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Corrosion Behavior of Stainless Steel and Aluminum in a Downstream Environment of CF_4/O_2 Microwave Plasma

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The corrosion characteristics of type 316 stainless steel, component metals of the steel (Fe, Cr, Ni, and Mo), and Al in the downstream effluent of a CF_4/O_2 plasma have been examined as a function of temperature (25-300°C) and feed gas composition (0-30 vol % O_2). Type 316, Fe, and Ni showed weight gains due to the formation of surface reaction films, which consist predominantly of involatile metal fluorides and grow parabolically with exposure time. Pure Cr and Mo exhibited weight losses due to the formation of volatile metal fluorides or oxyfluorides. The corrosion rate of these metals increased with increasing temperature, while that of Al was less than the limit of detection at all temperatures examined. The corrosion rates of Cr and Mo increased with increasing O_2 content of the reactant gas and reached maxima at ~20 vol % O_2 , whereas those of type 316, Fe, and Ni were nearly independent of the O_2 content. At 300°C, Cr_2O_3 films underwent etching in a similar manner as Cr metal, while Fe₂O₃, NiO, and Al₂O₃ films transformed into involatile fluorides or oxyfluorides. Mass spectrometric analyses suggested that F atoms and O_2 molecules are dominant species responsible for corrosion in the downstream effluent. The phase stability diagrams estimated metal fluorides to be the thermodynamically favored reaction products on the metals exposed to the effluent. (O = 2002 The Electrochemical Society. [DOI: 10.1149/1.1479157] All rights reserved.

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Dry etching techniques such as plasma etching (PE), reactive ion etching (RIE), and chemical dry etching or chemical downstream etching (CDE) are indispensable for the fabrication of very large scale integrated (VLSI) circuits.¹ Etching of component materials of VLSI circuits occurs by reactions with active species formed in a low-pressure glow discharge. In addition to chemical etching, physical sputtering and ion-enhanced etching also play an important role in RIE processes. A mixture of CF₄ and O₂ is widely used as a reactive gas for PE, RIE, and CDE processing. Fluorine atoms formed in the plasma of the mixture react with Si, SiO₂, and Si₃N₄ to produce volatile SiF₄, leading to etching effects.² The same etching mechanism is realized for metals of W, Mo, and Ta and their silicides.²⁻⁴

Metals like stainless steel or Al are used as reactor materials to maintain a high vacuum and to provide an electrode for high frequency discharges. Reactions with chemically active plasma species can also occur on the reactor walls and on the surface of metal tubing and components in vacuum systems, resulting in corrosion. However, knowledge of the corrosion behavior of construction materials used for dry etching systems is still limited. Bell et al.⁵ reported that in chemical vapor deposition (CVD) of W using WF₆ as a precursor, stainless steel reactor materials react with WF_6 to form gaseous corrosion products, which leads to the contamination of deposited W films. In a previous study,⁶ we examined corrosion characteristics of pure metals and alloys, such as Al, Ti, Cr, Fe, Co, Ni, Cu, Mo, Ta, W, type 304 and 316 stainless steels, and Alloy 600, in a downstream reactor of a CF₄-11 vol % O₂ microwave plasma. It was found that metals such as Ti, Cr, Mo, Ta, and W suffered from corrosion leading to weight loss, and their corrosion rate increased with rising temperature.⁶ At 300°C, Fe and stainless steels showed a weight gain due to the formation of thick surface reaction films.⁶ Weight changes of Al, Co, Ni, Cu, and Alloy 600 were less than or close to the limit of detection, while thin surface reaction films were detected on these metals by Auger electron spectroscopy (AES).⁶ In order to reveal the corrosion mechanism of the materials for dry etching systems, however, more information is needed about the influence of temperature and feed gas composition on the corrosion reaction kinetics. A knowledge of the corrosion behavior of metal oxides is also needed to explain the corrosion mechanism because stainless steels and Al are initially covered with oxide films.

The purpose of the present study is to elucidate the corrosion behavior of stainless steel and Al in the downstream effluent of a CF_4/O_2 plasma. To realize this purpose, the corrosion rates of type 316 stainless steel, its component metals (Fe, Cr, Ni, and Mo) and pure Al were first measured as a function of temperature and O_2 addition. The corrosion behavior of Fe_2O_3 , Cr_2O_3 , NiO, and Al_2O_3 thin films formed by metallorganic chemical vapor deposition (MOCVD) was then examined by measuring the changes in the thickness and composition of the films. Gas-phase analysis was performed to determine the kind and concentration of reactive species in the downstream effluent of the plasma. Furthermore, the thermodynamic stability of metal oxides and fluorides was examined through the calculation of phase stability diagrams for metal-fluorine-oxygen systems.

Experimental

Specimens.—The specimens used were type 316 stainless steel, component metals of the steel (Fe, Cr, Ni, Mo), and Al, whose analytical composition and heat-treatment conditions are listed in Table I. The size of the stainless steel, Fe, Ni, and Al specimens was $30 \times 18 \times 2$ mm, and that of Cr and Mo $18 \times 7 \times 2$ mm. The specimens were polished with SiC paper and diamond paste to a 1 μ m finish and then degreased ultrasonically in acetone. Except for the exposed area, the surfaces of the specimens were covered with vacuum evaporated Al films 100 nm thick. As described later, Al is not subject to corrosion under the conditions of this experiment.

The Fe₂O₃, Cr₂O₃, NiO, and Al₂O₃ films were prepared on Pt substrates using a cold wall low-pressure MOCVD apparatus described in a previous paper.⁷ Iron(III), chromium(III), and nickel(II) acetylacetonate compounds [Fe(O₂C₅H₇)₃, Cr(O₂C₅H₇)₃, and Ni(O₂C₅H₇)₂], and aluminum triisopropoxide [Al(O-*i*-C₃H₇)₃] were employed as precursors. Nitrogen (99.999 vol %) was used as a carrier gas of the precursors and oxygen (99.9 vol %) as a reactant gas. The temperatures of the precursors and the flow rates of N₂ and O₂ are listed in Table II. The deposition of the films was performed at 350°C.

Apparatus and techniques for corrosion test.—The apparatus used for corrosion tests consists of a feed gas controlling system, a microwave plasma generator, a reaction chamber, and an evacuation system.⁶ Using a microwave power supply (EBIC, MR-301), microwaves with a frequency of 2.45 GHz were transmitted through a coaxial cable to an Ebenson-type cavity, and a plasma was excited in

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Table I. Chemical composition (wt %) and heat-treatment conditions of type 316 stainless steel and pure metals used.

Element																	
	Specimen	С	Si	Mn	Cu	Р	S	0	Ν	Ni	Cr	Fe	Mo	Al	Ti	W	Heat-treatment
	Type 316	0.05	0.68	1.30	_	0.031	0.003		_	10.78	16.81	Bal.	2.14	_			1100°C, 60 min, WQ ^a
	Fe	0.001	0.0006	_	0.0006	0.002	0.001	0.036	0.0040	0.0002	0.0003	>99.95	_	_	_	_	850°C, 30 min, FCb
	Cr	0.003	0.002	0.0001	0.0002	_		0.0387	_	0.0006	>99.95	0.0048	_	0.0001		_	820°C, 5 min, WQ
	Ni	0.010	< 0.01		0.010	0.002	0.002	_	_	>99.9	_	0.010	_	_		_	1000°C, 30 min, WQ
	Mo	0.003	0.003	_	_	0.002	0.002	0.0050	0.0010	0.0010	_	0.010	>99.95	0.002	0.001	0.030	1200°C, 60 min, ACc
	A1	_		_	_		_							>99.7	_	_	400°C, 60 min, FC

^a Water quenching.

^b Furnace cooling.

^c Air cooling.

a quartz discharge tube 12 mm diam. The reaction chamber was located 15 cm downstream from the discharge region. The specimens were placed on an aluminum holder in the reaction chamber and heated by a built-in heater. The reaction chamber and surround-ing tubing were all made of type 304 stainless steel.

Mixtures of CF₄ (99.999 vol %) and O₂ (99.99 vol %) were used as reactant gases. The composition of the gas mixtures was varied between 0 and 30 vol % O₂ by flow rate, while the total flow rate was kept constant at 45 sccm. The pressure of the reaction chamber was increased from 33 to 35 Pa by a microwave discharge, but it was approximately independent of feed gas composition. Prior to corrosion tests, the reaction chamber was evacuated by a rotary pump until the pressure became lower than 0.133 Pa. The specimen was then heated to a given test temperature in the range of 25 to 300°C. After the specimen temperature was stabilized, the reactant gas was introduced into the discharge tube and the microwaves with a power of 80 W were applied to generate a plasma. After exposure for a given time, the specimen was cooled down to room temperature in vacuum.

Corrosion rates were evaluated from weight changes measured by weighing specimens to a precision of 0.01 mg before and after the test. The thickness of surface reaction films formed on the specimens was measured by ellipsometry. The relative phase retardation, Δ , and the relative amplitude reduction, $\tan \Psi$, were mesured at a wavelength 546.1 nm and at an angle of incidence 60° using a rotating analyzer automatic ellipsometer. The thickness and optical constants of the films were determined using a theoretical $\Delta vs. \Psi$ curve which fits the experimental data with minimal error. The theoretical $\Delta vs. \psi$ curves were calculated using Drude's exact optical equations for a three-medium (ambient-film-substrate) model.⁸

The chemical composition of the specimen surface was analyzed by Auger electron spectroscopy (AES) combined with Ar^+ ion sputtering using JEOL JAMP-7100 Auger microprobe. The sputtering rate was determined to be 0.085 ± 0.005 nm s⁻¹ by comparing the sputtering time with the film thickness measured by ellipsometry. The quantitative analysis of elements was performed using relative

Table II. Conditions for deposition of oxide thin films by MOCVD.

				Flow rate (sccm ^a)				
		Tempera	ture (°C)	Carrier gas	Reactant gas			
Oxide	Precursor	Precursor	Substrate	(N ₂)	(O ₂)			
Fe ₂ O ₃	$Fe(O_2C_5H_7)_3$	160	350	300	300			
Cr_2O_3	$Cr(O_2C_5H_7)_3$	140	350	500	500			
NiO	$Ni(O_2C_5H_7)_2$	160	350	800	400			
Al ₂ O ₃	$Al(O-i-C_2H_7)_3$	130	350	200	200			

^a sccm: standard cubic centimeters per minute.

sensitivity factors, which were preliminarily determined from AES spectra collected for standard oxides and fluorides with known composition.

Gas-phase analysis by optical emission spectroscopy and mass spectrometry.—Optical emission spectra were measured using a UV-visible spectroscopy system consisting of a grating spectrometer (Acton Research Co., SpectraPro 150) and a charge-coupled device (CCD) detector (Princeton Instruments Inc., TE/CCD-512-TK/1-UV and ST-135). An optical fiber was used to convey light from the quartz discharge tube to the spectrometer. A small amount of Ar (3.2 vol %) was added to the CF₄/O₂ mixture for argon actinometry measurements, one of the plasma diagnostic methods.⁹ It has been demonstrated that the addition of Ar in a small quantity (<5 vol %) does not perturb the discharge properties of a CF₄/O₂ mixture.^{10,11}

Mass spectra of the downstream effluent of the plasma were collected using a conventional quadrupole mass spectrometer (QMS; ULVAC, MSQ-300) which was operated at a fixed electron impact energy of 70 eV. The pressure of the QMS chamber was reduced by a factor of 2×10^{-5} relative to that of the reaction chamber (35 Pa).

Results and Discussion

Corrosion behavior of metals at 300°C.—PE and RIE processing is usually carried out at temperatures lower than 100°C. However, the temperature of a barrel-type PE reactor using a RF discharge reaches 200°C.¹² With a microwave discharge, the temperature around a discharge tube rises to 250-300°C.¹³ The wall temperature of an inductively coupled plasma (ICP) reactor increases up to ~300°C, depending on applied power and processing time.¹⁴ In light of these facts, the maximum test temperature in the present study was set at 300°C. The initial experiments were performed at 300°C using a reactant gas of CF₄-11 vol % O₂.

Figure 1 shows the weight change, ΔW , as a function of exposure time, t_{exp} , for type 316 stainless steel, Fe, Ni, Cr, Mo, and Al exposed to the effluent of a CF₄-11 vol % O₂ plasma at 300°C. The weight of the stainless steel, Fe, and Ni increases parabolically with increasing time. This suggests that solid reaction products are formed on the surface of the steel and the metals. The weight of Cr and Mo decreases linearly with time, indicating that these metals undergo etching. From the slopes of the $\Delta W vs. t_{exp}$ plots, the corrosion rates of Cr and Mo at 300°C are given as 0.037 and 0.15 g m⁻² s⁻¹, respectively. The weight changes of Al were always less than the limit of detection (±0.01 g m⁻²).

Figure 2a shows the AES depth profile of type 316 stainless steel after 10 min exposure at 300°C to the effluent of a CF₄-11 vol % O₂ plasma. Fluorine is detected through the surface reaction film ~120 nm thick, while oxygen exists only in a superficial layer of the film (Fig. 2a). This suggests that fluorination occurs on the stainless steel surface. From the concentration profile of F, it is evident that the surface film has a two-layer structure, an outer layer consisting



Figure 1. Weight change, ΔW , as a function of exposure time, t_{exp} , for type 316 stainless steel, pure Fe, Cr, Ni, Mo, and Al exposed to downstream effluent of CF₄-11% O₂ plasma at 300°C.

of higher metal fluorides, such as FeF_3 , and an inner layer consisting of lower metal fluorides, such as FeF_2 . In addition to metal elements coming from major alloying components (Fe, Cr, Ni, Mo), a large amount of Mn can be detected in a superficial layer extending to the depth of a few nanometers. To clarify in-depth variations of metal elements in the film, the cationic mole fractions of Fe, Cr, Ni, Mo, and Mn were calculated from Fig. 2a and plotted as a function of depth in Fig. 2b. In the superficial layer, Mn is deeply enriched and the other metals are depleted. Except for this layer, Cr is slightly depleted and Ni is slightly enriched. Molybdenum exists in the inner layer but is depleted in the outer layer. There is no significant enrichment of Cr and Mo in the steel matrix. These facts reveal that a certain amount of Cr and Mo may be lost during the corrosion test at 300°C.

AES depth profiles obtained for Fe and Ni after 10 min exposure are shown in Fig. 3a and b, respectively. The surface reaction films formed on these metals consist predominantly of parent metal fluorides, indicating that fluorination reactions occur on Fe and Ni. The film on Ni can be regarded as a single layer of NiF₂, because it contains only a small amount of O and Mn on the topmost surface (Fig. 3b). On the other hand, the concentration profiles of O and F for the film on Fe suggest that the film is composed of at least two layers, an outer layer consisting of Fe oxide and an inner layer consisting of Fe fluoride (Fig. 3a). The outer layer extends to the depth of ~50 nm and contains a significant amount of F and impurity elements, such as Ti, Cr, and Mn. The composition of the inner fluoride layer is close to FeF₂.

The thickness of the outer layer of the film on Fe varied from experiment to experiment, independent of exposure time. This layer



Figure 2. AES depth profile of type 316 stainless steel after exposure to downstream effluent of CF_4 -11% O_2 plasma for 10 min at 300°C.

is thought to originate from the oxide film formed before plasma excitation. In the present study, the plasma was excited after a CF_4/O_2 mixture was introduced and its composition was adjusted manually to a given value. Therefore, the specimens were exposed to the gas mixture for a short period without discharge. During this period, Fe reacts with O_2 in the gas mixture to form an oxide film. The time required for adjusting the feed gas composition was typically 20 s but was different from experiment to experiment. Oxidation of Fe is also possible during a heating period under vacuum with a pressure level of ~0.1 Pa.

Figure 4 shows AES depth profiles of Cr (a), Mo (b), and Al (c) exposed to the effluent of a CF₄-11 vol % O₂ plasma for 30 min at 300°C. It can be seen from Fig. 4a and b that the surface reaction films containing both O and F exist on the etched surface of Cr and Mo. These films are significantly thin compared with those formed on stainless steel and Fe. The O concentration parallels the F concentration through the depth profiles except the topmost surface. This suggests that the films consist of an oxyfluoride phase or a mixture of oxide and fluoride phases. The surface film on Al is very thin and has a two-layer structure, an outer layer consisting of a single oxyfluoride phase or a mixture of oxide and fluoride phases and an inner layer consisting of an oxide phase (Fig. 4c). The oxygen content of the inner layer seems to be low compared with that of stoichiometric Al_2O_3 . The inner layer is extremely thin (~2 nm or less), so that the AES signal from this layer and that from the Al substrate often overlap each other. This makes it difficult to know the exact concentration of elements of interest.

It has been reported that thin films of Si oxyfluoride, SiF_xO_y , are present on the Si surfaces etched in a CF_4/O_2 plasma¹⁵ and downstream of the plasma.¹⁶ The AES depth profiles shown in Fig. 4a and b reveal that similar oxyfluorides may be formed on Cr and Mo as reaction intermediates. However, there is another source of oxygen.



Figure 3. AES depth profiles of pure Fe and Ni after exposure to downstream effluent of CF_4 -11% O₂ plasma for 10 min at 300°C.

That is, oxygen detected on the etched surface of Cr and Mo may be due to exposure in air when the specimens were transferred from the corrosion test system to the AES system. It is well recognized that many inorganic fluorides are hygroscopic, and thus water vapor has a deleterious effect on fluoride thin films.¹⁷ For example, sputterdeposited CrF_3 films react with water vapor to decompose into Cr_2O_3 and HF.¹⁸ Such degradation of the CrF_3 films was observed after exposure to air with 100% relative humidity (RH) for more than 15 h.¹⁸ When the films were kept in a dry desiccator (<40% RH), no degradation occurred after 10 months.¹⁸ Although detailed experiments are required to determine whether oxygen uptake occurs in the reaction chamber or in air, it is suggested that at least a fluorine-containing thin film is formed on Cr and Mo as a reaction intermediate layer.

The growth process of surface reaction films on stainless steel, Fe, and Ni was examined using ellipsometry. The experimental Δvs . Ψ data for type 316 stainless steel fit a theoretical curve calculated for the growth of a film with an optical constant N_2 = 1.50-0.018*i*. Although the AES depth profile of the stainless steel (Fig. 2a) suggests that the surface film on the steel has a twolayer structure, the film can be optically treated as a homogeneous single layer. This reveals that the optical constant of the outer layer is close to that of the inner layer. The same measurement and analysis were performed on Fe and Ni. The optical constants of surface reaction films on Fe and Ni were found to be $N_2 = 1.52-0.03i$ and 1.45-0.00*i* at 546.1 nm, respectively. The thickness, *d*, of the films formed on type 316 stainless steel, Fe, and Ni at 300°C is plotted against exposure time, t_{exp} , and the square root of t_{exp} in Fig. 5a and b, respectively. For each metal, the film thickness increases paraboli-



Figure 4. AES depth profiles of pure Cr, Mo, and Al after exposure to downstream effluent of CF_4 -11% O₂ plasma for 30 min at 300°C.

cally with increasing time, indicating that the film formation kinetics follows a parabolic rate law. From the slope of $d vs. t_{exp}^{1/2}$ plot (Fig. 5b), one can determine the parabolic rate constant of film growth, k_p . The parabolic rate constant at 300°C changes in the following order: Fe ($k_p = 20.0 \text{ nm s}^{-1/2}$) > type 316 ($k_p = 5.0 \text{ nm s}^{-1/2}$) \geq Ni ($k_p = 0.32 \text{ nm s}^{-1/2}$). It is noted that when the linear portion of $d vs. t_{exp}^{1/2}$ plot for Ni is extrapolated, the line does not pass through the origin. This indicates that the growth of very thin films, probably less than 10 nm in thickness, does not obey a parabolic rate law.

Influence of temperature on corrosion rate.—The corrosion tests were carried out at various temperatures ranging from 25 to 300°C in the effluent of a CF₄-11 vol % O₂ plasma. A significant amount of weight loss was observed for Mo tested at room temperature, while the weight change of Cr became less than the limit of detection at temperatures lower than 100°C. The growth of surface reaction films on stainless steel, Fe, and Ni also became slow as the test temperature decreased. At temperatures lower than 150°C, the thickness of the film on Ni never exceeded 10 nm even after exposure for a long time (~2 h). The error in the film thickness determined by ellipsometric measurements was relatively large (around ± 2 nm), because the measurements were not performed *in situ* in the reaction



Figure 5. Thickness of surface reaction film, *d*, as a function of exposure time, t_{exp} , (a) and square root of t_{exp} (b) for type 316 stainless steel, pure Fe, and Ni exposed to downstream effluent of CF₄-11% O₂ plasma at 300°C.

chamber. For these two reasons, it was difficult to determine the exact growth kinetics of surface films on Ni at temperatures below 150°C.

Arrhenius plots of corrosion rates for type 316 stainless steel and its component metals (Fe, Cr, Ni, and Mo) are shown in Fig. 6. The parabolic rate constant of film growth, $k_{\rm p}$, and the linear rate of weight loss, $-\Delta W/\Delta t$, were employed for representing the corrosion rates of the stainless steel, Fe, and Ni (Fig. 6a), and Cr and Mo (Fig. 6b), respectively. The corrosion rate of each metal increases with rising temperature, following an Arrhenius equation. From the slopes of the log k_p vs. 1/T plots, the apparent activation energies, $E_{\rm a}$, of overall corrosion reaction can be derived as 23.1, 27.3, and 22.6 kJ mol⁻¹ for type 316 stainless steel, Fe, and Ni, respectively. These activation energies are lower than the corresponding energies of fluorination reaction of metals in a molecular fluorine atmosphere, 39.7 kJ mol⁻¹ for stainless steel,¹⁹ 35.2 kJ mol⁻¹ for Fe²⁰, and 41.7 kJ mol⁻¹ for Ni.¹⁹ From Fig. 6b, the apparent activation energies of the corrosion reaction for Cr and Mo are given as 39.8 and 24.7 kJ mol^{-1} , respectively.

Influence of feed gas composition on corrosion rate.—The corrosion tests were performed at 300°C with varying O₂ content in the feed gas from 0 to 30 vol %. The weight changes of type 316 stainless steel, its component metals, and Al after the test for 30 min are plotted against the O₂ content of the feed gas in Fig. 7. The corrosion rates of the stainless steel, Fe, and Ni are approximately independent of the O₂ content, while those of Cr and Mo markedly change with the O₂ content. When the O₂ content is increased from 0 to 20 vol %, the corrosion rates of Cr and Mo increase by approximately a factor of ten and then decrease gradually as the O₂ content is increased further. It has been reported that the etch rates of Si^{16,21,22} and SiO₂^{13,21} in downstream reactors with a CF₄/O₂ plasma go through a maximum as the O₂ content increases.



Figure 6. Arrhenius plots of parabolic rate constant of film growth on type 316 stainless steel, pure Fe, and Ni (a) and the corresponding plots of corrosion rates for pure Cr and Mo (b) in downstream effluent of CF_4 -11% O_2 plasma.

Corrosion behavior of thin oxide films.—The reaction of Fe_2O_3 , Cr_2O_3 , NiO, and Al_2O_3 thin films, formed on Pt substrates by MOCVD, with the downstream gas of a CF_4/O_2 plasma was examined using ellipsometry and AES. The Fe_2O_3 , Cr_2O_3 , and NiO films were crystalline and the Al_2O_3 film was amorphous. The effect of Al_2O_3 film on corrosion prevention in a CF_4/O_2 plasma etching system is especially important, because anodized aluminum is used as a reactor and electrode material in CF_4/O_2 plasma etching systems.²³ Turbomolecular pumps used in dry etching systems employ anodized Al alloy blades to prevent corrosion attacks by aggressive reactant gases.²⁴

The experimental $\Delta vs. \Psi$ data for a Cr₂O₃ film exposed to the effluent of a CF₄-11 vol % O₂ plasma at 100°C fit a single theoretical curve calculated for the etching of a film with an optical constant $N_2 = 2.10-0.05i$, indicating that the Cr₂O₃ film undergoes uniform etching without changing optical properties. The film thickness decreased linearly with time and the slope of the film thickness d vs. exposure time t_{exp} plot provides the etch rate of the film. The etch rates of Cr₂O₃ films as a function of temperature and feed gas composition are summarized in Fig. 8a and b, where the etch rate, $-\Delta d/\Delta t$, is plotted against the reciprocal of the test temperature (a) and the O₂ content of the feed gas (b), respectively. The etch rate changes with the test temperature and the O₂ content in a similar manner as the corrosion rate of Cr metal (Fig. 6b and Fig. 7b). The apparent activation energy of the etching reaction for the Cr₂O₃ film (41.0 kJ mol⁻¹) is approximately the same as that for Cr metal



Figure 7. Weight change, ΔW , as a function of O₂ content of CF₄/O₂ mixture for type 316 stainless steel, pure Fe, Cr, Ni, Mo, and Al at 300°C.

 $(39.8 \text{ kJ mol}^{-1})$. These results indicate that even if a Cr_2O_3 film exists on a metal surface, it will be removed in the initial stage of corrosion and does not work as a protective film.

In contrast to Cr₂O₃ films, Fe₂O₃, NiO, and Al₂O₃ films did not suffer from etching. However, the changes in experimental Δ and Ψ values suggested that the optical constants of Fe₂O₃, NiO, and Al₂O₃ films decreased with increasing exposure time. This is due to the change in chemical composition of the films. Figure 9 shows AES depth profiles for Fe₂O₃ (a), NiO (b), and Al₂O₃ films (c) exposed to the effluent of a CF_4 -11 vol % O₂ plasma at 300°C. Fluorine is detected through the depth profiles of every oxide films. This suggests that the Fe_2O_3 , NiO, and Al_2O_3 films are subject to fluorination, leading to the formation of fluorides or oxyfluorides. In the case of the NiO film exposed for 60 min, the outer region of the film extending to the depth of \sim 35 nm is converted into a fluoride layer containing a small amount of O (Fig. 9b). After prolonged exposure, NiO was completely transformed into NiF2. The F concentration in the surface region of Fe₂O₃ and Al₂O₃ films is also higher than that in the inner region of the films (Fig. 9a and c). This reveals that the superficial layer of these films is highly fluorinated. The thickness of such a highly fluorinated layer is a few nanometers for the Al₂O₃ film. From these results, it is evident that Fe₂O₃, NiO, and Al₂O₃ films react with fluorine to form involatile fluorides or oxyfluorides. In other words, these oxide films do not act as a barrier against fluorine penetration. The inner fluoride layer on Fe shown in Fig. 3a is thought to be formed by the penetration of F through a preexisting oxide layer.

Kim *et al.*²⁵ examined the etching behavior of Al_2O_3 films, formed by plasma-enhanced CVD (PE-CVD), in a RIE reactor with a CF₄/O₂ plasma. They found that the surface monolayer of the Al_2O_3 film is fully fluorinated in the form of AlF_3 and the subsurface layer is partially fluorinated in the form of AlO_3F_y . Our results



Figure 8. Etch rate as a function of temperature (a) and O_2 content of feed gas (b) for Cr_2O_3 film exposed to downstream effluent of CF_4/O_2 plasma.

on MOCVD-Al₂O₃ films, which show the formation of a highly fluorinated layer on the topmost surface of the film (Fig. 9c), is consistent with the results obtained by Kim *et al.*²⁵ Concerning to the interaction between NiO and molecular fluorine, Haendler *et al.*²⁶ have studied the reaction of NiO powders with F₂ at elevated temperatures. They found that NiO does not react appreciably with F₂ at 300°C, but the reaction occurs in 97% yield at 325°C and is completed at 375°C. The incompletely fluorinated powders consisted of NiF₂ and NiO phases, and there was no evidence for the formation of an oxyfluoride phase.²⁶ The AES depth profile shown in Fig. 9b indicates that the outer region of the NiO film is fluorinated to NiF₂ when exposed to the effluent of the plasma at high temperatures.

Gas phase analysis.—In the optical emission measurements of the plasma, argon actinometry^{10,11,23,27} was used for monitoring relative changes in F and O concentrations. That is, the ratio of the intensity of the F emission line at 703.7 nm to that of the Ar line at 750.4 nm, $I_{\rm F}/I_{\rm Ar}$, and the corresponding intensity ratio for the O emission line at 844.6 nm, $I_{\rm O}/I_{\rm Ar}$, were measured as a function of volume percent of O₂ in the feed gas. It was found that when O₂ was added to a CF₄ plasma, the $I_{\rm F}/I_{\rm Ar}$ ratio first increased from 1.28 at 0 vol % O₂ to 1.69 at 15 vol % O₂, and then decreased to 1.37 at 40 vol % O₂. Kastenmeier *et al.*^{13,21} have observed a similar change in the $I_{\rm F}/I_{\rm Ar}$ ratio for a CF₄/O₂ microwave plasma excited in a quartz discharge tube. The $I_{\rm O}/I_{\rm Ar}$ ratio increased gradually from 0.25 at 0 vol % O₂ to 0.75 at 15 vol % O₂, after which it increased quickly to 2.94 at 40 vol % O₂. That is, the concentration of O atoms tends to grow rapidly, as the O₂ content in the feed gas is increased beyond



Figure 9. AES depth profiles of Fe_2O_3 , NiO, and Al_2O_3 films after exposure to downstream effluent of CF_4 -11% O_2 plasma at 300°C.

the point at which the maximum F concentration is attained. Such a trend is identical to that observed by other investigators. 11,28,29

We performed mass spectrometric analyses of CF_4/O_2 mixtures in a reaction chamber with and without a microwave discharge. In the absence of discharge, a series of peaks due to the species formed by the electron impact ionization of CF_4 and O_2 in the QMS ionizer were observed; O^+ at 16 amu, F^+ at 19 amu, CF_2^{2+} at 25 amu, CF^+ at 31 amu, O_2^+ at 32 amu, CF_3^{2+} at 34.5 amu, CF_2^+ at 50 amu, and CF_3^+ at 69 amu. With a discharge, the peak intensity of the species related to CF_4 (for example CF_3^+ at 69 amu) and oxygen (O_2^+ at 32 amu) decreased, while that of F (F⁺ at 19 amu) and HF (HF⁺ at 20 amu) increased. At the same time the peaks due to reaction products such as CO (CO⁺ at 28 amu) and CO₂ (CO₂⁺ at 44 amu) increased substantially and new peaks assigned to COF_2 (COF⁺ at 47 amu and COF_2^+ at 66 amu) and SiF₄ (SiF₃⁺ at 85 amu) appeared. The formation of SiF₄ indicates etching of the quartz discharge tube.

Figure 10 shows the concentration of some representative species in the reaction chamber as a function of the O_2 content of the feed gas. With the addition of O_2 , the concentration of CF_4 and O_2 decreases, while that of F, HF, CO_2 , and COF_2 increases. The concentration of F, HF, and CO_2 reaches a maximum at ~20 vol % O_2 , and that of COF_2 shows a maximum at ~13 vol % O_2 . A slight increase in the concentration of O is observed when the plasma is



Figure 10. Difference between plasma-on and plasma-off intensities of O, F, HF, CO_2 , COF_2 , O_2 , and CF_3 peaks in mass spectra as a function of O_2 content of feed gas.

excited. The dependence of the O concentration on the O₂ percent in the feed is similar to that of the CO₂ concentration. This indicates that the O⁺ peak at 16 amu is attributed primarily to fragmentation of CO₂. The computer simulation of concentration profiles for CF₄/O₂ plasmas suggest that, except for an oxygen-rich plasma (for example CF₄-75 vol % O₂), the concentration of O atoms decreases rapidly to a quite low level when the gas leaves the discharge region.³⁰ The initial increase in the F concentration by the addition of O₂ is consistent with the results reported by other researchers^{13,31} and can be explained by the oxidation of fluorine-containing species, such as CF₂ and CF₃ radicals, in the plasma.³¹⁻³⁴

A comparison between Fig. 7b and Fig. 10 reveals that the corrosion rate of Cr and Mo is related to the concentration of F atoms in the gas phase. To examine the quantitative relationship between the corrosion rate and the atomic F concentration, we estimated the F concentration from the QMS data. It is generally difficult to measure directly the atomic F concentration by mass spectrometry. This is because F atoms react with residual H₂O and hydrocarbons to form HF before arriving at a QMS ionizer. To evaluate semiquantitatively the F concentration, Smolinsky and Flamm³¹ assumed that the HF⁺ peak appeared in mass spectra of downstream gases was due to F atoms from the discharge. The same assumption was made in the present study, and the sum of partial pressures of F and HF, evaluated from the corresponding QMS peak intensities, was used to calculate the concentration of F atoms in the reaction chamber. The estimated F concentration varied between 1.0×10^{19} and 3.9 $\times 10^{20}$ m⁻³ as the O₂ content of the feed gas was changed between 0 and 40 vol %. If a part of the F atoms are already hydrogenated before arriving at the surface of specimens, the calculation method used in the present study leads to an overestimation of the atomic F concentration. Therefore, the atomic F concentration reported in this paper should be regarded as semiquantitative.

Figure 11 exhibits the corrosion rates of Cr (a) and Mo (b) at 300° C as a function of atomic F concentration. There is an approximately linear relationship between the corrosion rate and the F con-



Figure 11. Weight loss, ΔW_{loss} , of pure Cr and Mo at 300°C as a function of atomic F concentration in downstream effluent of CF₄/O₂ plasma.

centration. Therefore, it is suggested that the presence of F atoms is responsible for the corrosion of the metals in the downstream effluent of CF_4/O_2 plasmas.

Thermodynamic stability of metal oxides and fluorides in downstream effluent of CF_4/O_2 plasmas.—The experimental results of the present study suggest that fluorine atoms are the dominant reactive species leading to corrosion of metals in the downstream effluent of CF_4/O_2 plasmas and the corrosion proceeds through the formation of parent metal fluorides, *i.e.*, fluorination. However, there also exists a large amount of molecular oxygen in the downstream gas. There is a possibility that metals react with oxygen as well as with fluorine. The phase-stability diagrams of metal-fluorine-oxygen systems were calculated using standard Gibbs free energies of formation for fluorides and oxides, which are available in thermodynamic data tables.^{35,36} The calculation method is described in the previous paper.⁶

Figure 12 illustrates the phase-stability diagrams of metalfluorine-oxygen systems for Fe (a), Cr (b), Mo (c), and Ni and Al (d) at 300°C. It can be seen that the present experimental condition, which is indicated by a black diamond mark (\blacklozenge), is in the stable region of metal fluoride for all the metal-fluorine-oxygen systems examined. This is valid even if the margin of error for the estimation of P_F and P_{O_2} is taken into account. It is therefore suggested that the chemical reaction of metals with F atoms is thermodynamically more favorable than the corresponding reaction with O₂ molecules. There is a possibility that metal oxyfluorides are formed as corrosion products or intermediates. However, it was difficult to examine the stability of oxyfluorides, because there was not enough thermodynamic data of metal oxyfluorides available to calculate phasestability diagrams including these compounds.

The phase-stability diagrams of Cr-HF-O₂ and Ni-HF-O₂ systems at 300°C were also calculated. From the systems, we found that the experimental condition sits on the boundary between the



Figure 12. Phase stability diagrams of metal-fluorine-oxygen systems for Fe (a), Cr (b), Mo (c), and Ni and Al (d) at 300°C.

stable region of oxide and that of fluoride. This reveals that metal fluorides are not completely stable if HF exists as an alternative of F in the effluent of CF_4/O_2 plasmas.

The experimental results of the present study show that Cr is etched due to the formation of a volatile compound, such as CrF_4 as discussed later, and Ni is fluorinated to NiF₂. These results agree with the prediction deduced from the phase-stability diagrams for metal-F-O₂ systems but are inconsistent with the expectation based on the corresponding diagrams for metal-HF-O₂ systems. Consequently, F atoms are involved in the corrosion of metals in the downstream effluent of CF_4/O_2 plasmas containing 0 to 30 vol % O₂, and the possibility that HF molecules play an important role in the corrosion process would be excluded.

Figure 13 shows the temperature-dependence of the vapor pressure of metal fluorides and oxyfluorides.³⁵⁻⁴⁰ The melting point and the boiling point of the compounds^{41,42} are also shown in the figure. The volatility of compounds is somewhat arbitrarily defined as a vapor pressure larger than 0.0133 Pa (10^{-4} Torr) .¹ This pressure is shown as a dotted line in Fig. 13. In the temperature range examined (25-300°C), the vapor pressures of MoF₅, MoF₆, and MoOF₄ are high enough to vaporize or sublimate. Chromium(IV) fluoride, CrF₄, is also volatile at temperatures higher than 100°C, while lower Cr fluorides, CrF₂ and CrF₃, have low vapor pressures. Therefore, it is presumed that Cr and Mo are subject to etching due to the formation of the highly volatile compounds, CrF₄ for Cr, MoF₅, MoF₆, or MoOF₄ for Mo. The vapor pressures of Fe(II), Fe(III), Ni(II), and Al(III) fluorides are low at temperatures below 300°C. Therefore, these metal fluorides can exist on the metal surface as solid reaction products.

Conclusions

The corrosion characteristics of type 316 stainless steel, its component metals, and Al in the downstream effluent of CF_4/O_2 plasmas, generated in a quartz discharge tube by microwaves, have been examined as a function of temperature and feed gas composition. The results are summarized as follows.

1. Type 316 stainless steel, Fe, and Ni show weight gains due to the formation of surface reaction films, consisting predominantly of involatile metal fluorides. The film formation reaction follows a



Figure 13. Logarithmic of vapor pressure, P_v , of metal fluorides and oxy-fluorides as a function of the reciprocal of temperature, 1/T.

parabolic rate law, when the film thickness exceeds 10 nm. The parabolic rate constant of film growth increases with rising temperature, following an Arrhenius relationship, while it is approximately independent of O_2 content of the feed gas (0-30 vol %).

2. Pure Cr and Mo exhibit weight losses due to the formation of volatile metal fluorides or oxyfluorides. The dependence of the corrosion rate on temperature obeys an Arrhenius relationship. At a given temperature, the corrosion rate increases with increasing O_2 content of the feed gas and reaches a maximum at around 20 vol % O_2 , where the maximum concentration of F atoms in the gas phase is attained.

3. Pure Al shows excellent corrosion resistance against the downstream effluent of the plasma. No weight change was detected in the measurement. A very thin film consisting of an involatile outer fluorine-containing layer (AlO_xF_y or AlF_z + AlO_t) and an inner oxide layer is formed on Al in the effluent.

4. The Cr_2O_3 , Fe_2O_3 , NiO, and Al_2O_3 thin films formed by MOCVD undergo fluorination, when exposed to the effluent of the plasma. The Cr_2O_3 films are subject to etching in a similar manner as Cr metal, due to the formation of a volatile reaction product. The Fe_2O_3 , NiO, and Al_2O_3 films are transformed into involatile fluorides or oxyfluorides.

5. Reactive species responsible for corrosion of metals in the downstream effluent of the plasma are F atoms and O_2 molecules. The corrosion rates of Cr and Mo are approximately proportional to the concentration of F atoms in the effluent.

6. The phase-stability diagrams calculated for metal-fluorineoxygen systems suggest that in the effluent metal fluorides are thermodynamically favored for all metals examined. The vapor pressure of metal fluorides determines whether corrosion results in etching (Cr and Mo) or the formation of solid reaction films (stainless steel, Fe, Ni, and Al).

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