Research Paper

Fluorine Plasma Corrosion Resistance of Anodic Oxide Film Depending on Electrolyte Temperature

Jae-Soo Shin^a, Minjoong Kim^a, Je-beom Song^b, Nak-gwan Jeong^b, Jin-tae Kim^{b,c,*}, and Ju-Young Yun^{b,c,*}

^aDaeJeon University, Daejeon 34520, Republic of Korea

^bKorea Research Institute of Standards and Science, Daejeon 34113, Republic of Korea

^cUniversity of Science and Technology, Daejeon 34113, Republic of Korea

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Abstract Samples of anodic oxide film used in semiconductor and display manufacturing processes were prepared at different electrolyte temperatures to investigate the corrosion resistance. The anodic oxide film was grown on aluminum alloy 6061 by using a sulfuric acid (H₂SO₄) electrolyte of 1.5 M at 0°C, 5°C, 10°C, 15°C, and 20°C. The insulating properties of the samples were evaluated by measuring the breakdown voltage, which gradually increased from 0.43 kV (0°C) to 0.52 kV (5°C), 1.02 kV (10°C), and 1.46 kV (15°C) as the electrolyte temperature was increased from 0°C to 15°C, but then decreased to 1.24 kV (20°C). To evaluate the erosion of the film by fluorine plasma, the plasma erosion and the contamination particles were measured. The plasma erosion was evaluated by measuring the breakdown voltage after exposing the film to CF₄/O₂/Ar and NF₃/O₂/Ar plasmas. With exposure to CF₄/O₂/Ar plasma, the breakdown voltage of the film slightly decreased at 0°C, by 0.41 kV; however, the breakdown voltage significantly decreased at 20°C, by 0.83 kV. With exposure to NF₃/O₂/Ar plasma, the breakdown voltage of the film slightly decreased at 0°C, by 0.38 kV; however, the breakdown voltage significantly decreased at 20°C, by 0.77 kV. In addition, for the entire temperature range, the breakdown voltage decreased more when sample was exposed to NF₃/O₂/Ar plasma than to CF₄/O₂/Ar plasma. The decrease of the breakdown voltage was lower in the anodic oxide film samples that were grown slowly at lower temperatures. The rate of breakdown voltage decrease after exposure to fluorine plasma was highest at 20°C, indicating that the anodic oxide film was most vulnerable to erosion by fluorine plasma at that temperature. Contamination particles generated by exposure to the CF₄/O₂/Ar and NF₃/O₂/Ar plasmas were measured on a real-time basis. The number of contamination particles generated after the exposure to the respective plasmas was lower at 5°C and higher at 0°C. In particular, for the entire temperature range, about five times more contamination particles were generated with exposure to NF₃/O₂/Ar plasma than for exposure to CF₄/O₂/Ar plasma. Observation of the surface of the anodic oxide film showed that the pore size and density of the non-treated film sample increased with the increase of the temperature. The change of the surface after exposure to fluorine plasma was greatest at 0°C. The generation of contamination particles by fluorine plasma exposure for the anodic oxide film prepared in the present study was different from that of previous aluminum anodic oxide films.

Keywords: Fluorine plasma, Anodizing, Sulfuric acid, In-situ particle monitoring, Electrolyte temperature

I. Introduction

The plasma etching process, in the semiconductor and display manufacturing processes, is a dry etching process using plasma to pattern electric circuits in a vacuum. This process is a preferred etching method, because it enables excellent minimum length and large-area uniformity in semiconductor devices. During the process, metal parts of the etch equipment are exposed to fluorine plasma, and thus generate contamination particles due to erosion and defects, contaminating the semiconductor substrate and reducing the process yield. To solve this problem, the corrosion resistance of the metal parts is improved through

anodic oxidation, in which metallic materials are connected to an anode and dipped into an electrolyte to grow a porous oxide film through electric oxidation [1-6]. Anodic oxidation is a metal surface treatment technology frequently used in the industry due to its high reproducibility and the excellent physical and chemical durability of the resulting products. The electrolyte composition, temperature, and current density are important factors that determine the properties of the oxide film in anodic oxidation. In particular, anodic oxidation using sulfuric acid (H₂SO₄) is less costly, enables rapid formation of thick anodic oxide films, and yields excellent physical properties [7,9]. Recently, with the increase of plasma-based process steps and the demand for high precision, studies have been continuously conducted on the properties of anodic oxide films [10]. However, in contrast to the long-term research on process conditions of

*Corresponding author
E-mail: jyun@kriss.re.kr

anodic oxidation and structural and physical properties, plasma corrosion resistance has not been sufficiently analyzed or reported.

In the present study, for the manufacturing of films having high corrosion resistance to fluorine plasma, the surface of the oxide films was controlled [11-16] by varying the temperature of the electrolyte and the corrosion of the film was observed after exposure to fluorine plasma. In particular, contamination particles generated by the exposure of an anodic oxide film to fluorine plasma were evaluated to represent an actual process. In addition, scanning electron microscopy (SEM) images of the films were acquired to observe changes of the surface structure depending on the temperature and the exposure to fluorine plasma.

II. Experimental

Film samples of aluminum 6061 alloy (Alfa Aesar, Table. 1) were prepared at a size of 300 mm × 300 mm. The samples were subjected to sonication for 30 minutes in ethanol (99.999%) to clean the surface. In addition, to reduce the roughness of the sample surface, electropolishing was performed for 60 s at 25 V and 600 s at 20 V using an electrolyte prepared by mixing 1200 ml of ethanol (99.999%) and 300 mL of perchloric acid (60%) (1:4) as a chiller to keep the temperature at 20°C. The material for the cathode was SUS306; the distance to the anode was 80 mm. Then, electrolyte polishing was performed on both sides of the samples, and the resulting samples were rinsed with water for 60 s.

After the electrolyte polishing, the backsides of the samples were masked using PET tape. The electrolyte for anodizing was prepared by mixing 126 ml of sulfuric acid and 1374 ml of deionized water (1.5 M). A CCA-1111 chiller (EYELA) was used to control the temperature of the electrolyte, and the anodizing was performed at 0°C, 5°C, 10°C, 15°C, and 20°C for 3600 s using a magnetic stirrer (300 rpm). The material for the cathode was SUS306; the distance to the anode was 80 mm.

The breakdown voltage was measured using TOS-9201 equipment (KIKUSUI); the breakdown voltage was determined as the voltage at which a current of 4 mA flowed when the voltage was increased at a rate of 15 V/

Table 1. Al6061 alloy Chemical analysis

Element	Wt%
Cu	0.278
Cr	0.130
Fe	0.143
Mg	0.962
Mn	0.015
Si	0.465
Ti	0.013
Zn	0.058

Figure 1. In-situ particle monitoring System (ISPM).

s (KS C 6521).

Changes of the surface were observed using an S-4800 field emission scanning electron microscope (FE-SEM, HITACHI). The samples were exposed to plasma by using the Inductively Coupled Plasma-Reactive Ion Etching (ICP-RIE) device shown in Figure 1. The base pressure was 2.5E-6 Torr; the working pressure was controlled at 3E-2 Torr. Two fluorine gases, CF₄ and NF₃, were respectively mixed with O₂ and Ar at a mixing ratio of 6:5:1 to form the plasma. The top ICP power was 500 W; the bottom bias power was 300 W. The distance between the bottom sample loading position and the top ICP was 120 mm.

The number of particles generated by the radical and physical reaction of Al₂O₃ on the sample surface due to the plasma exposure was measured using the in-situ particle monitoring system shown in Figure 2.

II. Results and Discussion

The thickness growth rate of the individual samples increased as the temperature of the electrolyte was increased, as shown in Figure 3.

Equations (1) and (2) are the formulae of the reactions occurring on the aluminum surface during the anodizing process.

Figure 2. Schematic diagram of ICP-RIE equipment.

Figure 3. Growth of film thickness depending on electrolyte temperature.

The thickness of the aluminum oxide is determined by Faraday's Law, shown in Equation (3):

$$t_{\text{Al}_2\text{O}_3} = \frac{17.6It}{\rho_{\text{Al}_2\text{O}_3}F} \quad (3)$$

In Equation (3), $\rho_{\text{Al}_2\text{O}_3}$ is the density of Al_2O_3 (3.62 g/cm³); F is the area of the aluminum surface (cm²), I is current in coulombs per second, t is time in second. The quantity of aluminum oxide is proportional to the quantity of electric charge passing through the electrolyte. The current density through the oxide film is defined as shown in Equation (4):

$$j = j_a + j_c + j_2 \quad (4)$$

where j_a , j_c and j_e are the densities of the anions, cations, and electron-contributed current. Since the electric conductivity of aluminum oxide is extremely low, j_a and j_c are the major factors influencing the charge transfer. Therefore, as the electrolyte temperature increased during anodizing, the current increased. As a result, the current density affecting the oxide film growth also increased, as shown in Figure 4.

With the increase of the electrolyte temperature, the rate of film thickness growth increased as the current density increased from 228.6 A/m² (0°C) to 233.8 A/m² (5°C), 311.7 A/m² (10°C), 467.5 A/m² (15°C), and 545.5 A/m²

Figure 4. Change of current density depending on electrolyte temperature.

Figure 5. Breakdown voltage depending on electrolyte temperature.

Figure 6. Decrease of breakdown voltage after exposure to fluorine plasma.

(20°C).

Figure 5 shows the variation of the breakdown voltage depending on the electrolyte temperature. The breakdown voltage gradually increased from 0.43 kV (0°C) to 0.52 kV (5°C), 1.02 kV (10°C), and 1.46 kV (15°C) as the electrolyte temperature increased from 0°C to 5°C, 10°C, and 15°C; the breakdown voltage then decreased to 1.24 kV (20°C). This indicates that, because the current density was increased too rapidly, the anodic oxide film did not grow as a compact film.

To evaluate the plasma corrosion resistance, the samples were exposed to $\text{CF}_4/\text{O}_2/\text{Ar}$ and $\text{NF}_3/\text{O}_2/\text{Ar}$ plasmas; then, the breakdown voltages were measured, as shown in Figure 6.

Figure 7. CF₄/O₂/Ar (6:5:1) plasma in-situ particles. Figure 8. NF₃/O₂/Ar (6:5:1) plasma in-situ particles. Figure 9. Change of the anodic oxide film surface depending on electrolyte temperature and exposure to CF₄/O₂/Ar plasma. Figure 10. Change of anodic oxide film surface depending on electrolyte temperature and exposure to NF₃/O₂/Ar plasma.

With exposure to CF₄/O₂/Ar plasma, the breakdown voltage slightly decreased at 0°C, by 0.41 kV; however, the breakdown voltage significantly decreased at 20°C, by 0.83 kV. With exposure to NF₃/O₂/Ar plasma, the breakdown voltage slightly decreased at 0°C, by 0.38 kV; however, the breakdown voltage significantly decreased at 20°C, by 0.77 kV. In addition, for the entire temperature range, the breakdown voltage decreased more with exposure to NF₃/O₂/Ar plasma than with exposure to CF₄/O₂/Ar plasma. The decrease of the breakdown voltage was lower in the anodic oxide film samples that were grown slowly at a lower temperature. The rate of the breakdown voltage decrease after exposure to fluorine plasma was highest at 20°C, indicating that the anodic oxide film was most vulnerable to erosion by fluorine plasma at that temperature.

Figures 7 and 8 show the number of contamination particles measured during exposure of the samples to the fluorine plasma. The numbers of the contamination particles were measured on a real-time basis while exposing the samples to the CF₄/O₂/Ar and NF₃/O₂/Ar

Element	Wt%
Cu	0.278
Cr	0.130
Fe	0.143
Mg	0.962
Mn	0.015
Si	0.465
Ti	0.013
Zn	0.058

plasmas, respectively. The number of contamination particles generated after exposure to the respective plasmas was lower at 5°C and higher at 0°C, whether the samples were exposed to CF₄/O₂/Ar plasma or NF₃/O₂/Ar plasma. In particular, for the entire temperature range, about five times more contamination particles were generated with exposure to NF₃/O₂/Ar plasma than with exposure to CF₄/O₂/Ar plasma.

Figures 9 and 10 shows FE-SEM images of the sample surface. The pore size and density of the non-treatment Al₂O₃ film sample increased with the increase of the electrolyte temperature. In particular, the change of the surface structure was distinctive at 20°C, indicating that the compactness of the structure decreased as the oxide film growth rate increased due to the increase of the current density on the surface. The pore size and density of the film surface exposed to CF₄/O₂/Ar plasma increased as the electrolyte temperature increased; the surface change was most prominent at 20°C. The pores of the films surface changed more after exposure to NF₃/O₂/Ar plasma than they did after exposure to CF₄/O₂/Ar plasma. Due to the physicochemical actions of Ar ions and fluorine radicals, in comparison with the non-treatment samples, the pore size in the samples that underwent fluorine plasma treatment increased; this increase was highest at 20°C.

IV. Conclusions

In the preparation of the anodic oxide films, the pore size and density on the surface increased with the increase of the electrolyte temperature. The breakdown voltage gradually increased from 0.43 kV (0°C) to 0.52 kV (5°C), 1.02 kV (10°C), and 1.46 kV (15°C) as the electrolyte temperature was increased from 0°C to 5°C, 10°C, and 15°C; the breakdown voltage then decreased to 1.24 kV (20°C).

The breakdown voltage was measured after sample exposure to fluorine plasma. With exposure to CF₄/O₂/Ar plasma, the breakdown voltage slightly decreased at 0°C, by 0.41 kV; however, it significantly decreased at 20°C, by 0.83 kV. With exposure to NF₃/O₂/Ar plasma, the breakdown voltage slightly decreased at 0°C, by 0.38 kV;

however, the breakdown voltage significantly decreased at 20°C, by 0.77 kV.

The number of contamination particles generated after the exposure to the respective plasmas was lower at 5°C and higher at 0°C, whether the samples were exposed to CF₄/O₂/Ar or NF₃/O₂/Ar plasma. In particular, for the entire temperature range, about five times more contamination particles were generated with exposure to NF₃/O₂/Ar plasma than with exposure to CF₄/O₂/Ar plasma.

The results of the present study may be applied to reduce contamination particles generated from the anodic oxide film used for parts of semiconductors and display manufacturing equipment. Further study may be needed on contamination particles generated by exposure of anodic oxide film to a fluorine plasma environment.

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