

Fluorine Passivation of Metal Surface for Self-Cleaning Semiconductor Equipment

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Fluorine Passivation of Metal Surface for Self-Cleaning Semiconductor Equipment

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Abstract—Fluorine passivation technology of metal surfaces for ULSI process equipment is investigated and passivated film quality is evaluated. Well-polished and pretreated bare surfaces of stainless steel and nickel are passivated with oxygen-free, high pure fluorine (O_2 and HF less than 1 ppm), and a uniform and stable passivated surface is obtained by introducing two step fluoridation, i.e., direct fluoridation and the succeeding thermal modification (heat treatment in nitrogen). The fundamental mechanism of the surface fluoridation is investigated by differential thermal analysis (DTA).

A chemical structure of the passivated films is examined by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Passivated films of stainless steel exhibit a double layer structure such as FeF_2 covered by CrF_2 , which has a lower vapor pressure than divalent metal fluorides such as FeF_2 , NiF_2 , and MnF_2 . It has been confirmed that the first fluoridation step produces a nonstoichiometric fluoride which is converted to the stoichiometric structure by thermal modification, i.e., the heat treatment of the fluoridated film in nitrogen. Passivation performance is achieved as a result of this thermal modification.

I. INTRODUCTION

FLUORINE passivation of metal surfaces is now recognized as an essential requirement for the progress of advanced semiconductor manufacturing equipment having a self-cleaning function [1] due to the corrosion-free characteristics. Self-cleaning means periodic inner surface cleaning of the process chamber by reaction gases such as Cl_2 , F_2 , etc. Thus the inner surface of the process chamber is not exposed to the clean room air due to this periodical gas phase cleaning, so that air components, mainly moisture, are not adsorbed on the inner surface. This allows realization of an ultraclean process environment [2], and drastically reduces the downtime of process equipment. Periodic gas-phase cleaning of process chambers has been used in practical process equipment [1]. But a large amount of plastic materials such as fluorocarbon resin is included in the chamber to prevent metal surface corrosion. Plastic materials produce a huge amount of outgassing such as moisture and hydrocarbon which drastically degrade the process environment, so that high quality processing such as low temperature and high selectivity performance are not carried out completely. In order to realize an ultraclean process environment for ad-

vanced processing, plastic materials must be removed from the inside of the process chamber. Corrosion-free gas-phase reaction systems with outgas-free performance for an ultraclean process environment can be achieved by the development of fluorine-passivation technology for metal surfaces. These two performances are essentially required to develop high quality and ultraclean processes in the field of ULSI manufacturing [3], [4].

Many kinds of specialty gases, indispensable for semiconductor manufacturing, have corrosive properties which cause particularly troublesome problems. For example, F_2 , HF, Cl_2 , and HCl are essentially reactive gases, and BF_3 , BCl_3 , SiF_4 , $SiCl_4$, SiH_2Cl_2 , $POCl_3$, WF_6 , MoF_6 , etc., become vigorously corrosive when exposed to moisture. Special gas supply systems which consist of vessels, tubing, valves, mass flow controllers, etc., made of stainless steel, are corroded by these reactive gases to cause the degradation of gas quality.

In gas phase reactors such as CVD and RIE systems having metallic process chambers, these halogen gases react and corrode metal surfaces resulting in a degradation of the process environment due to generation of particles and outgassing. These difficulties can be substantially overcome by the introduction of fluorine-passivated metal surfaces which exhibit corrosion-free characteristics to halogen gasses such as Cl_2 , F_2 , HCl, and HF. Fluorine-passivated materials may even make some now impractical processes possible. For example, selective deposition of tungsten is necessary for via hole filling at present, but it is not yet practical due to low-grade WF_6 and poor process equipment. This tungsten selective deposition is realized by a combination of ultraclean WF_6 and advanced process equipment made from fluorine-passivated metals. The periodic etching of deposited tungsten on the surface of the reactor by F_2 gas is used to maintain an ultraclean environment.

With respect to corrosion, there have been many investigations of metal surface fluoridation for corrosion rate and corrosion resistance. Nickel is known to have high corrosion resistance to fluorine and hydrofluoric acid, therefore many research studies of corrosion rates have been reported [5]–[7]. Kinetics and mechanism of fluoridation of nickel were investigated [8], [9], but there did not exist an evaluation of the quality of the passivated film. The only corrosion resistance data that has been reported is from thin films (on the order of 10 Å) formed at room temperature. And only the characteristics of the

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corrosion resistance of these films were reported on thin films (10-Å order) formed at room temperature [10], [11]. The kinetics of fluoridation on iron surfaces were reported [12]–[14], but these reports did not evaluate the corrosion-resistance characteristics.

Fluorine passivation technology has been applied to stainless steel having a smooth surface formed by electropolishing [15], [16], and practically utilized in the selective etching of native oxide from a silicon wafer using hydrogen fluoride gas [17], [18]. This paper describes the fluorine passivation of stainless steel and nickel in detail.

Pretreatments of metal surfaces and the kinetics of the passivation film formation are discussed in Section II. Section III describes the passivation procedure and the chemical structure of fluorine passivated films. The characteristics of corrosion resistance and outgassing of these films are given in Section IV. Section V describes the necessity of preparing a clean surface just before fluorine passivation. It also describes the thermal modification of fluoridated films, that is, the modification to the stoichiometric composition due to the heat treatment in nitrogen, the fluorine diffusion mechanism in fluoridated film, and the fine chemical structure of fluoridated film. The conclusion is given in Section VI.

II. REACTION OF FLUORINE WITH METAL SURFACE

A. Materials and Gas Supply System

Well-polished stainless steel and nickel are used for fluorine passivation. These metal surfaces are polished with mechanical and electric methods without accompanying a fragmented layer (Beilby layer). Mechanical polishing such as buff polishing is well known to generate a fragmented layer consisting of microcrystals having a thickness of about 1 μm [19]. Thus, electropolishing is essentially required to remove this fragmented layer. Surface roughness of these well-polished metal surfaces is evaluated ranging from 300 to 400 Å by surface profiler. Oxygen-free high pure fluorine and ultraclean nitrogen are used and their purity is evaluated by gas chromatography (GC), the Fourier transform infrared spectrometer (FT-IR), and dew point meter, to be less than 1 ppm for impurities such as O_2 , HF, SiF_4 , CF_4 , CO, CO_2 , HC, and H_2O . The supply system for ultraclean nitrogen and fluorine is an ultragas delivery system consisting of electropolished 316L stainless steel tubes, ultraclean valves, and other ultraclean components [20]–[25].

B. Differential Thermal Analysis (DTA) of Fluoridation

1. *Apparatus and Measurements:* Fluoridation conditions of stainless steel are investigated with DTA. The DTA system, consisting of nickel and monel parts and α -alumina furnace, can withstand fluorine corrosion up to 500°C.

A 304 stainless steel foil ($5 \times 5 \times 0.02$ t) is placed in the sample holder and the system environment is replaced with nitrogen. It is confirmed with GC that oxygen concentration in the system has been reduced to 10 ppm or

less. Then the sample is heated to a specified temperature, and fluoridation is carried out by flowing fluorine gas. During the measurement, nitrogen is introduced into the thermogravimetry (TG) part to prevent fluorine corrosion. Owing to this procedure, the maximum concentration of fluorine in the DTA is limited to 25-percent F_2 in nitrogen.

2. *Pretreatment Conditions of Stainless Steel Surface:* Generally, stainless steel is covered with a native oxide film (20–30 Å). If the fluoridation is carried out without removing this native oxide film, perfect passivation is impossible. Therefore, removal of the native oxide film from the metal surface is a very important process.

The exothermic peak is observed in the initial stage of reaction of fluorine with stainless steel. The existence of a native oxide film on the stainless steel surface reduces the exothermic peak when compared with that of a bare surface of stainless steel as shown in Fig. 1.

The removal condition of native oxide film on the surface is examined by four types of pretreatment as shown in Table I. It is seen in Table I that the exothermic peak area starts to exhibit constant value (8.2–8.4) from the pretreatment with diluted hydrofluoric acid after more than 1 min. When the pretreatment is not enough to remove a native oxide film from the metal surface, the exothermic peak area becomes smaller than the constant value as shown in Table I. From these results, it is confirmed that native oxide film can be completely removed by pretreatment with diluted hydrofluoric acid after more than 1 min. To avoid the reoxidation of metal surfaces, the samples have been transferred in nitrogen environment from the pretreatment chamber to the fluoridation chamber.

3. *Fluoridation Temperature:* Iron is the major component of stainless steel and is well known to take fluoridated forms as FeF_2 or FeF_3 . Fig. 2 indicates the temperature dependences of DTA and TG signals of synthesized FeF_2 in diluted fluorine gas in nitrogen. The exothermic fluoridation is confirmed from DTA signal increase at temperatures higher than 265°C, where the simultaneous increases of TG signal indicates a weight increase, i.e., the formation of FeF_3 .

The optimum fluoridation temperature of stainless steel is determined by X-ray diffraction (XRD) measurement. Three hundred and four stainless steel foil samples have been fluoridated at 250° and 275°C, respectively, based upon DTA information. Fig. 3 shows the XRD pattern of the fluoridated surface. The XRD pattern clearly indicates the single phase structure (FeF_2) of the fluoridated surface at 250°C, while there appears coexistence of FeF_2 and FeF_3 in the fluoridated film at 275°C. The fluoridation of 304 stainless steel foil should be carried out at a temperature lower than 265°C in order to suppress the formation of FeF_3 structure, because the fluoridated film may be cracked by the coexistence of FeF_3 . In the fluoridation procedure, the phase change temperature from FeF_2 to FeF_3 is defined as a critical temperature. This critical temperature strongly depends on the composition and crystal structure of stainless steel. For example, the crit-

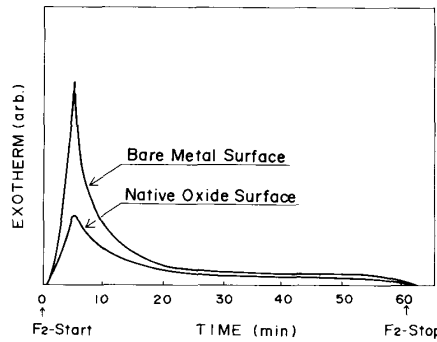


Fig. 1. DTA curve of the fluoridation of a stainless steel surface. F₂ concentration: 25 percent in N₂, fluoridation temperature: 220°C.

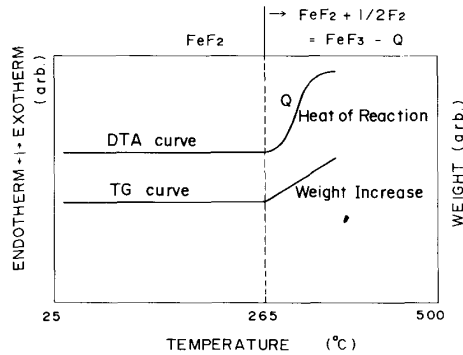


Fig. 2. DTA and TG (thermogravimetry) curve for the fluoridation of synthesized FeF₂. F₂ concentration: 25 percent in N₂.

TABLE I
HEAT OF REACTION OF STAINLESS STEEL WITH FLUORINE (DTA
CONDITION: TEMPERATURE 220°C, F₂ CONCENTRATION
25 VOL PERCENT)

Pretreatment of Surface	Exothermic Peak Area
Temp. and Time	(cm ² /100mg)
NH ₄ OH-H ₂ O ₂ : 90°C 10min	5.4
NH ₄ OH-H ₂ O ₂ : 90°C 10min -- HF : R.T. 30sec	4.8
NH ₄ OH-H ₂ O ₂ : 90°C 10min -- HF : R.T. 1min	8.2
HF : R.T. 30sec	7.0
HF : R.T. 1min	8.4
HF : R.T. 5min	8.4
HF : R.T. 10min	8.2
IPA : R.T. 5min -- HF : R.T. 30sec	6.9
IPA : R.T. 5min -- HF : R.T. 1min	8.2
NH ₄ OH-H ₂ O ₂ (NH ₄ OH:30% H ₂ O ₂ :H ₂ O=1:4:20)	
HF (50% HF:H ₂ O=1:100), IPA (isopropyl alcohol)	

ical temperatures are 265°C for 304 stainless steel foil having a thickness of 20 μm, 220°C for 304 stainless steel plate, and 300°C for 316L stainless steel plate. The detail of this critical temperature will be described in succeeding papers [26].

Fig. 4 shows the XRD pattern for fluoridated nickel surfaces produced at 350° and 400°C. NiF₂ · 4H₂O structure is found to remain in the case of 350°C fluoridation.

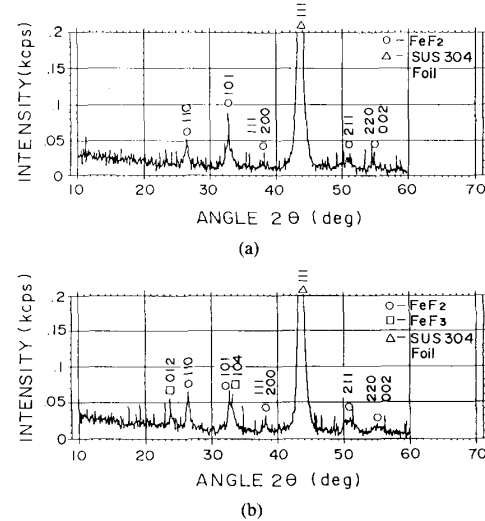


Fig. 3. X-ray diffraction (XRD) pattern of the fluoridated films of 304 stainless steel foil surfaces. (a) Fluoridation temperature: 250°C. (b) Fluoridation temperature: 275°C.

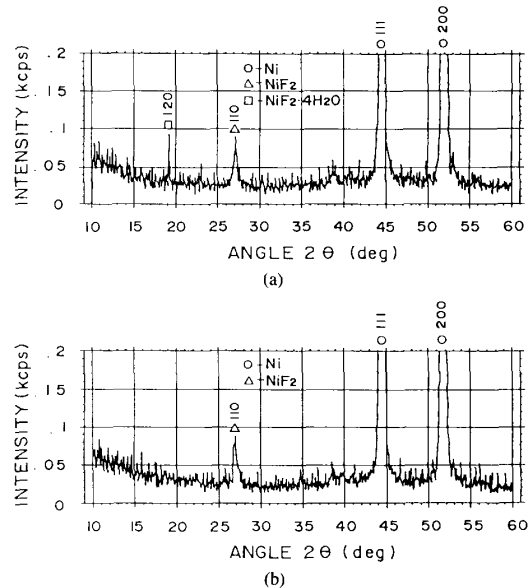


Fig. 4. XRD pattern of the fluoridated films of nickel surface. (a) Fluoridation temperature: 350°C. (b) Fluoridation temperature: 400°C.

The formation of NiF₂ · 4H₂O is caused by adsorbed moisture on the nickel surface. It is seen from Fig. 4 that a surface of nickel fluoridated at 400°C exhibits a single phase structure, such as NiF₂. Fluoridation at temperatures higher than 450°C causes cracking of the film. The optimum fluoridation temperature for nickel has been determined to be in the range of 350°-450°C.

C. Reaction Rate and Activation Energy

The rate and activation energy of reaction of fluorine with 316L stainless steel and nickel are measured using a

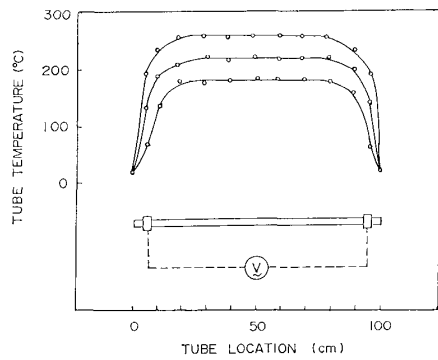


Fig. 5. Apparatus for the study of metal fluoridation kinetics and the tube temperature distribution along the length.

1/4-in tube 1 m in length. The fluoridation apparatus is shown in Fig. 5. The apparatus consists of electropolished 316L stainless steel and all metal valves of 316L stainless steel.

The native oxide of the sample tube is removed by pretreatment with 1:100 HF (0.5-percent HF solution) for 1 min, and the tube is baked at 250°C in nitrogen for 1 h to remove adsorbed moisture. The desorbed moisture from the tube is confirmed with a dew point meter (with a detection limit of -100°C). The tube is heated directly with an electric current controlled within 1 A [27]. The tube temperature's distribution along the length is shown in Fig. 5. The tube is evacuated at the reaction temperature, and fluorine gas is introduced to the pressure of 760 torr. The reaction rate is measured by fluorine consumption at 180°C, 220°C, 260°C for stainless steel and 300°C, 400°C, 500°C for nickel. The pressure in the tube is kept within 10 torr of the initial pressure by intermittent additions of fluorine as the pressure drops. Fluorine consumption is measured by accumulation of the pressure-drop reading at suitable time intervals. The reaction order (n) and reaction rate (K) are obtained from the diffusion equation [8] $W^n = Kt$ as shown in Fig. 6, where W is consumed fluorine weight and t is time. In addition, the film thickness is shown in Fig. 6. The reaction order indicates that the fluoridation of stainless steel and nickel follows a roughly parabolic rate law.

The relation between the rate constants of the reaction K and reciprocal temperature ($1/T$) is plotted in Fig. 7, and the activation energy obtained is 9490 cal/mol (0.41 eV) for stainless steel and 9950 cal/mol (0.43 eV) for nickel. In past research, the activation energy of metals

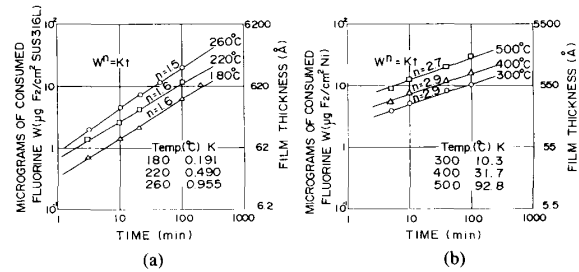


Fig. 6. Logarithmic plots of reaction rates of 316L stainless steel and nickel with fluorine at (a) 180°, 220°, 260°C for 316L stainless steel and (b) 300°, 400°, 500°C for nickel.

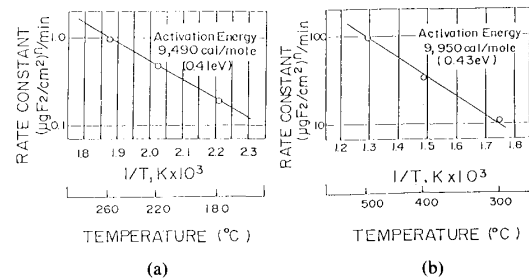


Fig. 7. Arrhenius plot of the rate constants for the reaction of 316L stainless steel with fluorine at (a) 180°, 220°, 260°C for 316L stainless steel and (b) 300°, 400°, 500°C for nickel.

by fluoridation has been reported to be 5600 cal/mol (0.24 eV) for stainless steel [28], 17 000 cal/mol (0.73 eV) for nickel [8], and 8400 cal/mol (0.36 eV) for iron [14].

III. PASSIVATION OF METAL SURFACE

A. Passivation Procedure

Stainless steel is baked at 250°C in nitrogen for 1 h before fluoridation. The desorbed moisture in the chamber is confirmed with a dew point meter (with a detection limit of -100°C). Fluorine is introduced into the chamber and the fluoridation is carried out at 220°C for 80 min. Fluorine is completely purged off from the chamber by nitrogen after fluoridation, and then the fluoridated stainless steel surfaces is heat treated at 320°C in nitrogen for 1 h to improve the film quality. The crystal structure is determined at fluoridation temperature, and the FeF_2 structure formed in the fluorine environment is not converted to the FeF_3 structure in nitrogen even if the temperature is increased higher than the critical temperature.

B. Structure of Fluorine Passivated Surface

The XPS analysis of the surface chemical composition of a passivated film formed on 316L stainless steel surface is shown in Fig. 8. It is confirmed that the top surface composition of the passivated film is CrF_2 . The elements O and C detected at initial sputter time come from adsorption of H_2O , O_2 , and CO_2 in clean room air.

The XPS analysis of the chemical composition of passivated film, formed on the chemically polished nickel

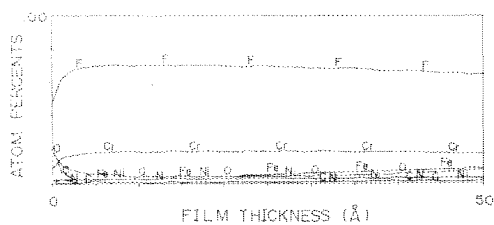


Fig. 8. Depth profile of X-ray photoelectron spectroscopy (XPS) spectra from the top surface of passivated 316L stainless steel. 316L stainless steel: electropolished piece. Fluoridation: 220°C, 80 min, heat treatment: 320°C, 60 min.

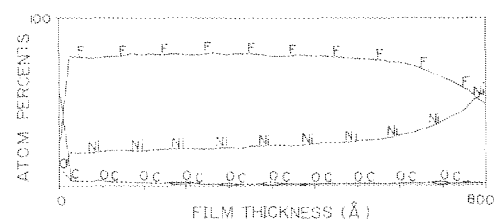


Fig. 9. Depth profile of XPS spectra from a passivated nickel surface. Nickel: chemically polished piece. Fluoridation: 400°C, 80 min, heat treatment: 500°C, 60 min.

piece by fluoridation at 400°C for 80 min and heat treatment at 500°C in nitrogen for 1 h is shown in Fig. 9. The passivated film is composed of the NiF_2 structure without the incorporation of a $\text{NiF}_2 \cdot 4\text{H}_2\text{O}$.

IV. EVALUATION OF FLUORINE PASSIVATED SURFACE

A. Corrosion Resistance of Passivated Stainless Steel Surface for Chlorine

The average roughness of 360 Å before passivation is improved to the level of 160 Å by a two step passivation procedure. Thus the passivated surface becomes smoother than the original surface. This smooth surface is maintained after the corrosion test described below.

The surface roughness and corrosion resistance of electropolished tubes are markedly superior to those of bright-annealed or cold-worked tubes.

The corrosion test of the passivated electropolished 316L stainless steel tube was carried out in an industrial grade chlorine environment. The experimental conditions are an exposure time of 28 h, chlorine pressure of 1 kg/cm², and a temperature of 25°C. Fig. 10 shows an SEM photograph of the inner surfaces of the tube after the corrosion test. It is seen from Fig. 10 that the unpassivated stainless steel surface is corroded completely while the passivated surface shows negligible change.

The unpassivated surface and the passivated surface of a chemically polished 316L stainless steel piece were exposed to a chlorine pressure of 5 kg/cm² for 72 h at 25°C. The SEM photograph and XRD pattern of the surfaces before and after the corrosion test are shown in Figs. 11 and 12, respectively. These figures indicate that the passivated surface is not corroded even in this high pressure

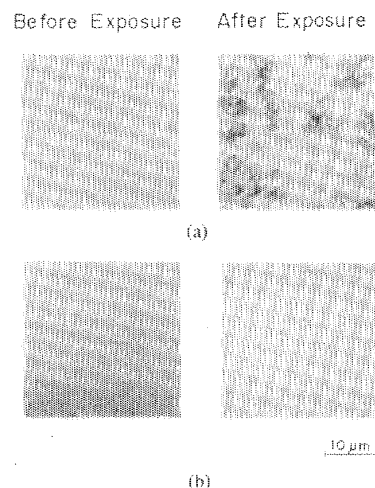


Fig. 10. SEM photograph of (a) unpassivated and (b) passivated 316L stainless steel surfaces exposed to Cl_2 at normal pressure. 316L stainless steel: 1/4-in electropolished tube, exposure environment: 100-percent Cl_2 at 1 kg/cm² (25°C, 28 h). Fluoridation: 220°C, 80 min, heat treatment: 320°C, 60 min.

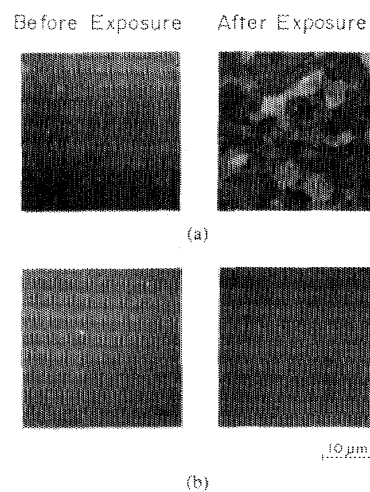


Fig. 11. SEM photograph of (a) unpassivated and (b) passivated 316L stainless steel surfaces exposed to Cl_2 at high pressure. 316L stainless steel: chemically polished piece, exposure environment: 100-percent Cl_2 at 5 kg/cm² (25°C, 72 h). Fluoridation: 220°C, 80 min, heat treatment: 320°C, 60 min.

chlorine environment though the unpassivated surface is completely corroded to form $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$.

B. Corrosion Resistance of the Passivated Surfaces in Wet Hydrogen Fluoride Gas

Fig. 13 shows SEM photographs of unpassivated and passivated 316L stainless steel surfaces after the cyclic test of exposing them to wet hydrogen fluoride gas (HF: 5 vol percent, H_2O : 1 vol percent, N_2 : 94 vol percent) and heating them in nitrogen. As can be seen, there is no significant corrosion of the passivated stainless steel surface, while the unpassivated stainless steel surface is vigorously corroded.

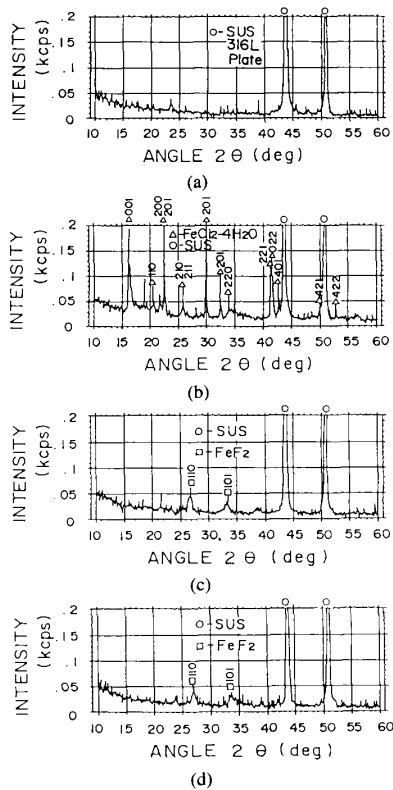


Fig. 12. XRD pattern of 316L stainless steel surfaces exposed to Cl_2 at higher pressure: (a) unpassivated surface before exposure, (b) unpassivated surface after exposure, (c) passivated surface before exposure, (d) passivated surface after exposure. 316L stainless steel: chemically polished piece, exposure environment: 100-percent Cl_2 at 5 kg/cm^2 (25°C , 72 h). Fluoridation: 220°C , 80 min, heat treatment: 360°C , 60 min.

The unpassivated and passivated surfaces of nickel were exposed to wet hydrogen fluoride gas (HF: 5 vol percent, H_2O : 1 vol percent, N_2 : 94 vol percent) at the pressure of 1 kg/cm^2 for 14 days at 25°C , and the degrees of corrosion were observed by SEM photographs. Significant corrosion was not seen on the passivated surface as shown in Fig. 14, while the unpassivated nickel surface was completely corroded although nickel was considered to have high corrosion resistance to hydrogen fluoride.

C. Structure Stability and Gas Desorption Characteristics of the Fluorine Passivated Surface

The structural stability of passivation films is evaluated by heating the passivation films formed on the 1/4-in electropolished 316L stainless steel tube, where HF molecules released from passivation films are measured by atmospheric pressure ionization mass spectrometry (APIMS) [29]. Ionization current intensities from APIMS are illustrated for three samples having three different thermal modification temperatures such as 320° , 350° , and 400°C in Fig. 15 (a)–(c). HF molecules are detected at the tube surface temperature of 100°C for the sample thermally modified at 320°C as shown in Fig. 15 (a),

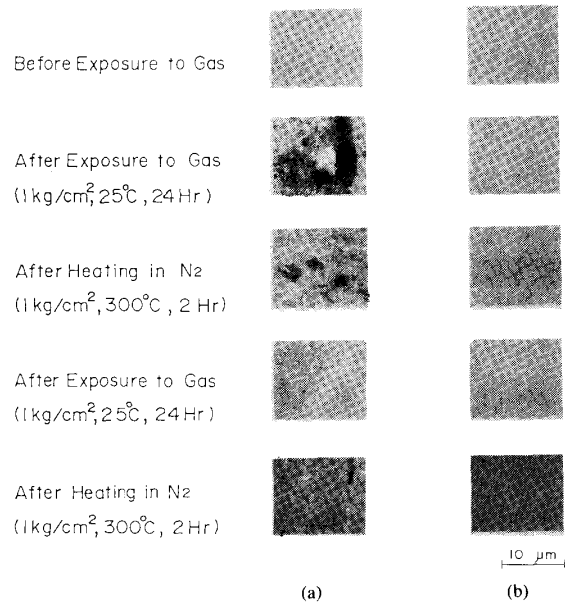


Fig. 13. SEM photograph of (a) unpassivated and (b) passivated 316L stainless steel surfaces exposed to wet hydrogen fluoride gas and cyclically heated. 316L stainless steel: chemically polished piece, wet hydrogen fluoride gas: HF 5, H_2O 1, N_2 94 (vol percent). Fluoridation: 220°C , 80 min, heat treatment: 320°C , 60 min.

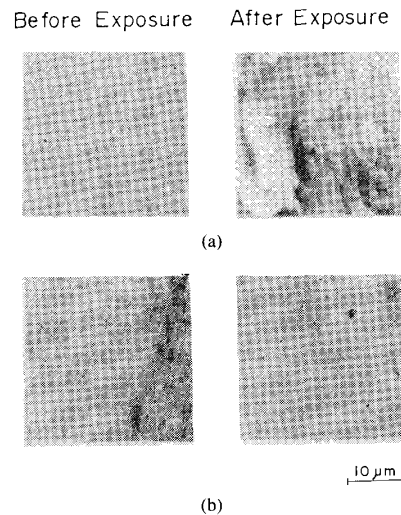


Fig. 14. SEM photograph of (a) unpassivated and (b) passivated nickel surfaces exposed to wet hydrogen fluoride gas. Nickel: chemically polished piece, wet hydrogen fluoride gas: HF 5, H_2O 1, N_2 94 (vol percent), exposure environment: at 1 kg/cm^2 (25°C , 14 days). Fluoridation: 400°C , 80 min, heat treatment: 500°C , 60 min.

while HF molecule release temperature is increased up to 400°C with an increase of thermal modification temperature up to 350°C as shown in Fig. 15 (b). In case the thermal modification temperature is increased to 400°C , HF molecules are not detected even if the tube surface temperature is increased up to 500°C as shown in Fig. 15 (c) and (d). 316L stainless steel generates cracks along

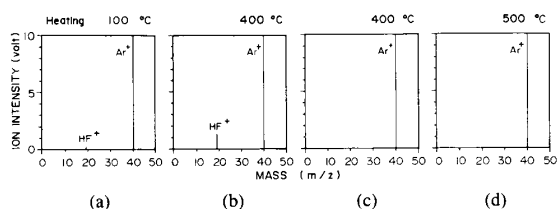


Fig. 15. Temperature dependence of the outgassing for thermal modification temperature. Thermal modification: (a) 320°C, (b) 350°C, (c) 400°C, (d) 400°C.

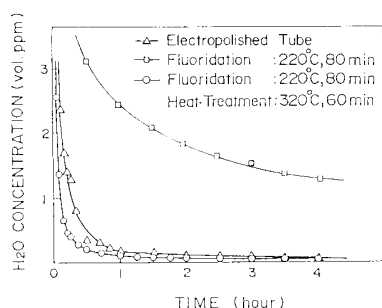


Fig. 16. Time dependence of the moisture level in nitrogen gas passed through unpassivated and passivated tubes at 25°C.

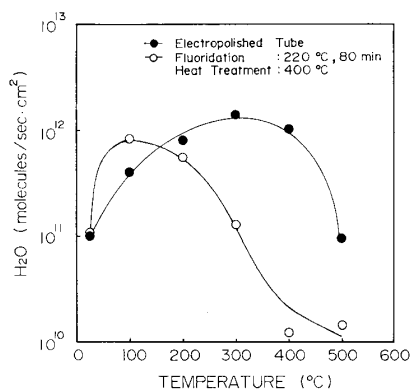


Fig. 17. Number of H₂O molecules desorbed from unit area in the temperature range 25° to 500°C.

the grain boundary when it is heated to temperatures higher than 500°C.

Outgassing (H₂O) characteristics of the unpassivated surface and passivated surface are evaluated with dew point meter [30], [31] and APIMS [29] using a 1/4-in electropolished 316L stainless steel tube having a length of 1.5 m and results are shown in Figs. 16 and 17. Moisture desorption of these tubes at room temperature is plotted as a function of time after these tubes are exposed to clean room air of 25°C and 50-percent humidity for 2 days as shown in Fig. 16, where the flow rate of N₂ is set at 0.5 l/min. Moisture desorption from fluoridated metal surface is also illustrated in Fig. 16. It is clearly seen from Fig. 16 that nonstoichiometric fluoride film exhibits a huge amount of adsorption of moisture molecules, re-

vealing a poor desorption characteristic. The passivated metal surface exhibits a desorption characteristic almost equal to the electropolished metal surface at room temperature.

The number of H₂O molecules desorbed from the unit area are plotted as a function of tube surface temperature in Fig. 17. The thermal modification temperature is set at 400°C in these passivated surfaces. The number of H₂O molecules from passivated surfaces is much smaller than that from unpassivated surfaces at temperatures higher than 200°C. These data indicate that H₂O molecules are adsorbed physically on the passivated metal surface while they are adsorbed chemically on the bare metal surface.

V. DISCUSSION

A. Clean Surface and Pure Fluorine for Passivation

Metal surfaces are usually covered with a native oxide and adsorbed moisture even after the surfaces have been electropolished to exhibit very smooth flatness. These must be removed completely before the start of passivation procedure. Fluorine reacts with adsorbed moisture and produces oxygen and hydrogen fluoride that attack the metal surface as a secondary reaction. Existence of oxygen in fluorine has been reported to promote severe corrosion of metal surfaces by many studies [5], [13], [14].

High purity fluorine with an oxygen content of less than 1 ppm and high purity nitrogen with a moisture content of less than 10 ppb are used in this work. Surfaces of stainless steel and nickel are completely pretreated to remove the native oxide and adsorbed moisture. As the result, the XPS spectrum of the passivated surface with the pretreatment indicates a very low oxygen signal as shown in Fig. 18 compared with no pretreatment. Both a clean metal surface and pure fluorine are absolutely required for the formation of a uniform and high quality passivated films, exhibiting good adhesion and excellent corrosion-free characteristics.

B. Thermal Modification of Fluoridated Film

Past research has reported that fluoridated nickel films became a nonstoichiometric fluorine-excess structure, i.e., NiF_{2+α} [32]. NiF_{2.2-3.0} structures on fluoridation of nickel at 230°–500°C are seen by XPS spectrometry [33]. However, it has not been elucidated whether the nonstoichiometric structure of these films is due to excess fluorine in interstitial or lattice sites. The improvement of the nonstoichiometric structure has not been carried out at all.

This work for the first time recognizes that the nonstoichiometric structure exists in direct fluoridated films of nickel and stainless steel even when the fluoridation is carried out in an ultraclean environment. However, it has been demonstrated experimentally that these nonstoichiometric structures are converted to stoichiometric structures by heat treatment in a clean nitrogen environment; the authors call this process thermal modification.

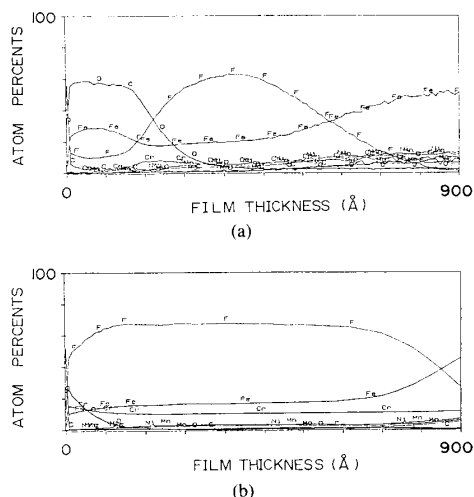


Fig. 18. XPS spectra of the 316L stainless steel surface fluoridated (a) without removal of native oxide (no pretreatment) and (b) with removal (pretreatment).

In order to enhance the effect of thermal modification, 24-h thermal treatment of fluoridated films of 316L stainless steel is carried out at 400°C as shown in Fig. 19(b), where the depth profile of chemical composition evaluated by XPS analysis is illustrated. Fig. 19(a) shows the depth profile of chemical composition of fluoridated films at 220°C for 80 min. The thermal modification effect is clearly observed in Fig. 19, where the nonstoichiometric structure with a mole ratio $[F]/[Fe] = 2.27$ is converted to the stoichiometric structure with a mole ratio $[F]/[Fe] = 2.00$ by thermal modification. Fig. 19 indicates an increase of film thickness after the thermal modification due to the excess fluoride diffusion to the interface of fluoride film and stainless steel. Thermal modification simultaneously accompanies a formation of thin CrF_2 layer (less than 100 Å) on the stoichiometric FeF_2 layer for stainless steel surface as shown in Fig. 8. In Fig. 19(b), however, CrF_2 on the stoichiometric FeF_2 is converted to Cr_2O_3 due to remaining moisture in nitrogen during long time thermal modification. The thermal modification, has a great impact on the performance of the passivated materials because a high corrosion resistance is only obtained by the stoichiometric structure film. On the other hand, the direct fluoridated film without thermal modification does not have enough corrosion resistance. The nonstoichiometric structure is itself unstable, and is stabilized by thermal modification. The difference in corrosion resistance between the thermal modification film and direct fluoridated film is made clear in Tables II and III where corrosion-resistance characteristics have been evaluated for vigorously corrosive environments such as 100-percent Cl_2 (Table II) and wet hydrogen fluoride gas (Table III). It is found that a thermally modified stainless steel with a surface thickness greater than 660 Å exhibits complete corrosion resistance as shown in Tables II and III. The ther-

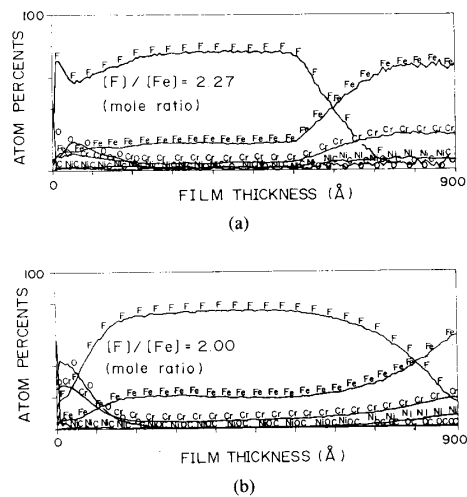


Fig. 19. Depth profile of XPS spectra from (a) a direct fluoridated 316L stainless steel surface (fluoridation: 220°C, 80 min) and (b) a thermal modified 316L stainless steel surface (fluoridation: 220°C, 80 min, thermal modification: 400°C, 24 h).

TABLE II
THE CORROSION RESISTANCE TO Cl_2 AND WET HYDROGEN FLUORIDE GAS OF THE THERMAL MODIFIED STAINLESS STEEL SURFACE (CORROSION RESISTANCE TO 100-PERCENT Cl_2 AT 100 PERCENT, 1 h)

Thickness of Fluoridated Film Å	Consumption of Cl_2	
	Fluoridated Surface $\mu g/cm^2$	Thermal Modified Surface $\mu g/cm^2$
0	5.0	5.0
400	3.0	2.0
660	1.0	0
1040	0.9	0

316L Stainless Steel : 1/4" electropolished tube
Wet Hydrogen Fluoride Gas : HF 5, H₂O 1, N₂ 94 (vol%)
* Fluoridation : at 220°C for 0-2hr in 100%F₂
** Thermal Modification : at 320°C for 2hr in N₂

TABLE III
THE CORROSION RESISTANCE TO Cl_2 AND WET HYDROGEN FLUORIDE GAS OF THE THERMAL MODIFIED STAINLESS STEEL SURFACE (CORROSION RESISTANCE TO WET HYDROGEN FLUORIDE AT 25°C, 72 h)

Thickness of Fluoridated Film Å	Evaluation by SEM	
	Fluoridated Surface	Thermal Modified Surface
0	very weak	very weak
400	very weak	strong
660	weak	very strong
1040	weak	very strong

316L Stainless Steel : 1/4" electropolished tube
Wet Hydrogen Fluoride Gas : HF 5, H₂O 1, N₂ 94 (vol%)
* Fluoridation : at 220°C for 0-2hr in 100%F₂
** Thermal Modification : at 320°C for 2hr in N₂

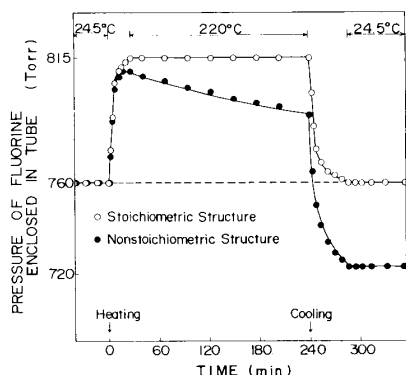


Fig. 20. Time variation of fluorine pressure due to heat cycle for nonstoichiometric structure and stoichiometric structure. Stoichiometric structure: fluoridation at 220°C for 80 min in 100-percent F_2 , thermal modification at 320°C for 24 h in N_2 . Nonstoichiometric structure: fluoridation at 220°C for 80 min in 100-percent F_2 .

mal modification effect is also recognized for nickel surfaces. It is concluded that the thermal modification is the key technology for metal surface passivation.

C. Fluorine Diffusion Mechanism

Fluorine can reach the metal surface by diffusion through a fluoride film even for low temperatures [9]. In this work, the reaction rate of stainless steel with fluorine is shown to follow roughly a parabolic rate law as shown in Fig. 6 due to fluorine diffusion through the fluoride films. Therefore, the thickness of the fluoride films increases with an increase of fluoridation time even at low temperatures, such as 180°–300°C. The fluorine diffusion is due to the nonstoichiometric structure of the fluoridated film. Therefore, it is expected that the fluorine cannot diffuse through the stoichiometric structure after the thermal modification treatment.

The barrier effect for the fluorine diffusion is evaluated by experiments, the results of which are shown as expressed in open circles in Fig. 20. Fluorine enclosed in a thermal modified tube is heated to the fluoridation temperature of 220°C. Fluorine consumption for 240 min was examined by pressure drops of fluorine gas after cooling to the initial temperature. The pressure of fluorine enclosed in tube does not change within the detection limit of 0.5 torr which corresponds to a fluorine consumption of $0.12 \mu\text{m}/\text{cm}^2$, i.e., equivalent to a thickness of 7 Å. This confirms that the stoichiometric structure does not permit diffusion of fluorine. On the contrary, as for the nonstoichiometric fluoride films, fluorine is continuously consumed as expressed in solid circles in Fig. 20, when the temperature is increased to 220°C. Therefore, the pressure of fluorine enclosed in the tube decreases by a factor of 36 torr after the sample is returned to the initial temperature, resulting in an increase of film thickness of 500 Å. The thermal modification has been confirmed to convert the nonstoichiometric structure to the stoichiometric structure of fluoride films which then serves as a

diffusion barrier to fluorine itself. It has the great significance in passivation technology.

D. Fine Structure of Passivated Film

It has been reported that chromium in stainless steel migrates to the surface by heating at 1000°C [34]. In the case of the oxygen passivation process, it has been shown that the top surface composition of the passivated film formed at 400°–500°C is chromium oxide [35]. The various properties of the oxygen passivated film result from this chromium oxide. The same phenomenon is observed in the thermal modification process in fluorine passivation, but the migration of chromium in fluorine passivation film occurs at the temperature range of 300°–400°C, lower than in oxygen passivation. It is considered that a high electronegativity of fluorine contributes to this phenomenon. The fluorine passivated surface of stainless steel covered with CrF_2 may be useful in high temperature reactive chambers, because CrF_2 has the lowest vapor pressure in the divalent metal fluorides such as FeF_2 , NiF_2 , and MnF_2 .

VI. CONCLUSION

Fluorine passivation technology for stainless steel and nickel has been investigated. For the clean surface passivation, fragmented layer free bare metal surfaces prepared by mechanical polishing or electropolishing, followed by native oxide removal procedure and oxygen-free high pure fluorine were used, with the O_2 and HF concentrations suppressed to less than 1 ppm.

The fundamental kinetics for the fluorine passivation has been studied. The rate constants of fluoridation of stainless steel and nickel have been determined to be $0.955 (\mu\text{g } F_2/\text{cm}^2)^{1.5-1.6}/\text{min}$ at 260°C and $35 (\mu\text{g } F_2/\text{cm}^2)^{2.7-2.9}/\text{min}$ at 400°C, respectively. The activation energy of fluoridation of stainless steel is 9490 cal/mol (0.41 eV) at temperatures of 180° to 260°C and that of nickel is 9950 cal/mol (0.43 eV) at 300° to 500°C. The fluoridated surface structure of 304 stainless steel foil is FeF_2 at temperatures less than 265°C, and changes to FeF_3 at temperatures higher than 265°C, followed by cracking. The critical temperature for this phase change has been confirmed to depend on the composition and crystal structure of stainless steel. The critical temperatures are 220°C for 304 stainless steel plate and 300°C for 316L stainless steel plate. It is recognized that the major component in the top surface of the passivated film is CrF_2 which has the lowest vapor pressure in the divalent metal fluorides such as FeF_2 , NiF_2 , and MnF_2 .

The fluoridated surface structure of nickel has been determined to be NiF_2 at the temperatures between 350° and 450°C. Fluoridation under 350°C forms $\text{NiF}_2 \cdot 4\text{H}_2\text{O}$ by the reaction with the remaining moisture on the surface and fluoridation above 450°C causes cracking of NiF_2 film.

Evaluation of corrosion resistance of passivated films of stainless steel and nickel was carried out in Cl_2 (100 percent) at 1 kg/cm² (25°C) or 5 kg/cm² (25°C) and

wet hydrogen fluoride gas (5 vol percent HF, 1 vol percent H₂O, and 94 vol percent N₂) at 1 kg/cm² (25°C). The passivated films on the surfaces of stainless steel and nickel are confirmed to have corrosion resistance to the reactive gases. The passivated film of stainless steel has a higher desorption rate of adsorbed moisture for inert gas flow, compared to an unpassivated surface.

We have been originally confirmed that improved passivation performance is achieved by means of the thermal modification of the nonstoichiometric surface structure formed by an introduction of two step fluoridation process, i.e., a combination of direct fluoridation and succeeding thermal modification. Direct fluoridation produces nonstoichiometric fluorides on the metal surfaces which are converted to a stoichiometric structure by the succeeding heat treatment in nitrogen, i.e., thermal modification. With stainless steel surface fluoridation, the nonstoichiometric iron fluoride FeF_{2.27} is converted to the stoichiometric iron fluoride (FeF₂), covered by a thin CrF₂ layer (less than 100 Å), by succeeding thermal modification.

It is confirmed that the stoichiometric fluoride structure does not permit the diffusion of fluorine even at the fluoridation temperature. This newly developed passivation technology gives the completely corrosion-free metal surfaces performance for vigorously corrosive gases such as Cl₂, F₂, HCl, and HF, so that a self-cleaning function, i.e., periodical gas phase cleaning of the inner surface of the process chamber, is feasible in advanced semiconductor manufacturing equipment.

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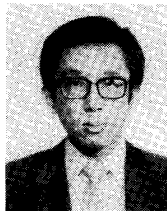


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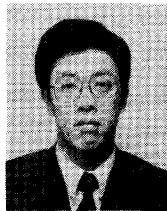
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