluminum fluoride due to the chemical reaction with the chlorine trifluoride gas, the aluminum substrate is assumed to suffer from no etching and has no influence on the etching behavior of the SiC$_2$N$_2$O$_2$ film, which was formed on the top surface of the substrate. The substrates were then cut into 10 × 10 mm pieces.

Because the aluminum substrates were stored in ambient air for a long time, the surface was considered to be sufficiently covered with a native oxide and airborne organic contaminants, similar to semiconductor silicon wafers. In order to obtain a clean surface, the sample surface was exposed to argon plasma typically for 1 min at 6 Pa and room temperature, at Step (A) shown in Fig. 1(b).

During Step (B) in Fig. 1(b), the monomethylsilane and nitrogen gases were added at 5%–60% and 0%–80%, respectively, to the ambient argon for 5–10 min. The total pressure and the electric current were 10–30 Pa and 1–16 mA, respectively. The purity of the monomethylsilane, argon and nitrogen gases was 99,9999%. They were used without further purification. The oxygen incorporation into the film was assumed to come from the trace amount of gases containing oxygen atoms, such as O$_2$, H$_2$O, CO$_2$ and CO, in the gases. In addition, the chamber wall material was empirically known to be the origin of the oxygen. The oxygen concentration might influence on the anticorrosive behavior; it has been reported to have a relationship with the partial pressures of monomethylsilane, nitrogen and argon gases.14

The obtained film was first exposed to the concentrated hydrogen chloride aqueous solution (conc HCl aq soln) at room temperature for 1 min in order to quickly evaluate the anticorrosive behavior, similar to the previous study.10 If there were any pinholes and cracks, the hydrogen chloride could enter through them to reach the aluminum substrate surface and cause serious etching. Unfortunately, the hydrogen chloride gas could not be used for this purpose, because it might cause too fast etching to perfectly delete the substrate.

Next, the obtained SiC$_2$N$_2$O$_2$ film was placed in the etching reactor, as shown in Fig. 2(a). The sample was heated by infrared light coming from halogen lamps in ambient nitrogen. The nitrogen flow rate was 1 slm at atmospheric pressure. The temperature was adjusted to that between room temperature and 400 °C. The chlorine trifluoride gas was then introduced at the concentration of 100% and at the flow rate of 50 sccm for 1 min, while the nitrogen gas was terminated. After terminating the chlorine trifluoride gas, the nitrogen was again supplied at 1 slm. The sample was cooled to room temperature and was taken out from the etching reactor.

The film surface morphology was observed using a scanning electron microscope (SEM) (VE-8800, Keyence, Tokyo). The film thickness and chemical bonding conditions were ex situ evaluated by...
X-ray photoelectron spectroscopy (XPS) (Quantera SXM, ULVAC-PHI Corp., Tokyo, Japan). The depth profile was obtained along with the sputtering. The thickness removed by one sputtering operation was 21 nm in this study.

Results and Discussion

Hydrogen chloride.—Figure 3(a) shows the initial aluminum substrate surface. The aluminum surface had a smooth appearance without any large hillocks and pits. Next, one drop of the concentrated hydrogen chloride aqueous solution (conc. HCl \textit{aq} soln) was placed on the sample surface at room temperature for 1 min. The aluminum surface was significantly etched and showed an obviously rough morphology having large pits, as shown in Fig. 3(b).

Next, the SiC\textsubscript{N}O\textsubscript{f}lm having the nitrogen concentration of about 3% was evaluated. As shown in Fig. 3(c), the 84-nm-thick SiC\textsubscript{N}O\textsubscript{f}lm surface did not show any change after the etching by the conc. HCl \textit{aq} soln for 5 min. Similarly, the 168-nm-thick SiC\textsubscript{N}O\textsubscript{f}lm surface had no pits and no roughening after the etching by the conc. HCl \textit{aq} soln for 10 min. The results were the same for those having the other nitrogen concentrations. Thus, the SiCNO film surface was expected to suffer from no etching due to pinholes and cracks by the conc. HCl \textit{aq} soln at room temperature.\textsuperscript{10}

Figure 1. (a) PECVD reactor and (b) process used in this study. Step (A) is the surface cleaning by argon plasma and Step (B) is the SiC\textsubscript{N}O\textsubscript{f}lm deposition using monomethylsilane, nitrogen and argon gases.

Figure 2. (a) Etching reactor and (b) process for exposure of samples to chlorine trifluoride gas.
Chlorine trifluoride gas.—The anticorrosive behavior of SiC\textsubscript{x}N\textsubscript{y}O\textsubscript{z} films having the nitrogen concentration of 3, 10 and 25\% were studied using the exposure to the chlorine trifluoride gas for 1 min at various temperatures.

Figure 4 shows the thickness change in the film, which was formed using monomethylsilane, nitrogen and argon gases at the concentrations of 20, 20 and 60\%, respectively, at the total pressure of 15 Pa and at the average electric current of 2.5 mA for 5 min. The average nitrogen concentration in the film was about 3\%. As shown in Fig. 4, the film thickness did not change by the exposure to the chlorine trifluoride gas at room temperature. Thus, the film containing the 3\% nitrogen was not etched by the chlorine trifluoride gas. At the temperature of 230 °C, the etching was considered to occur, because the film thickness slightly decreased. The occurrence of etching was clearly recognized at 330 and 380 °C, at which temperatures the etching depths were about 10 and 15 nm, respectively. Based on Fig. 4, with the increasing etching temperature, the etching depth increased.

The surface concentration of silicon, carbon, nitrogen, oxygen and fluorine was evaluated by XPS as shown in Fig. 5. Before the exposure to the chlorine trifluoride gas, the concentration of silicon, carbon and oxygen was about 30\%, while that of nitrogen was about 3\%. Additionally, the fluorine concentration was confirmed to be 0\%.

After exposure to the chlorine trifluoride gas at room temperature for 1 min, the surface concentration of fluorine increased to about 8\%. The fluorine concentration at the surface was nearly constant in the temperature range between room temperature and 380 °C. In contrast, the nitrogen concentration at the surface decreased to less than that of fluorine. The carbon concentration slightly decreased at the temperatures higher than 330 °C. This was consistent with the previous study,\textsuperscript{15} which showed that the carbon film could be etched off in the temperature range higher than 300 °C.
Although the surface concentration of silicon, carbon, and oxygen seemed to change, no clear trend could be recognized. The silicon, carbon, nitrogen, oxygen, and fluorine concentrations in the film were evaluated by XPS, accompanied by a shallow sputtering of the surface. Figure 6 shows the various concentrations at the depth of 21 nm from the surface. The concentrations of silicon, carbon, nitrogen, oxygen, and fluorine were 50, 30, 5, 15, and 0%, respectively, in the temperature range of room temperature to 380 °C for the exposure to the chlorine trifluoride gas. Thus, the content of the film after the etching by the chlorine trifluoride gas did not change. Additionally, fluorine was not present at the depth of 21 nm.

In order to evaluate the fluorine diffusion into the film in detail, the depth profiles of the silicon, carbon, nitrogen, oxygen, and fluorine concentration were measured, as shown in Fig. 7. This film was formed under the same conditions as that for the films shown in Figs. 5 and 6.

Based on the quick increase in the aluminum concentration and the existence of an oxygen peak, the film thickness was evaluated to be about 90–100 nm. In the depth range from 20 to 80 nm, the silicon, carbon, nitrogen, and oxygen concentrations were nearly the same values as those shown in Fig. 6. Focusing on the fluorine, the concentration of fluorine was limited to the vicinity of the surface, based on the results shown in Figs. 5–7. Thus, the fluorine diffusion through the film having a nitrogen concentration of 3% during the exposure to the chlorine trifluoride gas was negligible, even at 380 °C.

In order to evaluate the influence of nitrogen, the nitrogen concentration in the film was increased to 10% by adjusting the nitrogen gas concentration during the film formation. The 500-nm-thick SiC$_3$N$_2$O film was formed at the monomethylsilane, nitrogen and argon gas concentrations of 20, 40, and 40%, respectively, at the total pressure of 20 Pa for 5 min and at the average electric current of 5 mA. The obtained film was exposed to the 100% chlorine trifluoride gas at room temperature for 1 min. The surface morphology is shown in Fig. 8. The surface had many crater-like circles, the diameters of which were widely scattered from several to 50 μm. The surface was considered to be significantly etched even at room temperature.

The depth profiles of the silicon, carbon, nitrogen, oxygen, and fluorine in the SiC$_3$N$_2$O film shown in Fig. 8 were measured by XPS. Figure 9 shows that the film thickness was found to be about 450 nm from the oxygen peak and the increase in the aluminum concentration. The average concentrations of the silicon, carbon, nitrogen, and oxygen were about 50, 30, 10, and 10% and were nearly constant in the film, respectively. In contrast, the fluorine concentration at the surface was nearly 10%; it decreased along with the depth from the surface. The fluorine might diffuse from the surface to about a 150-nm depth.

Next, the SiC$_3$N$_2$O film having the nitrogen concentration of 25% was formed. The depth profiles of the silicon, carbon, nitrogen, and oxygen in the obtained film are shown in Fig. 10. A 240-nm
thick SiC\textsubscript{x}N\textsubscript{y}O\textsubscript{z} film was formed at the monomethylsilane, nitrogen and argon gas concentrations of 10, 80 and 10\%, respectively, at the total pressure of 20 Pa for 10 min and at the average electric current of 9 mA. This film had not yet been etched.

In this study, the obtained film simply suffered from etching, without any peeling from the aluminum substrate after the etching at high temperatures. Thus, the obtained films were considered not to significantly shrink.

**Influence of nitrogen concentration.—**The influence of the nitrogen concentration in the film on the etching behavior by the chlorine trifluoride gas is summarized. As shown in Figs. 10 and 11, the 240-nm-thick SiC\textsubscript{x}N\textsubscript{y}O\textsubscript{z} film containing 25\% nitrogen was quickly and entirely removed within 1 min at room temperature. At the nitrogen concentration of about 10\%, the SiC\textsubscript{x}N\textsubscript{y}O\textsubscript{z} film of about 50-nm thick was removed within 1 min at room temperature. Thus, the decrease in the nitrogen concentration in the SiC\textsubscript{x}N\textsubscript{y}O\textsubscript{z} film from 25\% to 10\% made the etching rate low. Simultaneously, the surface morphology significantly changed, as shown in Fig. 8; the fluorine diffusion in the SiC\textsubscript{x}N\textsubscript{y}O\textsubscript{z} film reached to about a 150-nm depth. Thus, the SiC\textsubscript{x}N\textsubscript{y}O\textsubscript{z} film containing a 10\% nitrogen concentration was recognized to still be less anti-corrosive.

In contrast, the SiC\textsubscript{x}N\textsubscript{y}O\textsubscript{z} film containing a 3\% nitrogen concentration showed a significantly low etching rate at room temperature. Even at 380 °C, the etching rate was less than 20 nm min\textsuperscript{-1}. Taking into account that the etching rate of silicon carbide at 400 °C is about 1 \mu m min\textsuperscript{-1},\textsuperscript{11, 12} the nitrogen concentration of 3\% is considered to cause no deterioration of the anti-corrosive behavior. Such a trend is consistent with the etching behavior difference between the silicon carbide\textsuperscript{12} and silicon nitride.\textsuperscript{9} The chemical reaction mechanism to cause such a difference should be clarified in the future study. Particularly, the hydrogen concentration in the silicon nitride film\textsuperscript{15} should be additionally taken into account.

Overall, the increase in the nitrogen concentration in the SiC\textsubscript{x}N\textsubscript{y}O\textsubscript{z} film was shown to significantly reduce the anti-corrosive behavior to the chlorine trifluoride gas at 100%. However, taking into account that the chlorine trifluoride gas is a significantly strong etchant, the high-nitrogen concentrated film is expected to work as the coating film in a moderately harsh ambient. Additionally, the coating film is expected to be easily and quickly removed, when the film is not necessary. Thus, the nitrogen concentration in the film should be chosen and adjusted corresponding to the role of the SiC\textsubscript{x}N\textsubscript{y}O\textsubscript{z} film. Being removable can be an advantage for the manufacturing process.

**Conclusions**

The anti-corrosive behavior of the SiC\textsubscript{x}N\textsubscript{y}O\textsubscript{z} film was studied by means of an exposure to 100\% chlorine trifluoride gas at atmospheric pressure and various temperatures. A SiC\textsubscript{x}N\textsubscript{y}O\textsubscript{z} film was formed on an aluminum substrate without any heating assistance at 10–20 Pa using monomethylsilane, nitrogen and argon gases by the plasma-enhanced chemical vapor deposition method. The exposure to the concentrated hydrogen chloride aqueous solution showed that the obtained film did not have any pinhole and crack. The etching and the fluorine diffusion became significant with the increasing temperature and with the increasing nitrogen concentration in the film. The anticorrosive behavior is expected to be adjustable by changing the nitrogen concentration in the film.

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