Investigation of fluoride layer of yttria coatings prepared by aerosol deposition method

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The fluorination of Yttria (Y₂O₃) coatings in the inner chamber wall of a plasma-etching equipment causes a process drift. In this paper, we investigate the relationship between the microstructure and fluoride layer of Y₂O₃ coatings prepared by aerosol deposition (AD) method compared with Y₂O₃ coatings prepared by atmospheric plasma spraying (APS) and ion plating (IP). The plasma corrosion of AD-coating, which has a highly dense microstructure without any pores, proceeded homogeneously and the specific surface area maintained its initial smooth surface. Moreover, F atoms slightly penetrated the AD-coating and formed a very thin, 45-nm fluoride layer after plasma exposure. The total area of the surface fluoride layer did not increase with plasma exposure time because the surface remained smooth. Therefore, Y₂O₃ coating prepared by AD can suppress surface fluorination and process drift compared with Y₂O₃ coatings prepared by APS and IP.

Key-words: Yttria, Aerosol deposition, Process drift, Plasma corrosion, Fluorination

1. Introduction

Integrated circuits in semiconductor devices continue to be rapidly scaled down to enable their high integration in devices. The International Roadmap for Devices and Systems indicates that the technology node of semiconductor logic devices will reach a size of 5 nm in 2020 and 3 nm in 2022.1) Owing to the rapid scaling-down of integrated circuits, wafer-to-wafer etching reproducibility has become a major concern in plasma-etching processes. It has been reported that chemical composition changes because of the fluorination of inner chamber wall surfaces after plasma exposure causes process drift, such as changes in etching rates, etching profiles, etching selectivity, or etching uniformity.2)–6) Yttria (Y₂O₃) ceramics have been widely used as plasma-resistant materials for the inner chamber wall of plasma-etching equipment.7)–21) They have a low plasma corrosion rate and can significantly reduce particle contamination than conventional ceramics such as alumina (Al₂O₃) or quartz (SiO₂).11)–14) This lower plasma corrosion rate can be explained based on the sublimation enthalpy of fluoride, which is a reaction product of ceramics during the fluorine plasma process. The surfaces of Y₂O₃, Al₂O₃, and SiO₂ are easily fluorinated in fluorine plasma such that fluoride layers are deposited on the surfaces. However, yttrium(III) fluoride (YF₃) has higher sublimation enthalpy (481 kJ/mol) than aluminum fluoride (AlF₃) (301 kJ/mol) and silicon tetrafluoride (SiF₄) (25.8 kJ/mol), and it is more stable in a fluorine-based plasma environment.11)–14) Therefore, Y₂O₃ is more slowly removed from the surface than Al₂O₃ and SiO₂ in plasma-etching processes. However, the fluorination of Y₂O₃ causes a process drift. In this phenomenon, the Y₂O₃ surface of the inner chamber wall is gradually fluorinated (Y–F bond is formed), and F atoms in the plasma are consumed during the fluorination process. However, when fluorination is completed, the fluoride layer releases F atoms into the plasma.9) Therefore, to control the process drift, it is important to understand the fluorination behavior and reduce the fluorination of plasma-resistant materials such as Y₂O₃. Although some studies have investigated the chemical composition effects of plasma-resistant materials on their fluorination behavior, studies focusing on the effects of their microstructures are very few.

Moreover, Y₂O₃ coatings prepared by aerosol deposition (AD) have been reported to exhibit superior plasma resistance in the reduction of particle contaminants than coatings prepared by other methods (e.g., thermal spraying).22)–23) The Y₂O₃ coatings prepared by AD, which have highly dense microstructures without pores, are
homogeneously plasma corroded and maintain their initial smooth surface after plasma exposure. Furthermore, the plasma corrosion behaviors of the AD-coating based on their microstructures is also considered to affect its fluorination behavior, and it is estimated that the AD-coating can potentially reduce fluorine penetration and process drift, but it has not been confirmed until now.

In this study, the relationship between the microstructure and fluoride layer was investigated to verify whether Y2O3 coatings prepared by the AD method are effective in suppressing the process drift. We also compare Y2O3 coatings prepared by the AD method with Y2O3 coatings prepared by atmospheric plasma spraying (APS) and ion plating (IP).

2. Experimental methods

The microstructure and fluorination behavior of Y2O3 coating samples prepared by the AD method were compared with Y2O3 coating samples prepared by APS and IP. The coating samples were formed on Al2O3 substrates. The thicknesses of the coatings prepared by APS, IP, and AD were approximately 100, 8, and 10 μm, respectively. For APS and IP coating, commercial samples were used in this study. Regarding the process temperature, APS-coating was formed at 5000–10000 °C plasma arc, IP coating was prepared at approximately 500 °C, and AD-coating was formed at room temperature.

Figure 1 presents a schematic of the AD system used in this study. The deposition chamber was evacuated with a vacuum system. The Y2O3 ceramic powder (average particle size: 0.3–0.4 μm, purity: 99.99 %) in the aerosol chamber was dispersed with a nitrogen carrier gas with a flow rate of 10 L/min to generate aerosols. The aerosols were then accelerated by the gas pressure difference between the deposition chamber and the aerosol chamber and were injected from the nozzle at subsonic speed. Afterward, the ceramic powder was fractured and deformed by colliding it with a substrate. Ceramic films were then formed in the desired area by oscillating the substrate with an X–Y–Z stage. The pressures in the deposition and aerosol chambers were 90–150 Pa and 45–60 kPa, respectively. The distance from the substrate to the nozzle was set to 10 mm. The cross section of the Y2O3 coatings was observed by scanning electron microscopy (SEM; SU-8220, HITACHI Co., Ltd., Japan) after ion milling (IM4000PLUS, HITACHI Co., Ltd., Japan) using Ar ion beam.

The Y2O3 coatings were partially masked with polyimide films and then placed on the bottom electrode of an inductively coupled plasma-reactive ion etching equipment (MUC-21 RV-APS-SE, Sumitomo Precision Products Ltd., Japan). A mixture of CHF3 (flow rate: 100 sccm) and O2 (flow rate: 10 sccm) gases was then introduced into the chamber of the plasma-etching equipment. The chamber pressure was 0.5 Pa. The power of the coil and bias were 1000 and 500 W, respectively. The frequency of the coil and bias was 13.56 Hz. The Y2O3 samples were exposed to fluorine plasma for 60 min. After the exposure, the surface morphology and developed interfacial area ratio (Sdr), which is the surface texture parameters in ISO 25178, were measured using a laser scanning microscope (LSM; LEXT OLS4500, Olympus Co., Japan). This Sdr parameter is expressed as the percentage of the definition area’s additional surface area contributed by the texture as compared to the planar definition area. The cross section of the Y2O3 coating after plasma exposure was observed by SEM, and Y, O, and F elemental mapping was analyzed by energy-dispersive X-ray spectrometry (EDX; XFlash5060FQ, Bruker Co., Ltd., USA). The crystal structures of the Y2O3 coatings before and after plasma exposure were observed by X-ray diffraction (XRD; X’Pert3 Powder, Malvern Panalytical Co., Ltd., Netherlands and UK). Furthermore, atom concentration and peak separations of the photoelectron spectrum from Y3d of the Y2O3 coatings after plasma exposure were measured by X-rays photoelectron spectroscopy (XPS; PHI Quantera II, ULVAC-PHI Inc., Japan) using a monochromatic AlKα X-ray source at a pass energy of 280 eV. The sputtering times of the XPS measurement were 0, 50, 100, 500, and 2500 s, using focused Ar ion beam. The cross section of the Y2O3 coating prepared by AD was observed by transmission electron microscopy (TEM; JEM-2010F; JEOL Ltd., Japan), and line analysis of Y, O, and F elements was conducted using EDX (Genesis, EDAX Inc., USA).

3. Results and discussion

Figure 2 presents the LSM images of as-prepared Y2O3 coating samples (IP: a-1; APS: b-1; AD: c-1) and their surfaces after plasma exposure (IP: a-2; APS: b-2; AD: c-2). Some pores were observed on the as-prepared surfaces of IP- and APS-coating. It was found that if there were pores in their microstructure, these pores were selectively plasma corroded, and plasma corrosion marks reflecting their pore shape were formed and their surface roughness was increased.24 Therefore, in IP- and APS-coating, plasma corrosion progressed mainly in the pores and the surface roughness increased on these surfaces. However, pores were not observed on the surface of AD-coating before and after plasma exposure. Figure 3 shows developed interfacial area ratio (Sdr) of Y2O3 coatings prepared by APS, IP, and AD, before and after plasma exposure for 60 min. Plasma exposure increased the Sdr of IP coating.
from 0.02 to 0.05 and the Sdr of APS-coating from 0.02 to 0.07, respectively. However, the Sdr of the AD-coating remained almost unchanged after plasma exposure. Thus, IP- and APS-coating exhibited a significant increase in surface area after plasma exposure, whereas the AD-coating maintained its initial smooth surface after plasma exposure.

The cross-sectional SEM images of the microstructures of Y$_2$O$_3$ coatings prepared by APS, IP, and AD before plasma exposure are shown in Fig. 4. Lamellar structures, which were generated by the cooling and solidification of raw material particles in a molten or semi-molten state unique to the thermal spraying method after substrate collision, were observed on the APS-coating. In addition, several fine lateral pores between the lamella structures as well as several pores larger than 10 $\mu$m were observed. Furthermore, columnar structures unique to the IP coating formed by crystal growth were observed on the IP coating in a direction perpendicular to the substrate and vertical pores were observed among these columnar structures. IP is a process wherein a reaction gas and vapor-deposited metal atoms are reacted on the surface of a substrate to form a film. Therefore, it is easy to grow crystals in a specific direction, and it is considered to have a unique structure containing pores between the crystal-grown columnar structures. On the contrary, the AD-coating had highly dense structures without pores. These dense structures occur by the reduction of crystallite size by fracture or plastic deformation of raw material powder during the AD process. These phenomena do not require thermal energy, only the kinetic energy of particles impacting the substrate at subsonic speeds.$^{25}$

Figure 5 shows the cross-sectional SEM images of the microstructures of Y$_2$O$_3$ coatings prepared by APS, IP, and AD after plasma exposure for 60 min. In this study, the IP coating was corroded 1.4 $\mu$m from the initial surface after 60 min of plasma exposure. The APS- and AD-coating were corroded 0.7 $\mu$m from the initial surface after 60 min of plasma exposure. For APS-coating, mortar-like corrosion marks generated from the plasma corrosion of large pores were observed with an increase in surface roughness. For IP coating, the plasma corroded the edge of the vertical pores among the columnar structures selectively with an increase in surface roughness. However, the AD-coating was plasma corroded homogeneously, and distinct plasma corrosion marks were not observed.

Figure 6 shows SEM images and EDX elemental (Y, O, and F) mappings of Y$_2$O$_3$ coatings prepared by APS, IP,
and AD after plasma exposure for 60 min. For IP coating, F atoms were detected, especially around the vertical pores, and they penetrated to a depth of 3–8 μm from the coating surface. This suggests that in microstructures, such as IP coating with vertical pores, F atoms in the plasma can easily penetrate the coating. In the case of APS-coating, F atoms were detected in a large crater on the surface. The F atoms may be owing to residues deposited during fluorine plasma corrosion. However, F atoms were not detected inside APS-coating. Meanwhile, the APS-coating had many closed pores, as presented in Fig. 4. However, these closed pores were isolated from the plasma environment and did not affect the penetration of F atoms. In the case of AD-coating, F atoms were not detected on the surface and inside the coating. However, APS and AD-coating detected fluorine on the outermost surface via XPS and TEM analysis (Figs. 8–10) described later. As the fluorinated layer is very thin, it is considered that the SEM-EDX shown in Fig. 6 could not detect the fluorine on the outermost surface due to its limited resolution.

Figure 7 shows XRD patterns and crystal structures of Y₂O₃ coatings prepared by APS, IP, and AD before and after plasma exposure for 60 min. Before plasma exposure, a diffraction peak around 2θ = 48.5° attributed to the (440) plane in the cubic crystal of Y₂O₃ was detected in IP-coating. However, after plasma exposure, a diffraction peak around 2θ = 47.8° attributed to the (110) plane in the rhombohedral crystal of YOF was detected.
clear peak shift suggests crystal structure change due to the fluorination of Y$_2$O$_3$. On the other hand, only peaks attributed to the cubic crystal of Y$_2$O$_3$ were detected before and after plasma exposure in APS- and AD-coating, except peaks attributed to the rhombohedral crystal of Al$_2$O$_3$, which was the substrate.$^{28}$ As the fluorination of APS and AD was extremely thin, no change was observed in the crystal structure.

Figure 8 shows atom concentration of Y$_2$O$_3$ coatings measured by XPS after plasma exposure of APS-, IP-, and AD-coating at Ar sputtering times of 0, 50, 100, 500, and 2500 s. At sputtering time of 0 and 50 s, large amounts...
of C and F atoms were detected in all coating samples. Plasma treatment using CF$_x$-based gas forms a fluorocarbon layer on the surface of the etching material. Thus, C and F atoms with sputtering time of 0 and 50 s indicate the fluorocarbon layer formed on the Y$_2$O$_3$ coating surfaces. In IP coating, F, Y, and O atoms were detected at sputtering times of 100, 500, and 2500 s. This suggests that the F atoms have deeply penetrated the IP coating. In the case of APS-coating, F, Y, and O atoms were detected at sputtering time of 100 s and slightly at 500 s. For AD-coating, F, Y, and O atoms were detected at sputtering time of 100 s. In the APS- and AD-coating, the F atoms penetrated only the surface, suggesting that the fluoride layer is very thin.

Figure 9 shows the peak separations of the photoelectron spectrum of Y$_3$d measured by XPS after plasma exposure of APS-, IP-, and AD-coatings at Ar sputtering times of 50 and 500 s. XPS after plasma exposure of APS-, IP-, and AD-coatings at Ar sputtering times of 50 and 500 s. For the IP coating, bonding energies originating from Y–O and Y–F were detected at sputtering times of 50 and 500 s, respectively. The Y–F bonding energy consisted of Y$_3$d$_{5/2}$ (159.5 eV) and Y$_3$d$_{3/2}$ (161.5 eV) peaks, whereas Y–O bonding energy comprised Y$_3$d$_{5/2}$ (157.2 eV) and Y$_3$d$_{3/2}$ (159.2 eV) peaks. For APS- and AD-coating, although bonding energies originating from Y–O and Y–F were detected at sputtering time of 50 s, they were hardly detected at sputtering time of 500 s for Y–F. Similar to IP coating, the surfaces of Y$_2$O$_3$ coatings prepared by APS and AD were fluorinated and their chemical bonding changed. However, these fluoride layers were considered to be much thinner than IP coating.
Figure 10 shows cross-sectional TEM images and EDX line analysis (Y, O, and F) of Y₂O₃ coatings prepared by AD after plasma exposure for 60 min. The AD-coating had a highly dense structure with a crystal size of 10–20 nm. Moreover, F atoms were detected in the Y₂O₃ coating from the surface to a depth of 45 nm by EDX line analysis. The fluoride layer of AD-coating was much thinner than that of IP coating whose thickness was ³6-8µm, as shown in Fig. 6. Thus, the microstructure of Y₂O₃ coating significantly influences its fluorination behavior.

Figure 11 presents the schematic of the fluorination behavior of Y₂O₃ coatings prepared by IP, APS, and AD. APS-coating has several fine lateral pores and pores larger than 10µm, which were generated by cooling and solidification of raw material particles in a molten or semi-molten state unique to the thermal spraying method after substrate collision. IP coating has vertical pores, which were formed due to the difference in crystal growth direction. In this study, the pores formed more clearly by the surface roughness of the Al₂O₃ substrate. On the contrary, the AD-coating has highly dense structures without pores, which was formed by the reduction of crystallite size by fracture or plastic deformation of raw material powder during the AD process. The plasma selectively corrodes the pores, producing corrosion marks, reflecting the unique pore shape of the coating process and increasing the surface roughness. In the case of IP coating, F atoms deeply penetrated the coating through its vertical pores and formed a thick YOF fluoride layer. Thus, the microstructures of IP are considerably susceptible to fluorine penetration. APS-coating had a large number of closed pores, but the closed pores were isolated from the plasma exposure environment; the F atoms slightly penetrate and diffuse into the coating, forming a thin fluorinated layer. However, with plasma corrosion of the APS-coating, large craters were formed owing to the large pores inside the APS-coating, and the specific surface area of the coating increases significantly. Therefore, the total area of the surface fluoride layer of the APS-coating is estimated to increase with plasma exposure time. Similar to APS-coating, F atoms slightly penetrated AD-coating, thereby forming a very thin fluoride layer. Besides, the plasma corrosion of AD-coating, which has a highly dense microstructure without any pores, proceeded homogeneously. Moreover, the specific surface area hardly changed and maintained initial smoothness. Therefore, the total area of the surface fluoride layer of AD-coating does not increase with plasma exposure time. In this study, Y₂O₃ coatings were etched over 0.7µm with high energy ion bombardments by bias power. So, the fluorinated layer thickness could be defined by the balance of fluorine diffusion and etching with ion bombardments. However, the inner walls of the plasma etcher, where the Y₂O₃ coatings were actually used, may have been exposed to etching and cleaning plasmas without high energy ion bombardments. Therefore, the fluorinated thickness of surface of Y₂O₃ coatings...
could be increased much for a long time operation than the result in this study.

These results suggest that fluorination behaviors of \( \text{Y}_2\text{O}_3 \) coatings are strongly affected by their microstructures. To reduce or control process drift, it is important to suppress chemical composition change, such as fluorination of the inner wall of plasma-etching equipment. Therefore, \( \text{Y}_2\text{O}_3 \) coating prepared by AD, which can suppress surface fluorination and maintain its initial smooth surface after plasma exposure, can suppress process drifts.

4. Conclusions

The relationship between the microstructures and fluoride layer of \( \text{Y}_2\text{O}_3 \) coatings prepared by AD method was compared with \( \text{Y}_2\text{O}_3 \) coatings prepared by APS and IP.

For IP coating, F atoms deeply penetrated the coating through its vertical pores and formed a thick fluoride layer.

For APS-coating, several closed pores in the coating did not affect the penetration of F atoms and formed a very thin fluoride layer. However, with plasma corrosion, large craters were formed owing to large closed pores, and the total area of the surface fluoride layer was increased with plasma exposure time.

For AD-coating, the F atoms slightly penetrated the coating and formed a very thin fluoride layer. AD-coating had a highly dense microstructure without any pores homogenously plasma corroded. Moreover, the total area of the surface fluoride layer did not increase with plasma exposure time.

Therefore, \( \text{Y}_2\text{O}_3 \) coating prepared by AD, which can suppress surface fluorination and maintain its initial smooth surface after plasma exposure, can suppress process drifts.

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