A Systematic Study and Characterization of Advanced Corrosion Resistance Materials and Their Applications for Plasma Etching Processes in Semiconductor Silicon Wafer Fabrication

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1. Introduction

Corrosion resistance is a quantitative measure of materials under study in a special corrosion environment. With a continuous development in semiconductor IC industry on silicon wafer fabrication and the rapid shrinkage of silicon wafer feature size as of to 32nm, 25nm and even smaller, the requirement on corrosion resistance chamber materials under high density plasma becomes extremely critical and difficult. Therefore, the study, characterization and new development of corrosion resistance chamber materials have been a critical task for technologists in semiconductor IC industry. Without the correct selection of corrosion resistance chamber materials, it is impossible for semiconductor IC industry to achieve current technology levels. Among steps of semiconductor wafer fabrication, plasma dry etching is the most difficult and comprehensive step which has a very high standard for the selection of corrosion resistance chamber materials.

Different from the traditional corrosion study, materials under high density plasma during dry etching processes should meet a comprehensive requirement. First of all, chamber materials must demonstrate a very high corrosion/erosion resistance under high density plasma during etching processes as well as in the defined wet chemicals. Since different etching processes use different reactive gases and chamber conditions, chamber materials selected have to vary in order to meet the variations of etch processes and chamber conditions. Secondly, chamber materials should have low particles and defects during etching processes because the particles and defects generated from chamber materials will fall on the silicon wafer, serve as the killer defects, and cause the loss of wafer production yield. Thirdly, chamber materials should avoid metal contamination issues on silicon wafer. The high metal contamination generated from chamber materials such as Na, K, Fe, Ni, Cr, Cu et al will electrically shorten the dies on a silicon wafer and directly impact wafer production yield. In addition to the above requirements for advance corrosion resistance chamber materials, chamber etching process stability and transparency, chamber impedance matching and stability, thermal and dielectric properties, capable of surface texturing, microstructure, wet cleaning compatibility, resistance to in-situ waferless plasma
Corrosion Resistance

dry cleaning (WAC), RF coupling/grounding efficiency, adhesion of etch by-products and polymer, bonding strength of surface coatings, fundamental mechanical properties, manufacture ability and reproducibility, and cost of the materials have to be considered as a whole. After reviewing the overall requirements of chamber materials, one can see that it is not an easy task to find a suitable chamber material for semiconductor IC wafer fabrication which can meet all the above requirements. A comprehensive study has to be performed in order to find and to determine the best chamber materials among the existing materials in the world for a special etching application. Due to the complexity, the qualification processes of a new advanced corrosion resistance material for plasma etching processes are not only very time-consuming, but also very expensive. The fundamentals and applications of plasma dry etching and the applications on equipment of semiconductor silicon wafer fabrication have been described and studied extensively [1-20].

Let's take some examples. During metal etch processes (etching aluminum line), Cl₂ and BCl₃ are the main reactive gases to etch aluminum. Ar, N₂, CF₄, CHF₃, C₂H₄, or O₂ are also used during etching and WAC processes. Therefore, the selected chamber materials have to demonstrate high corrosion (and erosion) resistance to these gases under the high density plasma. For silicon etch processes, SF₆, NF₃, HBr and HCl are the main reactive gases used to etch silicon. Other gases may also be used in the etching and WAC processes. The selected chamber materials should have a high corrosion resistance to both F-based gases and HBr corrosion. In particular, the corrosion of HBr mixed with a very tiny amount of water on the heat effected zone of stainless steel has been an issue for a long time. For dielectric etching processes, CₓFₓ based reactive gases are usually used with a high applied power in order to etch oxide. Chamber materials selected have to show high corrosion and erosion resistance at a relatively high temperature and high power. For special etch processes such as metal hard mask etch, MRAM etch, high K etch and Bevel etch, special process gases and chamber conditions are applied. Therefore, the requirements to corrosion resistance chamber materials may be different. Since some plasma etching processes even etch noble metals such as Pt, Ru and Ir, one has to find chamber materials which can survive in these aggressive plasma etching conditions. Therefore, chamber materials which are submitted to sputtering, chemical etching, ion-enhanced etching, as well as ion-enhanced inhibitor etching have to be studied and characterized thoroughly for each special etching applications. There is no any material which can meet all plasma etching applications. In summary, some of the key requirements of chamber materials is listed below [21-39]:

- Low erosion rate under vigorous plasma bombardment.
- Low chemical reaction rate under many chemistries such as Cl₂/BCl₃-containing plasma,
- Fluorine-containing plasma,
- HBr/HCl/Cl₂-containing plasma,
- Oxygen-containing plasma.
- Low transition metal transport to the workpiece.
- Low or zero particle contamination from surfaces.
- Strong interface bonding of surface coatings for long part lifetime.
- Excellent and repeatable dielectric properties for RF energy coupling.
- Pore-free ceramic materials and low porosity surface coating to avoid undercut corrosion and to eliminate substrate attack.
- Excellent adhesion of etch by-products and polymers.
- Excellent corrosion resistance in wet chemistry cleaning.
- Cost effective in manufacturing.
- Excellent repeatability from part to part and wafer to wafer.

The relationship among chamber materials used in semiconductor etching equipment, etching, wet cleaning, sputtering, and etch by-products is shown in Fig. 1[21, 22, 35, 36].

![Diagram showing the relationship among chamber materials, etching processes, precision wet cleaning and etch byproducts in a plasma etching chamber.](image)

**Fig. 1.** The relationship of chamber materials, etching processes, precision wet cleaning and etch byproducts in a plasma etching chamber [21, 22, 35, 36].

For etching process requirement, a metal etch film stack and common issues are shown in Fig. 2

![Diagram showing an etched metal film stack and common metal etch problems.](image)

**Fig. 2.** Aluminum metal film stack and common issues in etching processes [21, 22].

The killer defects which are generated during metal etching processes fall on metal lines and cause the loss of production yield in wafer fabrication. The killer defects may either come from chamber materials or etch by-products [21, 22, 23, 25, 27].
Fig. 3. Killer defects generated in aluminum metal etch processes.

The corrosion/erosion patterns of chamber materials showed three different patterns under plasma. Fig. 4 shows the three different patterns [21, 22, 28, 35, 36].

Fig. 4. Corrosion/erosion patterns of chamber materials under plasma etching (pictures are at 10,000x magnification). Model A indicates a uniform corrosion/erosion which can either be higher or low; Model B shows the attack at grains of materials; and Model C shows the attack at grain boundaries of materials.
In pattern A, chamber materials can be etched/sputtered by plasma uniformly. The etch rate can be very low or very high. The etch rate depends on the plasma chemistry, process recipe, and materials. For example, high purity Y$_2$O$_3$ has showed very high plasma resistance in both Metal and Silicon etch processes. A uniform corrosion/erosion pattern is observed [21, 22, 25, 30]. For anodized aluminum, a very high corrosion/erosion rate is observed under BCl$_3$-containing plasma during metal etch processes. In fact, an anodized aluminum film with a 75 μm in thickness (hot deionized water sealed) can only hold up to 1,800 wafers in some etch process recipes in production. This became a severe problem on the lifetime of anodized aluminum in aluminum etch processes. For Silicon etch processes, the lifetime of anodized aluminum has no issue because there is no obvious attack of reactive gases to anodized aluminum in Silicon etch processes. The only concern is the formation of AlOF on anodized aluminum surface when SF$_6$ and NF$_3$ are used in the etching processes. The formed AlOF can either have chamber particle issue or cause etch process shift due to the surface impedance change on anodized aluminum surface. The wet cleaning to fully remove AlOF film on anodized aluminum surface is very critical to achieve a consistent and reliable etching performance on wafer fabrication. Fig. 5 shows an anodized aluminum metal etch chamber after 1,800 wafer fabrication in production. The anodized aluminum is fully removed under Cl$_2$/BCl$_3$ high density plasma [21, 22, 25, 30]. The major attack of anodized aluminum is due to the chemical reaction between BCl$_3$ and Al$_2$O$_3$ under the high density plasma. The reaction rate of the attack to anodized aluminum highly depends on the gas concentration of BCl$_3$ and the plasma density. Chamber erosion test indicates that Cl$_2$ has little attack to anodized aluminum [21, 22, 25, 30].

$$\text{BCl}_3 + \text{Al}_2\text{O}_3 = \text{B}_2\text{O}_3 + \text{AlCl}_3$$

Fig. 5. Anodized aluminum is fully removed under Cl$_2$/BCl$_3$ plasma after only 1,800 wafers in production (about 60 RF hours). The special attacking pattern depends on the local plasma density and gas concentration.

The high density plasma reaction rate of BCl$_3$ with anodized aluminum or high purity alumina at different flow is shown in Fig. 6. The high reaction rate occurs on chamber top window due to both high density plasma and gas flow. On the chamber wall, the reaction
rate of BCl$_3$ with Al$_2$O$_3$ is almost a linear relationship, but the reaction rate is much lower than that on the chamber top window. It also indicates that without BCl$_3$ flow, the reaction rate of Cl$_2$ plasma has almost no attack to anodized aluminum or to high purity alumina. In the plasma reaction rate study, the total flow is fixed as of 205 sccm. The Argon gas flow is fixed at 40 sccm. The test starts at 165 sccm Cl$_2$ flow and zero flow of BCl$_3$, then 155 sccm Cl$_2$ flow and 10 sccm BCl$_3$ flow, until the final flow of Cl$_2$ is 85 sccm and BCl$_3$ flow is 80 sccm. The test coupons are either on chamber top window or on the chamber wall. Nine different types of anodized aluminum and high purity alumina are used in the test [21, 22, 25, 30]. The reaction rate is in the unit of mils per RF hour.

Fig. 6. The maximum reaction rate of Al$_2$O$_3$ at different BCl$_3$ gas flow under high density plasma [21, 22, 25, 30].

In pattern B, chamber materials suffered the attack of grains under plasma. CVD SiC grains can be attacked by Cl$_2$-containing plasma and SiC material cannot be used in aluminum etch processes as a chamber material. Grains of high purity ceramic (99.5% or higher alumina) can also be attacked by BCls in metal etch processes and the glass phases such as SiO$_2$, CaO, and MgO remain. It is obvious that BCl$_3$ can attack anodized aluminum and alumina under high density plasma. For high purity AlN, AlN grains are attacked by fluorine-containing plasma such as SF$_6$ and NF$_3$, the grain boundaries remain.

In pattern C, chamber materials are attacked at grain boundaries only. A typical example is high purity alumina (99.5% or higher in Al$_2$O$_3$), glass phases such as SiO$_2$, MgO, and CaO can react with fluorine-containing gases. In this case, grains of alumina remain. The formation of AlOF may occur on alumina surface. Fig. 7 shows a ceramic ESC surface which is covered by a layer of AlOF after exposure to plasma in silicon etch processes [35, 36].

A 33% atomic% of F is detected on electrostatic chuck ceramic surface (high purity alumina) indicating the formation of AlOF on high purity alumina surface under fluorine-containing
plasma. The chemical treatment to remove AIOF using TMAH (tetramethylammonia hydroxide) is also demonstrated in Fig. 8 [35, 36, 40].

Fig. 7. A uniform AIOF film (rainbow color) covers the ceramic surface of a used electrostatic chuck after silicon etch processes.

Fig. 8. The ceramic surface of a used electrostatic chuck contains about 33 atom% fluorine on the surface film with a rainbow color.
Since the limitation of the space of this chapter, anodized aluminum, boron carbide, and Y₂O₃ as chamber materials will be demonstrated.

2. Experimental and discussion

Since the limitation of the space of this chapter, anodized aluminum and boron carbide coating as chamber materials will be demonstrated and discussed in details.

All the ceramic and CVD test coupons (except anodized aluminum coupons) are polished to mirror surface finish with the average surface roughness less than 1.0 μ-in in Ra. The anodized aluminum coupons are anodized with the surface roughness less than 32 μ-in (as-received). The thermal spray coatings keep the as-coated surface. Ceramic and CVD coated coupons weigh the pre-test weight. Anodized aluminum and thermal spray coating coupons were measured to obtain the average coating layer thickness before test. All the test coupons were soaked in IPA for 5 minutes, wiped by both IPA and acetone, rinsed by deionized water (DIW) for 1 minute and baked at 110°C for 30 minutes. A special thermal conductive tape was used to mount the test coupons on locations in the etching chamber. Three locations were selected to mount the test coupons. Test coupons are mounted on chamber top window, chamber wall, and electrostatic chuck surface, respectively. Etching systems used in this study include Applied Materials 200mm and 300mm etching tools and Lam 2300 etching tools. During materials characterization on chamber wall, on chamber top window and on electrostatic chuck, a dummy aluminum wafer was used to cover the electrostatic ceramic surface. The etching process recipe keeps running for three minutes, followed by a cooling down process for about two minutes, than repeat the etching recipe. The minimum process time (RF hours) cycled is 120 RF hours and the longest process time cycled is 200 RF hours.

A typical process recipe under a 200mm etch tool is shown below [21, 22, 25, 30]:

**Step 1.** Plasma Etching & Dechuck Steps
- 12mT/85Cl₂/80BCl₃/40Ar/1600Ws/200Wb/45°C cathode/80°C wall & top window/7 Torr He flow/180 seconds.
- 100Ar/TFO/500Ws/100Wb/5sec.

**Step 2.** Cooling Down Step
- 12mT/200Ar/45°C cathode/80°C wall & top window/120 seconds.

Repeat process recipe (step 1 and step 2) until the accumulated RF hours achieve 120 RF hours or 200 RF hours, respectively.

After plasma etching processes, all the test coupons were removed from the chamber. A post wet cleaning was carried out to remove polymer, etch by-products, and other contaminants. All the coupons were then DIW rinsed and baked at 110°C for 30 minutes. Post weight measurements were carried out to obtain the average thickness loss per RF hour. For anodized aluminum and spray coating coupons, post thickness measurements were carried out in order to obtain the coating thickness loss per RF hour.

All the coupons are studied by SEM before and after plasma etching process. The corrosion/erosion rates of different test coupons are recorded and compared as mils per RF hour. Test coupons on etch chamber top window, chamber wall and on electrostatic chuck surfaces are shown in Fig. 9.

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Fig. 9. Test coupons in etching chamber are mounted on chamber top window (left) and on chamber wall (right) and on the dummy aluminum wafer on an electrostatic chuck surface (right, white surface).

Fig. 10 shows the test results of various materials obtained from worldwide suppliers. The letters of A, B, C, D et al represent the suppliers and their materials. Agreements were signed for not allowing to release the names of the worldwide suppliers and their materials. The plasma etching rate is in the unit of mils (1 mil = 25.4 μm). It is obvious that either YAG (solid solution of Al₂O₃ and Y₂O₃) and solid Y₂O₃ can reduce the plasma etching rate at the order of 40-50 times in comparison with the previously used chamber materials such as high purity alumina. That is the reason why Y₂O₃ has been as one of the leading chamber materials in plasma etching tools in the past 10 years for the leading semiconductor etching equipment companies.

![Graph showing the etch rate reduction of new chamber materials.](image-url)

Fig. 10. Test results of new and old chamber materials in plasma etching on chamber top window. The etch rate reduction of new chamber materials can reduce the etching rate by 40 to 50 times.
For test results on chamber wall, the etching rate of anodized aluminum from various suppliers w/wo hot DI water seal is between 0.050 to 0.070 mils / RF hour. For boron carbide coating through a thermal spray method, the etching rate is below 0.001 mils / RF hour. For sintered or hot pressed boron carbide, the etching rate is between 0.0001 to 0.0007 mils / RF hours. It is also obvious that the plasma etching resistance of boron carbide can improve the plasma resistance by 50 times or higher. In fact, boron carbide coated chamber has been using at worldwide wafer fabrication customer sites since 1998. 50 to 100 times chamber life improvement has been demonstrated since 1998 up to today [21, 22, 25, 30, 41].

In order to select the best configuration of surface coatings such as B₄C (boron carbide), three configurations are considered. Configuration 1 is the coating of B₄C on bare aluminum surface. Configuration 2 is the B₄C coating on anodized aluminum surface. Configuration 3 is the B₄C coating on anodized aluminum surface and then HL126 sealant is used to seal the pores in the spray coating layer. HL126 contains methacrylate esters and it can fill very tiny pores. The metal contamination levels of HL126 is pretty low. All metal levels are below 1 ppm except the sodium level at 57 ppm. Permabond HL126 is a high strength and low viscosity anaerobic threadlocker. Its properties are listed in the attached table below:

PHYSICAL PROPERTIES OF THE UNCURED ADHESIVE *

<table>
<thead>
<tr>
<th>Properties</th>
<th>Methacrylate Esters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Resin, Solid, %</td>
<td>100</td>
</tr>
<tr>
<td>Color</td>
<td>Green</td>
</tr>
<tr>
<td>Viscosity, cP, 25°C (77°F)</td>
<td>20</td>
</tr>
<tr>
<td>Consistency</td>
<td>Liquid</td>
</tr>
<tr>
<td>Gap Filling, in</td>
<td>0.005</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.09</td>
</tr>
<tr>
<td>Flash Point, °C (°F)</td>
<td>&gt;110 (230)</td>
</tr>
<tr>
<td>Shelf Life stored at or below 27°C (80°F), months</td>
<td>12</td>
</tr>
</tbody>
</table>

Electric Properties

| Dielectric strength, MV/m              | 11                   |
| Electric Resistance, ohm-cm           | 10¹⁵                |

Performance properties of the cured sealant

| Operating temperature °C (°F)         | 150 (300)           |

Table 1. Properties of HL126 sealant

The corrosion resistance of boron carbide coated coupons after plasma etching is tested by HCl bubble test method which was first proposed by Shih in 1992 and was used as a standard technique in anodization study for IC industry in 1994 [42]. The fundamental concept of the defined HCl bubble test method can be explained as follows. The dilute HCl solution can go through the pores and micro-cracks on coating and anodized aluminum layer to react with bare aluminum under the coating or under the anodized aluminum. When HCl reacts with aluminum alloy, hydrogen bubbles will generate. Streams of hydrogen bubbles can be observed and the time to start the continuous hydrogen bubbles can be recorded and compared for different coating configuration and different types of anodized aluminum before and after plasma etching processes. Shih [43, 44] has set up the method at two major semiconductor equipment companies since 1994 and the method has been widely accepted by worldwide anodization suppliers. The method is simple, low cost
and fast in comparison with ASTM standard salt spray test method [45, 46]. The test results show that boron carbide coating on anodized aluminum and sealed with HL126 provide the best corrosion resistance among the four configurations as shown in Fig. 11 [25].

Fig. 11. After plasma etching for 200 RF hours, Boron carbide coated anodized aluminum sealed with HL126 sealant provides the best corrosion in all configuration.

The wet cleaning compatibility of four configurations is also tested by soaking the large size B₄C coated rings in saturated AlCl₃ solution at pH=0 for 90 minutes, then put the rings in an environmental chamber to monitor the time when boron carbide coating starts to peel off. The test sequence is shown in Fig. 12 [25].

Fig. 12. Wet cleaning compatibility test of four configurations of boron carbide coated rings.
For coating on bare aluminum alloy, the entire coating layer peeled off during immersion in the saturated AlCl₃ solution at pH=0.0. The coating on anodized aluminum can hold 45 hours in the environmental chamber and the coating layer peeled off completely at 47 hours. Both coating on bare aluminum alloy and on anodized aluminum with the use of HL126 sealant can hold up to 114 hours in the environmental chamber without any failure. At 114 hours, the environmental chamber test was stopped. From the test results of HCl bubble test and wet cleaning compatibility test, coating on anodized aluminum with the use of HL 126 sealant can provide the best corrosion resistance. This configuration is selected as the final configuration as the new chamber wall material.

In order to qualify boron carbide coating as a new chamber material, many aspects have to be considered. One of the concerns is the impact to ICF (ion current flux). Three configurations are considered and compared in the etching chamber. The ICF of anodized aluminum chamber is used as the baseline. Boron carbide coatings on bare aluminum or on anodized aluminum are studied through ICF measurements. The results showed that the three configurations have the compatible ICF. The results of ICF measurements are shown in Fig. 13 [21, 22, 25, 30].

![Fig. 13. ICF measurements on the wafer during the use of three configuration chambers.](Fig. 13)

Another concern is the potential damage to gate oxide. The leakage current measurements on the gate oxide show that born carbide coating does not introduce damage to gate oxide. The measurements of leakage current of gate oxide are shown in Fig. 14 [21, 22, 25, 30].
Fig. 14. The leakage current of gate oxide in log scale indicates that there is no damage to gate oxide when a born carbide coated chamber is used.

The metal contamination using a boron carbide coated chamber has shown meeting the specification of metal contaminations such as Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Ti, and Zn in 1,000, 2,000, and 3,000 wafer marathons, respectively.

There is no metal contamination introduced when a high purity boron carbide coating is introduced as the new chamber wall coating.

The monitoring data of on-wafer aluminum etch rate, etch rate non-uniformity, defect and particle performance, and thickness measurements of boron carbide coating before and after plasma etching processes are shown in the following figures and tables. In Fig. 15, the particle data during a 3,000 wafer marathon are provided and compared with the specification requested by customers. It is obvious that new B₄C coated chamber wall can meet the requirement of particles. In this study, particles at and larger than 0.2 μm are recorded. The B₄C coated chamber wall can also provide excellent aluminum etch rate and etch rate non-uniformity through the entire 3,000 wafer marathon as shown in Fig. 16 [47].

The boron carbide coated chamber is also qualified through a 2,000 wafer marathon for etching of 0.15 μm feature size. Excellent aluminum etching performance is demonstrated as shown in Fig. 17 [48].

On a 300mm etch tool, boron carbide coated chamber was also used in a 1,000 wafer marathon. The boron carbide coated chamber meets all the requirements including aluminum etch rate and etch rate non-uniformity, etch profiles, defects and particles, metal contamination [49]. The particle performance at 0.12 μm or larger is the critical requirement. It is obvious that the boron carbide coated chamber can meet the requirement. The up limit of particle allowance at 0.12 μm or larger is defined as 50 adders/per wafer.

After plasma etching O₂/Cl₂ for 120 RF hours, the thickness of pre and post boron carbide coating on anodized aluminum is measured and the data are listed in Table 2.
Fig. 15. Gas-only and RF-on particles during a 3,000 wafer marathon. The up limit of allowance of defect and particles is defined as 50 adders/ per wafer.

Fig. 16. Al etch rate and etch rate non-uniformity during a 3,000 wafer marathon.
A Systematic Study and Characterization of Advanced Corrosion Resistance Materials and Their Applications for Plasma Etching Processes in Semiconductor Silicon Wafer Fabrication

Fig. 17. The boron carbide coated chamber shows an excellent aluminum etch performance on a feature size as of 0.15 μm through a 2,000 wafer marathon.

Fig. 18. Particle adders as of ≥ 0.12 μm size in a 1,000 wafer marathon on a 300mm etch tool. The boron carbide coating on anodized aluminum with HL126 sealant is used as the chamber coating to replace anodized aluminum.

<table>
<thead>
<tr>
<th>Location</th>
<th>Pre (mils)</th>
<th>STD(mils)</th>
<th>Post (mils)</th>
<th>STD(mils)</th>
<th>Delta</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (10 data)</td>
<td>17.60 0.413</td>
<td>17.98 0.236</td>
<td>+0.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B (10 data)</td>
<td>17.55 0.363</td>
<td>17.52 0.225</td>
<td>-0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C (10 data)</td>
<td>18.76 0.287</td>
<td>18.56 0.201</td>
<td>-0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 data</td>
<td>17.97 (average)</td>
<td>18.02 (average)</td>
<td>+0.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. The overall coating thickness before and after plasma etching under O₂/Cl₂ plasma for 120 RF hours.
It is obvious that there is little coating thickness loss after 120 RF hours under $O_2/Cl_2$ plasma. The main purpose of $O_2/Cl_2$ plasma is to test the performance of HL126 sealant under $O_2/Cl_2$ plasma condition.

After the detail study through a thorough process qualification, the new boron carbide coated chamber wall is used to replace the previously anodized aluminum surface. The new ceramic material such as YAG or $Y_2O_3$ is used to replace original high purity alumina. This configuration was introduced to semiconductor wafer fabrication for evaluation. Excellent etch performance, enhanced defect and particle reduction, and 50 to 100 times chamber lifetime improvement are reported. The production yield of the wafer fabrication also improved about 7% in production at the customer site (see Fig.19) [41]. The following data provide some of the information. The sequence of the data collection is as follows:

Baseline configuration using the old chamber hard ware submitted to gas-only and RF-on particle measurements without seasoning. After 1st RF-on particle measurement, five oxide wafers were used for seasoning the chamber, then RF-on particles were measured again. Two PR wafers were used to seasoning the chamber before final RF-on particle measurement. The test data are shown in Table 3 [41].

<table>
<thead>
<tr>
<th>Condition</th>
<th>Gas-only w/o seasoning</th>
<th>RF-on(1) w/o seasoning</th>
<th>RF-on(2) 5 ox seasoning</th>
<th>RF-on(3) 2 PR seasoning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Old chamber configuration</td>
<td>10</td>
<td>34</td>
<td>53</td>
<td>48</td>
</tr>
<tr>
<td>New chamber configuration</td>
<td>2</td>
<td>5</td>
<td>6</td>
<td>5</td>
</tr>
</tbody>
</table>

*: Unit in particle counts/wafer and particle adders at 0.2 $\mu$m or larger are recorded.

Table 3. Gas-only and RF-on particles of old and new chamber configurations

Fig. 19. Production yield improvement at wafer fabrication when new chamber material, hardware and best-known method are implemented.
About 7% production yield is reported in comparison with the old chamber configuration. The lifetime of chamber wall and chamber top window can improve about 50 times [41].

The new boron carbide coating has been introducing to worldwide wafer fabrication for over 10 years with over 1,000 chambers introduced to wafer fabrication in IC industry. The chamber lifetime has demonstrated to improve from the worse case as of 60 RF hours (1,800 wafers) under BCl₃/Cl₂ etching plasma to over 4,000 RF hours or longer in semiconductor wafer fabrication in the world. It also demonstrates that the chamber materials play a critical role in semiconductor etching equipment, particularly, for the cost reduction. A short comparison of anodized aluminum and boron carbide coating is highlighted in Table 4 [21, 22, 25, 30].

<table>
<thead>
<tr>
<th>Items</th>
<th>Anodized aluminum</th>
<th>Boron Carbide Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum etch rate</td>
<td>0.07 mils/RF hour</td>
<td>0.001 mils/RF hour</td>
</tr>
<tr>
<td>Minimum lifetime</td>
<td>1,800 wafers</td>
<td>120,000 wafers</td>
</tr>
<tr>
<td>Particle performance</td>
<td>normal*</td>
<td>better</td>
</tr>
<tr>
<td>Metal contamination</td>
<td>normal</td>
<td>better</td>
</tr>
<tr>
<td>Micro-cracks</td>
<td>yes</td>
<td>no, but with coating pores</td>
</tr>
<tr>
<td>Coating bonding</td>
<td>very high</td>
<td>less than anodized Al</td>
</tr>
<tr>
<td>Surface roughness</td>
<td>normal</td>
<td>higher</td>
</tr>
<tr>
<td>Polymer adhesion</td>
<td>normal</td>
<td>better</td>
</tr>
<tr>
<td>Wet cleaning recovery</td>
<td>normal</td>
<td>normal</td>
</tr>
<tr>
<td>Process performance</td>
<td>normal</td>
<td>normal</td>
</tr>
<tr>
<td>Production yield</td>
<td>normal</td>
<td>better</td>
</tr>
<tr>
<td>Gate oxide damage</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Water adsorption</td>
<td>normal</td>
<td>normal</td>
</tr>
<tr>
<td>Micro-hardness (100g)</td>
<td>360-450</td>
<td>3,000</td>
</tr>
<tr>
<td>Localized attack</td>
<td>yes, through cracks</td>
<td>no, with HL126 sealant.</td>
</tr>
<tr>
<td>Etch process window</td>
<td>normal</td>
<td>normal</td>
</tr>
<tr>
<td>Risk of undercut corrosion</td>
<td>no</td>
<td>no, with HL126 sealant</td>
</tr>
<tr>
<td>HCl bubble time</td>
<td>≤ 10 minutes (non hot DIW seal)</td>
<td>&gt; 50 hours, with HL126 sealant (after hot DIW seal)</td>
</tr>
<tr>
<td>Effect of base aluminum alloys to coating quality</td>
<td>yes, large impact</td>
<td>no</td>
</tr>
</tbody>
</table>

Table 4. Comparison of Anodized Aluminum and Boron Carbide Coating

Anodized aluminum has been using as the major etching tools surface coatings since 1980. It still received a lot of applications in plasma etching tools because of its low cost, easy to manufacture, easy to make large or small sizes of the parts, wide applications, easy to refurbish, and achieving good quality control at different suppliers in the world. Therefore, the study of anodized aluminum has always been a major task for the major semiconductor etching tool manufacturers. For high purity Y₂O₃ thermal spray coating, it has been qualified and applied as one of the major chamber components in plasma etching tools in the past 10 years. It is still one of the major materials as coating or as a solid sintered material which is used in plasma etching tools. At Lam Research Corporation, great attentions have been paid in the improvements and the new development of anodized aluminum and Y₂O₃ coatings.
These studies have been highlighted in John and Hong’s presentation [28, 31-33, 35-39] and the publications of the new anodized aluminum study with Mansfeld et al [38, 39].

The study and characterization of anodized aluminum and the methodology are shown below. But the techniques are not limited to the techniques listed below:

- Admittance measurements on anodized aluminum to check sealing quality.
- Micro-hardness on surface and through the anodized aluminum layer.
- SEM cross section and Eddy current meter for anodized layer thickness.
- X-ray diffraction for the phase analysis of anodized aluminum.
- SEM cross section of micro-structure and secondary phases observation.
- TEM analysis to estimate the barrier layer thickness.
- EDX analysis for element analysis on the surface or through the layer.
- ICPMS analysis to obtain the surface cleanliness before and after cleaning.
- GD-OES analysis of the depth profile of elements in anodized layer.
- HCl bubble test to obtain the acidic corrosion resistance of anodized layer.
- Dielectric voltage breakdown of the anodic layer.
- Color and color uniformity of the anodic film.
- Electrochemical impedance spectroscopy to obtain the overall impedance.
- Surface roughness and coating thickness and their variations.
- Taber abrasion test to obtain wear resistance of the anodic film.
- Microhardness on surface and through coating cross section.
- Coating weight.
- Erosion/corrosion rate under high density plasma with different chemistries.
- Raw aluminum alloys analysis through different manufacturing processes.
- Intermetallic inclusions and their chemical composition analysis.
- Thermal property of anodic film after thermal cycling at different temperatures.

Although there are so many techniques used in the anodized aluminum study, there are only key techniques which are selected as a routine quality monitoring of worldwide anodization suppliers. The basic techniques are surface roughness, thickness of anodic film, color and color uniformity, dielectric voltage breakdown, acidic corrosion resistance through HCl bubble test, electrochemical impedance in 3.5wt% NaCl solution, surface micro-hardness, SEM cross section to observe the anodic layer micro-cracks, and admittance under 3.5wt% K$_2$SO$_4$ solution at 1000 Hz. For the surface cleanliness of anodization, ICPMS analysis of post precision wet cleaning has been used as a standard technique for metal contamination control. Since the requirements to anodized aluminum quality, corrosion resistance, and surface cleanliness for plasma etching tools are much strict and higher than the traditional industry applications, improvements of corrosion resistance and surface cleanliness are always the tasks. Lam Research has defined the surface cleanliness and the corrosion resistance of anodized aluminum specification for a standard type III and advanced anodized aluminum [28, 31-33, 35-39, 44].

The reaction mechanism of aluminum oxidation is summarized by Macdonald [50] as a reasonable model. The oxides grow as bilayer structures with an inner layer due to movement of oxygen vacancies from metal/film interface and an outer layer due to the movement of cations outward from the film/environmental interface. The vacancy concentrations vary exponentially with distance. The cathode consumes electrons by evolving hydrogen and reducing oxygen. Barrier layer grows into metal phase via reaction.
Outer film grows via precipitation of Al$^{3+}$ due to hydrolysis. The fundamental reactions for anodized aluminum systems are shown as follows:

<table>
<thead>
<tr>
<th>Metal film</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $m + V_{M^{x'}} = M_{M} + Xe$</td>
<td>(3) $M_{M} = M^{x'} + V_{m^{x'}}$</td>
</tr>
<tr>
<td>(2) $m = M_{M} + (x/2) V_{o''} + Xe^-$</td>
<td>(4) $V_{o''} + H_{2}O = O_{o} + 2H$</td>
</tr>
</tbody>
</table>

The principal crystallographic defects are (1) vacancies: $V_{o''}$ and $V_{M^{x'}}$ for $MO_{x/2}$; (2) interstitials: $O_{i2^{-}}$ and $M_{ix^+}$. In fact, oxide films can be described as exponentially-doped semiconductor junctions. The fundamentals and process optimization of anodized aluminum have been studied thoroughly by Brace, Thompson, Wood, Mansfeld, and recent years by Shih through the comprehensive studies of anodization of different aluminum alloys, different anodization processes, and different manufacturing processes [51 – 60]. The interface model of anodized aluminum with hot DI water seal has been described by Mansfeld, Kendig, Shih and others [61- 72] as shown in Fig. 20.

Fig. 20. The typical interface model of anodized aluminum with a hot DI water seal.

$$Z(\omega) = R_{b} + R_{b}/[1+(j\omega C_{b}R_{b})^{\alpha_{2}}]+(R_{po}+CPE)/[1+(j\omega C_{po}(R_{po}+CPE))^{\alpha_{1}}]$$

where $C_{b} = \varepsilon\varepsilon_{0}A/D_{b}$; $C_{po} = \varepsilon\varepsilon_{0}A/D_{po}$ and CPE $= k(j\omega)^{n}$

$\varepsilon_{0} = 8.854 \times 10^{-14}$ F/cm and is the permittivity of free space.

In Fig.20, $C_{b}$ and $R_{b}$ are barrier layer capacitance and resistance, respectively. $R_{po}$ and CPE are the total impedance of the porous layer defined as $Z_{po}$ which equals to $R_{po} +$ CPE. $C_{po}$ is the capacitance of the porous layer. CPE represents the constant phase element (CPE). A two-time constant interface model and suitable values of $R_{b}$ and $Z_{po}$ indicate a good quality of anodized aluminum. $Z_{po}$ values highly depend on the quality control of hot DI water sealing process and it is very important for the improvement of the corrosion resistance of anodized aluminum [73-82]. $R_{b}$ values depend on the voltage applied during anodization as well as the overall process control during anodization. A uniform and thick barrier layer helps to improve the dielectric voltage breakdown of the anodized aluminum. Mansfeld and Shih [63-69] developed a software package specially for the analysis of electrochemical impedance spectroscopy (EIS) data of anodized aluminum and the software has been widely applied for EIS data analysis. The EIS data of the new anodized aluminum developed and qualified at Lam Research Corporation show that the anodized aluminum has no corrosion in 3.5wt% NaCl (similar to seawater) for 365 days as shown in Fig. 21 [28, 38].
The overall impedance and HCl bubble test results are shown in Table 5. EIS data of three test coupons after immersion in 365 days in 3.5wt% NaCl solution are analyzed using the software written by Shih and Mansfeld called “ANODAL” [63-69].

<table>
<thead>
<tr>
<th>Coupon ID</th>
<th>$Z_{po}$ (ohm-cm$^2$)</th>
<th>$R_{b}$ (ohm-cm$^2$)</th>
<th>HCl bubble time in hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>365D005</td>
<td>1.462x10$^7$</td>
<td>1.257x10$^{10}$</td>
<td>&gt; 24</td>
</tr>
<tr>
<td>365D107</td>
<td>1.568x10$^7$</td>
<td>1.641x10$^{10}$</td>
<td>&gt; 24</td>
</tr>
<tr>
<td>365D073</td>
<td>1.396x10$^7$</td>
<td>1.363x10$^{10}$</td>
<td>&gt; 24</td>
</tr>
</tbody>
</table>

Table 5. The overall impedance and HCl Bubble Time of Test Coupons After Immersion in 3.5wt% NaCl solution for 365 days (coupons were prepared in three different batches of anodization processes) [78].

The Bode-plots of the three EIS data after 365 day’s immersion in 3.5wt% NaCl solution is shown in Fig. 22. The anodized aluminum shows an excellent corrosion resistance and high quality of process control.

The complete EIS data analysis of the three test anodized aluminum samples is listed in Table 6 below. It is obvious that a consistent and an excellent corrosion resistance on both porous layer and barrier layer have been demonstrated. It is very important to improve the overall corrosion resistance of anodized aluminum through a well-controlled hot DI water sealing process. The parameters of hot DI water sealing tank water purity level, temperature range, sealing time, hot DI water pH value, and the pre-cleaning of the anodized aluminum before loading to the hot DI water tank will impact the quality of the sealing quality. The anodized anodization as a chamber coating for semiconductor IC industry moved from previously used non-sealed type III anodization or other types of non-sealed anodization to a well-controlled hot DI water sealed anodization for over 15 years because the hot DI water sealed anodized aluminum has demonstrated much better overall corrosion resistance in plasma etching chamber.
A Systematic Study and Characterization of Advanced Corrosion Resistance Materials and Their Applications for Plasma Etching Processes in Semiconductor Silicon Wafer Fabrication

Fig. 22. EIS Bode-plots of advanced anodized aluminum coupons in 3.5wt% NaCl solution for 365 days. Black – 365D005; Red – 365D107; Blue – 365D073.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>D005</th>
<th>D107</th>
<th>D073</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_p0 (nF)</td>
<td>9.15</td>
<td>9.20</td>
<td>9.33</td>
</tr>
<tr>
<td>C_b (μF)</td>
<td>8.45</td>
<td>9.19</td>
<td>8.97</td>
</tr>
<tr>
<td>Z_p0 (Mohm)</td>
<td>0.731</td>
<td>0.784</td>
<td>0.698</td>
</tr>
<tr>
<td>R_b (Mohm)</td>
<td>628.4</td>
<td>820.5</td>
<td>681.5</td>
</tr>
<tr>
<td>n</td>
<td>0.1814</td>
<td>0.1733</td>
<td>0.1733</td>
</tr>
<tr>
<td>α_1</td>
<td>0.887</td>
<td>0.900</td>
<td>0.887</td>
</tr>
<tr>
<td>α_2</td>
<td>0.958</td>
<td>0.930</td>
<td>0.940</td>
</tr>
<tr>
<td>A (area in cm^2)</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Chi-sq</td>
<td>2.785x10^{-3}</td>
<td>3.761x10^{-3}</td>
<td>2.775x10^{-3}</td>
</tr>
<tr>
<td>Z_p0 (ohm-cm^2)</td>
<td>1.462x10^7</td>
<td>1.568x10^7</td>
<td>1.396x10^7</td>
</tr>
<tr>
<td>R_b (ohm-cm^2)</td>
<td>1.257x10^{10}</td>
<td>1.641x10^{10}</td>
<td>1.363x10^{10}</td>
</tr>
</tbody>
</table>

Table 6. Detailed of EIS Data Analysis of test Samples D005, D107 and D073 after 365 Day’s Immersion in 3.5wt% NaCl Solution

In Table 6, α is called frequency dispersion which is related to surface inhomogeneties with different dimensions [83]. Chi-sq is the fitting error between the experimental data and fitted data at each frequency. The detailed calculation is shown as below [84] and is the sum of the fitting error at each frequency multiplying 100 and dividing the total data points.

\[
\text{Chi-sq} = (100/N) \sum \left( \frac{|Z_{\text{exp}}(f_i) - Z_{\text{fit}}(f_i)|}{Z_{\text{exp}}(f_i)} \right)
\]

TEM is also used to obtain the barrier layer thickness of different types of anodized aluminum [80]. In Fig. 23, a standard type III anodization achieves about 50nm thickness of the barrier layer. The thickness of a new anodization can be as thick as 100nm due to the higher voltage applied in the anodization process. The thicker barrier layer can provide a
higher barrier layer resistance during the EIS study as shown in Table 5 and Table 6. By combining both an excellent hot DI water seal processing to obtain an excellent corrosion resistance of the porous layer and a thicker barrier layer of the anodic film, the anodic film can hold 365 days in seawater without corrosion.

Fig. 23. TEM pictures of a standard type III hard anodization (left) and a mixed acid anodization (right) [80]

For acidic corrosion resistance of anodized aluminum, HCl bubble test is an easy and very effective method to obtain the corrosion resistance. From Fig. 24 below, one can see the good and poor anodized aluminum under the solution of 5wt% HCl solution (28, 31-33, 44, 78]. On the left of Fig. 24, there is no any hydrogen bubble generated under the attack of a strong acid within 2 hours immersion. It indicates a high quality of anodized aluminum. On the right of Fig. 24, anodized aluminum generates a lot of hydrogen bubbles in 5wt% HCl solution only after 10 minutes immersion in the acid. It indicates a poor anodized aluminum.

Fig. 24. Acidic corrosion resistance of two test coupons of anodized aluminum. On the left, anodized aluminum does not show any acidic corrosion in two hours and on the right, anodized aluminum shows severe acidic corrosion after only 10 minutes immersion in the acid.
The HCl bubble test can be processed at any position of etching chamber before and after etching process. In Fig. 25, one process chamber is studied on its corrosion resistance in 5.0wt% HCl solution [76]. This method has received a wide application for the corrosion resistance study of anodized aluminum.

Fig. 25. HCl bubble test on a used process chamber after 12,000 wafers processing. Six locations are selected to run the HCl bubble test [76].

A systematic study of anodized aluminum made of Al6061-T6 11” thick block was carried out. It is obvious that HCl bubble test can be studied at different thickness positions to compare the differences of corrosion resistance [77]. The detail positions of different tests are shown in Fig. 26. Eleven different test methods are applied to the study.

HCl bubble test can be carried at different thickness to evaluate the corrosion resistance at different thickness in a thick aluminum block [77].

The thermal properties of anodized aluminum have also been studied. One of the typical studies was published in the work with Mansfeld [39]. A lot of studied have been carried out at Lam through the years [39, 73-82]. All these studies show that anodized aluminum film can be degraded through the use at a relatively high temperature. Both porous layer and barrier layer can be impacted depending on the operation temperature. Radii before anodizing on aluminum parts have to be controlled and the micro-cracks at corners and edges depend on the type of anodized aluminum and final thickness of anodic layer.

High purity $Y_2O_3$ has advantages in comparison with anodized aluminum and ceramic such as high purity alumina in many aspects. First of all, it can reduce the plasma etching rate for both metal etch and silicon etch by a factor of 40 times. It can bring cost saving in etch tools for semiconductor wafer fabrication. It can also reduce metal contamination too. The comparison of anodized aluminum and thermal spray coating of high purity $Y_2O_3$ are summarized by John and Shih [28, 31]. The advantages of $Y_2O_3$ coated anodized aluminum are as follows:

- Particle and defect reduction due to the elimination of aluminum fluoride.
- Metal contamination reduction due to its lower transition metal content.
- Better resistance to dielectric breakdown due to a thicker coating.
- Chamber material lifetime improvement due to much lower etch rate under plasma.
- Cost reduction due to extensive chamber materials lifetime.
Corrosion Resistance

Fig. 26. A systematic study the anodized aluminum of Al6061-T6 11” thick block.

Although thermal spray and sintered $Y_2O_3$ has been widely using as one of the chamber materials in wafer fabrication, the study of this material as well as its coating has never been stopped because of the challenges. These studies for semiconductor IC wafer fabrication contain the following studies, but not limit to these techniques [28, 78].

- Impurity levels of raw powder.
- Particle size distribution of the raw powder.
- Impurity levels of the raw powder.
- Environmental control of coating processes.
- Optimization of coating process to reduce porosity and to eliminate non-melted particles.
- Coating thickness, roughness, color and the uniformities.
- Bonding strength and bending strength through pulling and bending tests.
- Dielectric voltage breakdown.
- Acidic corrosion resistance under 5wt% HCl solution.
- Micro-hardness.
- Overall admittance (coating/anodize/aluminum).
- ICPMS analysis for surface cleanliness.
- Surface particles after precision wet cleaning.
- Wet chemicals compatibility study.
- Porosity estimation through SEM cross section analysis.
- Overall impedance and interface model of coating through EIS study.
- Plasma resistance under both BCl$_3$/Cl$_2$ and SF$_6$/HBr gases.
In order to study $Y_2O_3$ coating on anodized aluminum, the following electrochemical cell configuration is used to study the overall impedance and interface model of the coated samples or parts as shown in Fig. 27 [28, 78].

![Electrochemical cell configuration during EIS study of $Y_2O_3$ coated anodized aluminum in 3.5wt% NaCl solution](https://example.com/electrochemical-cell-config.png)

Fig. 27. Electrochemical cell configuration during EIS study of $Y_2O_3$ coated anodized aluminum in 3.5wt% NaCl solution [78].

An interface model of $Y_2O_3$ coated anodize aluminum shows a three-time constant interface model indicating a $Y_2O_3$ coated layer, the porous layer of anodized aluminum, and the barrier layer of anodized aluminum as shown in Fig. 28 [28, 78]

![Proposed interface model of $Y_2O_3$ coated anodized aluminum in EIS study](https://example.com/interface-model.png)

Fig. 28. The proposed interface model of $Y_2O_3$ coated anodized aluminum in EIS study

Assuming that $C_c$, $C_{po}$ and $C_b$ are capacitances which represent the capacitances of $Y_2O_3$ coating layer, porous layer of anodized aluminum and barrier layer of anodized aluminum, respectively. The interface parameters can be obtained and the coating quality can be monitored. The interface model can be described as the following equation [28, 78].

$$Z(\omega) = \frac{R_b}{1+(j\omega C_b R_b)^{\alpha_3}} + \frac{(R_p + CPE)}{1+(j\omega C_{po}(R_p+CPE))^{\alpha_2}} + \frac{R_c}{1+(j\omega C_c R_c)^{\alpha_1}} + R_s$$
Where $Z$ is the total impedance, $R_b$ is the barrier layer resistance of anodization, $R_p$ is the porous layer resistance of porous layer of anodized aluminum, CPE is the constant phase element of the porous layer, $R_c$ is the coating resistance, and $R_s$ is the solution resistance.

Soaking three spraycoated $Y_2O_3$ on anodized aluminum in 3.5wt% NaCl solution for 7 days, the EIS data are shown in Fig.29. The EIS data indicate that samples coated at different time have the similar overall impedance and the quality control of coating process is consistent. The complete analysis of the EIS data using a three-time constant interface model is shown below (Table 7).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$ (ohm)</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>$R_c$ (ohm)</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>$R_p$ (ohm)</td>
<td>$1.2 \times 10^5$</td>
<td>$1.1 \times 10^5$</td>
<td>$1.2 \times 10^5$</td>
</tr>
<tr>
<td>$R_b$ (ohm)</td>
<td>$5.0 \times 10^7$</td>
<td>$5.0 \times 10^7$</td>
<td>$5.1 \times 10^7$</td>
</tr>
<tr>
<td>$K$ (ohm)</td>
<td>$8.0 \times 10^4$</td>
<td>$6.6 \times 10^4$</td>
<td>$7.5 \times 10^4$</td>
</tr>
<tr>
<td>$A$ (area in cm$^2$)</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>$Z_c$ (ohm-cm$^2$)</td>
<td>800</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td>$Z_{po}$ (ohm-cm$^2$)</td>
<td>$4.0 \times 10^6$</td>
<td>$3.5 \times 10^6$</td>
<td>$3.9 \times 10^6$</td>
</tr>
<tr>
<td>$Z_b$ (ohm-cm$^2$)</td>
<td>$1.0 \times 10^9$</td>
<td>$1.0 \times 10^9$</td>
<td>$1.0 \times 10^9$</td>
</tr>
</tbody>
</table>

Table 7. Interface parameters of three spraycoated $Y_2O_3$ on anodized aluminum

Fig. 29. EIS data of three spraycoated $Y_2O_3$ on anodized aluminum in 3.5wt% NaCl solution for 7 days. Excellent coating quality control is observed through the EIS study [28, 78].
3. Conclusions

- The revolutionary chamber materials study under high density plasma has opened a new scientific field in the characterization of materials. Meeting the comprehensive requirements of plasma etching tools in semiconductor wafer fabrication with the technology node shrinkage is not an easy task. The efforts and methodology developed through these studies have built up the foundation in the advanced materials characterization, development and application.

- A systematic study of chamber materials for plasma etching tools has been demonstrated. The materials studied include anodized aluminum, boron carbide coating, Y$_2$O$_3$ coating and sintered Y$_2$O$_3$ as well as the solid solution of aluminum oxide and yttrium oxide (YAG).

- In addition to the discussion of systematic study of anodized aluminum, an advanced anodized aluminum developed has shown no corrosion in seawater environment for 365 days.

- Thermal spray coating of boron carbide has been studied thoroughly. It has been introducing to worldwide semiconductor wafer fabrication since 1998. The coating has demonstrated over 50 times even 100 times lifetime improvement in production of semiconductor wafer fabrication and has been one of major chamber materials up to today.

- Y$_2$O$_3$ coating has also been studied thoroughly through the years since 2002. It has demonstrated longer chamber lifetime under plasma for both metal etch and silicon etch applications. It has been introduced to worldwide wafer fabrication since 2002 with a great cost saving and improved etch performance. As of today, it is still the major chamber coating of the current plasma etching tools.

- Lam Research Corporation has been putting great efforts and support for the new chamber materials development. It becomes more critical for semiconductor plasma etching equipment companies to develop new and advanced materials for current and next generation plasma etching feature size applications.

4. Acknowledgement

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Song, Dr. You Wang, Dr. Yan Chun, Dr. Qi Li, Dr. Allan Zhao, Joe Sommers, Dr. Griff O’Neil, Dr. Raphael Casaes, Dr. T. W. Kim, Dr. Lin Xu, Dr. Catherine Zhou, Dr. Yijun Du, Dr. Daxing Ren, Ho Fang, May He, Josh Cormier, Fangli Hao, Dr. Steve Mak, Dr. Gerald Yin, Dr. Xikun Wang, Dr. Danny Lu, Yoshi Tanase, Dr. Samantha Tan, Dr. Fuhe Li, Shang-I Chou, Tim. Su, John Holland, Peter Holland, Jason Augustine, Dr. Y. L. Huang, Lucy Chen, Jie Yuan, Hui Chen, Li Xu, Charlie Botti, Han Sellege, Dr. Arthur W. Brace, and many others.

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The book has covered the state-of-the-art technologies, development, and research progress of corrosion studies in a wide range of research and application fields. The authors have contributed their chapters on corrosion characterization and corrosion resistance. The applications of corrosion resistance materials will also bring great values to reader's work at different fields. In addition to traditional corrosion study, the book also contains chapters dealing with energy, fuel cell, daily life materials, corrosion study in green materials, and in semiconductor industry.

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