Research Paper

Plasma Corrosion in Oxalic Acid Anodized Coatings Depending on Tartaric Acid Content

Jae-Soo Shin[a], Je-Boem Song[b,c], Sin-Ho Choi[a,b], Jin-Tae Kim[b,d], Seong-Geun Oh[c], and Ju-Young Yun[b,d*]

[a]*Department of Materials Science and Engineering, Daejeon University, 300-716, Korea*
[b]*Vacuum Center, Korea Research Institute of Standards and Science, 305-600, Korea*
[c]*Department of Chemical Engineering, Hanyang University, 133-791, Korea*
[d]*Department of Nanomaterials Science and Engineering, University of Science and Technology, 305-333, Korea*

Abstract Study investigated the optimal anodizing conditions for fabricating an oxide film that produces less contamination in a corrosive plasma environment, using oxalic acid and tartaric acid. Oxide films were produced using sulfuric acid, oxalic acid, and tartaric acid electrolyte mixtures with various mole ratios. The oxide film made by adding 0.05 M tartaric acid to 0.3 M oxalic acid showed higher breakdown voltage and lower leakage current. Additionally, contamination particles were reduced during plasma etching, thus demonstrates that this mixture presented optimal conditions. However, higher tartaric acid content (0.1 M, 0.15 M) led to lower breakdown voltages and higher leakage currents. Also, it resulted in more cracking during thermal shock tests as well as the generation of more contamination particles during plasma processing.

Keywords: plasma corrosion, etching, particle monitoring, anodizing, anodic film, tartaric acid

I. Introduction

To ensure the productivity of fabrication processes in semiconductor and display manufacturing, it is important to reduce the generation of contamination particles within the plasma etching chamber. Contamination particles produced from coated parts often cause various failures in etching processes. This is because the etching process involves exposure to a highly reactive plasma environment. For this reason, the parts used in these chambers are coated with protective materials. The most widely used coating strategy is anodizing, which produces an oxide film that is highly resistant to heat and wear [1]. Anodizing generates an oxide film by immersing the metallic material to be coated in an electrolyte solution and applying voltage, thereby causing oxidization on the metal surface. Since different electrolyte solutions used in anodizing will produce oxide films with different qualities, the solution is the most important factor in the production of oxide films that are highly resistant to corrosion. When an electrolyte mixture is used, the composition of the mixture is a key factor determining the properties of the oxide film.

Sulfuric acid (H_2SO_4) electrolytes are often used in industries because of their economical advantage, and many studies have reported optimal conditions using sulfuric acid anodized coatings [2-5]. However, when sulfuric acid electrolytes are used, sulfuric acid ions remain in the oxide film, creating a film with low purity that is more susceptible to corrosion [6]. For this reason, anodizing processes using organic acids have been actively researched. The most widely used acids are oxalic ($C_2H_2O_4$), malonic ($C_3H_4O_4$), malic ($C_4H_6O_5$), tartaric ($C_4H_6O_6$) and citric ($C_6H_8O_7$) acids. Outstanding properties of oxide films generated from mixtures of inorganic and organic acids, such as tartaric-sulfuric acid, boric-sulfuric acid, and dilute sulfuric acid, have been reported [7-10]. However, insufficient research has been conducted on mixtures of organic acid electrolytes such as oxalic and tartaric acid.

Study investigated the quality of oxide films generated from different mixture ratios of oxalic acid and tartaric acid. The base electrolyte solution was produced using oxalic acid, and different amounts of tartaric acid were added to observe the resulting physical properties of the oxide films, such as thickness, breakdown voltage, and leakage current. Corrosion resistance under plasma exposure was also tested, comparing the amount of contamination particles generated in the process in real-time. Finally, the optimal tartaric-oxalic acid ratio in terms of reducing the production of contamination particles was investigated.

II. Experiment

The starting material used to generate the oxide film

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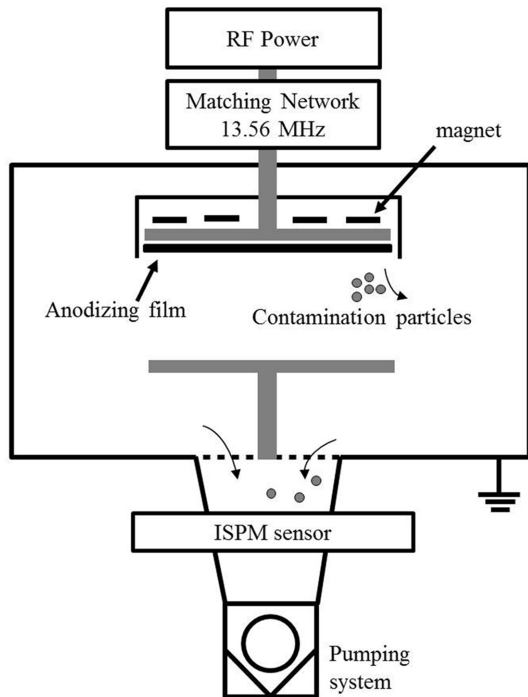E-mail: jyun@kriss.re.kr

Figure 1. Schematic diagram of the experimental setup and In-Situ Particle Monitoring (ISPM) sensor.

was 1 mm thick Al foil (99.99% aluminum, annealed, Alfa Aesar corp.) formed into a disc with 76 mm diameter. The Al foil was mechanically polished in order to remove scratches from its surface. Electropolishing was then conducted, using a mixture of ethanol and perchlorate (v/v=9:1) at 5°C and 20 V for 10 minutes, resulting in a final roughness of 0.2±0.02 μm, similar to a mirror surface. A teflon bath was used for the anodizing system while a Pt mesh was used as a counter electrode. Electrolyte solutions containing 0.3 M oxalic acid combined with varying concentrations of tartaric acid (0.05 M, 0.1 M, 0.15 M) were tested in the experiment. The oxide films were generated at 2°C electrolyte temperature, and 20 mA/cm^2 over a duration of 40 minutes.

Plasma resistance was tested using capacitively coupled plasma (CCP) and the equipment setup is shown in Fig. 1. A gaseous mixture of CF$_4$, Ar, and O$_2$ (16:4:3) was used. Under a total pressure of 200 mtorr, 100 W electrical power of 13.56 MHz frequency was applied for plasma etching. A light scattering In-Situ Particle Monitoring (ISPM) sensor [11] was used between the chamber and pump to measure the particles generated from the oxide films by plasma corrosion. After plasma etching the oxide film surfaces were observed with a FE-SEM (HITACHI Brucker S-4800). The electrical properties of the oxide film were measured using a withstanding voltage tester (TOS9200, KIKUSUI) to test breakdown voltages.

III. Results and Discussion

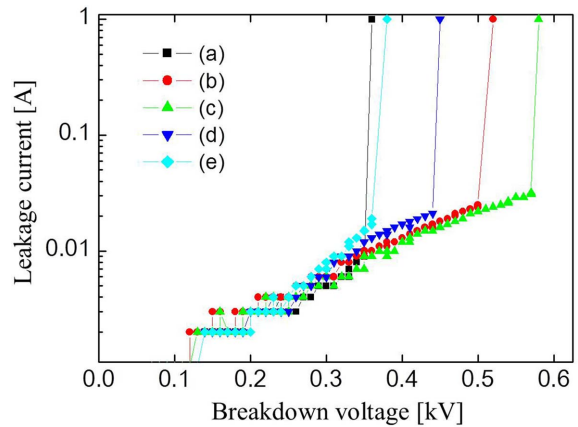The growth rate of the anodic aluminum oxide film

Figure 2. Leakage current vs. applied voltage for electrolyte types; (a) sulfuric acid 1.5 M, (b) oxalic acid 0.3 M, (c) oxalic acid 0.3 M, tartaric acid 0.05 M, (d) oxalic acid 0.3 M, tartaric acid 0.10 M, (e) oxalic acid 0.3 M, tartaric acid 0.15 M.

depends on the electrolyte mixture ratio. The sulfuric acid and tartaric-oxalic acid mixtures are as follows: (a) sulfuric acid 1.5 M, (b) oxalic acid 0.3 M, (c) oxalic acid 0.3 M, tartaric acid 0.05 M, (d) oxalic acid 0.3 M, tartaric acid 0.10 M, and (e) oxalic acid 0.3 M, tartaric acid 0.15 M. When applying a fixed current density of 20 mA/cm^2 with an anodizing duration of 40 minutes, the sulfuric electrolyte solution produced an oxide film of 25 μm thickness on the aluminum substrate, while the oxalic acid produced an oxide film of 20 μmthickness. The sulfuric acid resulted in a higher oxide film growth rate than the oxalic acid, consistent with refs. [12]. When tartaric acid was added to oxalic acid, the thickness remained constant at 20 μm, showing that the addition of tartaric acid had no impact on the growth speed.

Breakdown voltage refers to the highest voltage that the aluminum oxide film can withstand without being damaged. As the oxide-coated parts of plasma electrodes are connected to high frequency electrical power, leakage current and arcing on the oxide film surface can be produced. Therefore, it is important to enhance the insulating properties of the oxide film. A thicker oxide film has higher breakdown voltage. However, other problems may occur with changes in plasma impedance and impedance matching. The typical thickness for oxide films used in industries is 20-40 μm.

Fig. 2 shows leakage current measurements taken when the oxide film thickness was held constant at 20 μm. The breakdown voltage was 0.35 kV for the sulfuric acid oxide film and 0.51 kV for the oxalic acid oxide film, thus revealing significant enhancement when oxalic acid is used. The oxide film produced by adding 0.05 M tartaric acid to 0.3 M oxalic acid had slightly lower leakage current and higher breakdown voltage of 0.58 kV. Most of the leakage current can pass through the oxide film barrier which is only several nm thick. The enhanced breakdown voltage indicates that the tartrate anions make the oxide film barrier electrically strong. When higher concentrations
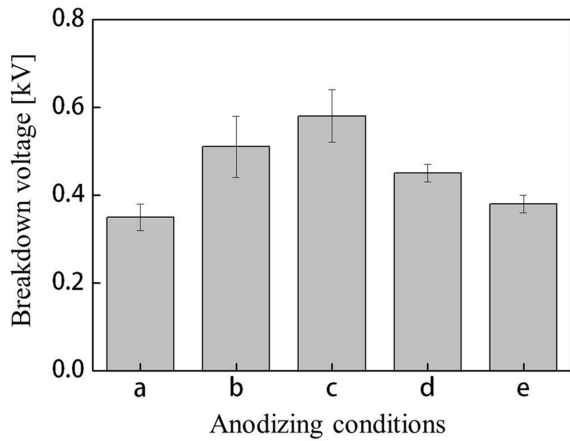
Figure 3. Breakdown voltage vs. electrolyte types; (a) sulfuric acid 1.5 M, (b) oxalic acid 0.3 M, (c) oxalic acid 0.3 M, tartaric acid 0.05 M, (d) oxalic acid 0.3 M, tartaric acid 0.10 M, (e) oxalic acid 0.3 M, tartaric acid 0.15 M.

of tartaric acid (0.1 M, 0.15 M) were added to 0.3 M oxalic acid, the oxide film growth was adversely affected. Fig. 3

shows the mean value of the breakdown voltage taken from 10 randomly selected, non-overlapping locations on the oxide film surface.

As the oxide-coated parts of plasma electrodes are heated during the plasma etching process, cracks on the oxide film surface may occur due to thermal stress. When cracks occur, contamination particles that affect plasma processing are abruptly increased, leading to failure. In order to evaluate the thermal stability of the oxide film surface, the oxide film was exposed to thermal cycling from room temperature to 300°C. Fig. 4 presents FE-SEM images of the oxide film surfaces after three iterations of thermal cycling. As seen in the FE-SEM images, wide cracks occurred on the sulfuric oxide film while a reduction in crack width was observed in the oxalic-tartaric oxide film. Cracks did not occur in the oxide film produced from 0.3 M oxalic acid combined with 0.05 M tartaric acid. Cracks typically occur due to weak bond strength along cell boundaries between pore walls [13]. The results showed
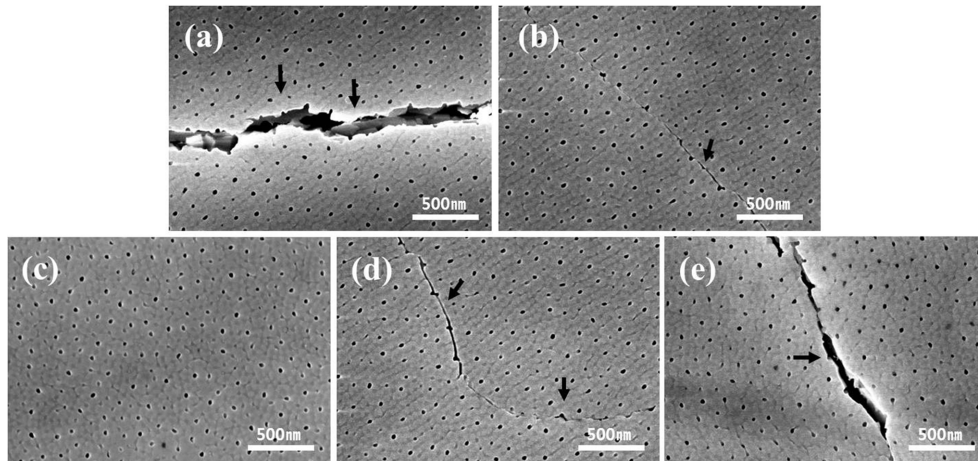

Figure 4. SEM images after heating shock for electrolyte types; (a) sulfuric acid 1.5 M, (b) oxalic acid 0.3 M, (c) oxalic acid 0.3 M, tartaric acid 0.05 M, (d) oxalic acid 0.3 M, tartaric acid 0.10 M, (e) oxalic acid 0.3 M, tartaric acid 0.15 M.
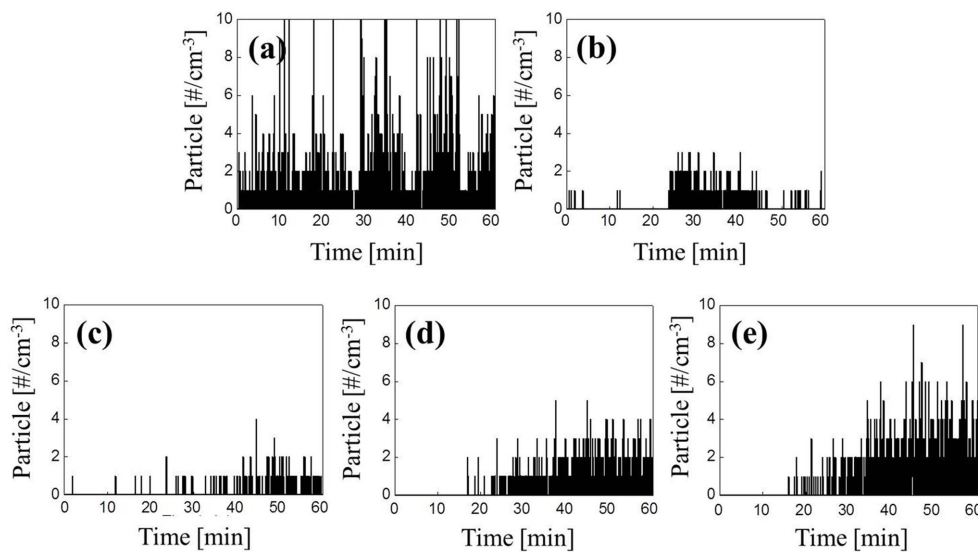

Figure 5. Real time monitoring of the particles generated during the plasma treatment for electrolyte types; (a) sulfuric acid 1.5 M, (b) oxalic acid 0.3 M, (c) oxalic acid 0.3 M, tartaric acid 0.05 M, (d) oxalic acid 0.3 M, tartaric acid 0.10 M, (e) oxalic acid 0.3 M, tartaric acid 0.15 M.
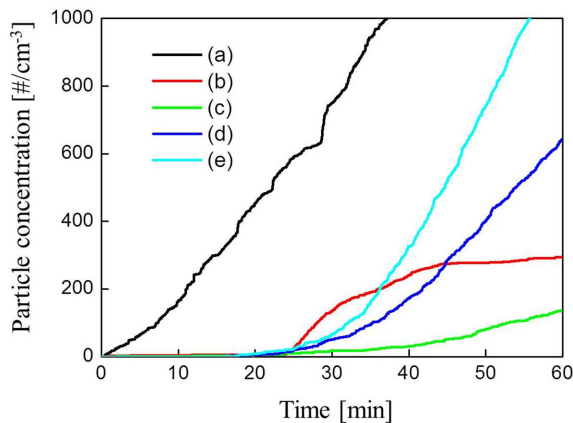
Figure 6. Accumulated particle concentration vs. plasma treatment time for electrolyte types; (a) sulfuric acid 1.5 M, (b) oxalic acid 0.3 M, (c) oxalic acid 0.3 M, tartaric acid 0.05 M, (d) oxalic acid 0.3 M, tartaric acid 0.10 M, (e) oxalic acid 0.3 M, tartaric acid 0.15 M.

that the bond strength in oxide films was increased with the use of the organic acids oxalic acid and tartaric acid.

To evaluate contamination particles generated during plasma etching, 13.56 MHz frequency and 100 W (5.5 W/ 10 cm^2 electrode surface area) power were applied to generate plasma. A gaseous mixture of CF_4, Ar, and O_2 was used under 200 mtorr pressure. As high density plasma was formed using magnets, the corrosion on the oxide film was accelerated. The contamination particles produced from plasma corrosion were measured using an ISPM sensor. Fig. 5 shows real-time measurements of particles 200 nm or larger, generated by exposing the oxide film to a plasma etching environment. The sulfuric acid oxide film produced a relatively larger amount of particles during plasma exposure. On the other hand, the oxalic acid and oxalic-tartaric oxide films generated fewer particles. Among the tested solutions, the mixture of 0.3 M oxalic acid and 0.05 M tartaric acid produced the best result.

Fig. 6 presents the real-time particle measurements. The amount of accumulated particles in the sulfuric oxide film is larger than that in the oxalic acid oxide films, as shown in Fig. 5. The addition of tartaric acid to oxalic acid led to an abrupt drop in the amount of particles. Fewer particles were generated when 0.05 M tartaric acid was added. Therefore, the best anodizing conditions for reducing the amount of contamination particles are using an oxalic acid base with a small amount of tartaric acid (0.05 M).

IV. Conclusion

The effect of anodizing electrolyte solution conditions on reducing the amount of contamination particles formed during plasma etching was investigated. After observing the oxide film properties and plasma corrosivity of oxide films produced with various mole concentrations of sulfuric acid, oxalic acid and tartaric acid, the following conclusions were drawn. The use of 0.3 M oxalic acid combined with 0.05 M tartaric acid led to a drop in leakage current and a high breakdown voltage of 0.58 kV in the oxide film that is generated. The oxide film remained free from cracks in a thermal cycling test. This oxide film also resulted in less contamination generated during plasma processing. It is expected that the present results can be exploited to increase the life-time of anodized oxide films used in plasma environments.

Acknowledgments

References

[1] A. Bautista, J. A. Gonzalez, and V. Lopez, Surf. Coat. Technol. 154, 49 (2002).
[2] W. Bensalah, K. Elleuch, M. Feki, M. Wery, and H. F. Ayedi, Surf. Coat. Technol. 201, 7855 (2007).
[3] H. H. Shih, and S. L. Tzou, Surf. Coat. Technol. 124, 278 (2000).
[4] L. Domingues, J. C. S. Fernandes, M. D. C. Belo, M. G. S. Ferreira, and L.G. Rosa, Corros. Sci. 45, 149 (2003).
[5] I. Tsangaraki-Kaplanoglou, S. Theohari, Th. Dimogerontakis, Y. M. Wang, H. H. Kuo, and S. Kia, Surf. Coat. Technol. 200, 2634 (2006).
[6] I. H. Chang, D.Y. Jung, and J. S. Gook, J. Kor. Inst. Surf. Eng. 45, 5 (2012).
[7] J. B. Song, J. T. Kim, S. G. Oh, J. S. Shin, J. R. Chun, and J. Y. Yun, Sci. Adv. Mater. 7, 127 (2015).
[8] EU Patent, EP 2055 810A2, (2009).
[9] M. Garcia-Rubio, P. Ocon, M. Curioni, G. E. Thompson, P. Skeldon, A. Lavia, and I. Garcia, Corros. Sci. 52, 2219 (2010).
[10] M. Garcia-Rubio, M.P. de Lara, P. Ocon, S. Diekhoff, M. Beneke, A. Lavia, and I. Garcia, Electrochim. Acta. 54, 4789 (2009).
[11] K. M. Takahashi, and J. E. Daugherty, J. Vac. Sci. A 14, 2983 (1996).
[12] J. Ren, and Y. Zuo, Appl. Surf. Sci. 261, 193 (2012).
[13] L. Woo, S. Kathrin, S. Martin, P. Eckhard, S. Roland, and G. Ulrich, Nature Nanotech., 3, 234 (2008).