Improving Corrosion Resistance of Plasma Etch Reactors Testing Anodize Coatings and Cleaning Methods

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Abstract

Plasma etch reactors are used extensively in the volume manufacturing of wireless and optoelectronic compound semiconductor devices. Many of the different plasma etch processes in the fabrication of these devices require the use of chlorine or bromine-based corrosive gases. Consequently, protection of the plasma exposed internal aluminum components in these reactors and the preventive maintenance procedures are critical to maintain system integrity and high throughput.

To aid in the evaluation and ranking of different anodized protective coatings for the reactor, an ex-situ accelerated chlorine-based corrosion resistance test has been developed. Results from analysis of these experiments are presented.

The corrosion resistance life test has also been used in the determination of the optimum preventive maintenance cleaning technique of these anodized coatings. Recommendations from this work are also reported.

INTRODUCTION

Due primarily to its ease of machinability and low cost, aluminum is often utilized for chambers and components for vacuum applications – including most plasma etching. Plasma etching of many materials in GaAs, InP, and GaN device manufacturing requires the use of corrosive gases. These corrosive gases and their reaction by-products can result in the degradation of exposed and unprotected components in the reactor chamber. While aluminum is well suited for medium and high vacuum applications, it is relatively reactive and consequently susceptible to chemical attack. [1, 2]

Aluminum naturally forms a tough resistant oxide, alumina, upon exposure to air that almost immediately protects it from further corrosion. Once that protective coating is removed in the absence of oxygen, the underlying aluminum is once again highly reactive. For plasma etch reactors using corrosive chlorine or bromine-based chemistries, this results in the need for protective coatings to be applied to the aluminum reactor components. Most often the technique of anodization is used to form a thick and dense protective alumina coating on these components.

While anodization extends the life of the reactor components, the coatings themselves are still subject to corrosive failure. There are two main mechanisms of failure. Firstly, for components subjected to ion bombardment during the plasma process, the anodized coating is slowly removed by ion assisted etching. The second mechanism results from the porous nature of the anodized coatings. Upon venting the reactor for maintenance or cleaning, the residual chlorinated etch by-products are hydrolyzed with moisture in the air to form HCl. Over time, this acid will break down the anodized coating. With this second mechanism, the lifetime of the anodized coating is dependent largely on the microstructure (porosity) of the anodized film in conjunction with the nature of the maintenance processes (i.e. mechanical abrasion, etc.) used to clean it.

In recent years, significant advancements have been made in anodized coatings technology particularly in the pertinent areas of corrosion resistance and mechanical hardness. [3] In this paper, an accelerated chlorine-based life test has been developed to compare a number of these advanced anodized coatings in order to identify a coating with improved corrosion resistance. The tests are based on sample coatings of each type and referenced against currently used coatings in plasma etch reactors. Following the initial tests between different coating types, the accelerated life test was also applied to examine the effects of abrasive cleaning methods on coating lifetimes. Based on this work, recommendations regarding cleaning methods for anodized reactor surfaces will be made.

EXPERIMENTAL

In this section, details on the different anodized sample coatings, the accelerated chlorine-based life test, and the cleaning techniques are described.

A) Anodized Coatings Evaluated

A total of five anodized coatings were evaluated. This includes samples of the commonly used coatings in many plasma reactors, hard anodized (Type III) that was supplied by two different coatings manufacturers. In Table I, details on the sample coatings and group category are presented.

As noted in the table, some of the details on the coatings preparation method are unknown as they are proprietary to the individual manufacturers.

TABLE I
DETAILS ON ANODIZED COATINGS EVALUATED

Sample Group #	Designation	Details
A	Current Anodize	Hard Anodized, Type III
B	Current Anodize	Hard Anodized, Type III
C	Advanced Anodize I	Proprietary Process
D	Advanced Anodize II	Proprietary Process
E	Advanced Anodize III	Proprietary Process

B) Accelerated Chlorine-based Life Test

The accelerated life test used to evaluate corrosion-resistance of the anodized coatings was the "HCl bubble test". In this test, the coating is immersed in a dilute HCl solution and visually monitored over several hours. When the coating breaks down, HCl attacks the underlying aluminum and released bubbles of H_2 are observed. Qualitatively, the onset of coating failure occurs when the first continuous stream of H_2 bubbles appears from anywhere on the coating surface. The HCl bubble test, a variant of the salt spray technique[4], is an established method for testing anodized coatings, and coating manufactureres often supply HCl bubble test corrosion-resistance results. However, due to variations in the test conditions, comparison of different coatings based on individual manufacturer supplied data has proven unreliable. Therefore, an in-house HCl bubble test was developed to evaluate the corrosion resistance of the various anodized coatings.

In order to more easily evaluate a number of coatings, small (~ 10 cm x 10 cm) test samples from each coatings manufacturer were used. For each test, a fresh solution of 5% (w/w) HCl solution was mixed. A Teflon ring with an inner diameter of about 3 cm and 0.5 cm high was adhered to each test sample with a silicone sealant and then filled with the HCl solution. A computer-interfaced digital camera was used to monitor the evolution of H_2 bubbles as the coating breaks down. To validate the results, 3 to 5 repeatability tests were performed on each coating type. Data for each sample was captured at 10 second intervals for up to a 24 hour time period or at least until clear evidence that complete failure of the coating had occurred.

The captured digital images were analyzed off-line and linked together to create a movie sequence of the experiment. Image time stamps were used to determine the coating failure times.

C) Cleaning Procedure Evaluation

As discussed earlier, in addition to withstanding the etch process and exposure to moisture, it is also important that the coating be able to withstand scheduled maintenance and cleaning procedures. While etch processes vary in terms of chamber condition, many processes require more than just a simple water / isopropyl alcohol wipe sequence in order to restore the reactor to a "clean" condition. One common practice for removing "tougher" etch by-products is to scrub the surface in the presence of water or isopropyl alcohol – typically with an abrasive cleaning pad. While this is effective in removing process residues, it can negatively impact the corrosion resistance of the anodized coating.

To simulate a typical cleaning procedure, a number of the coating samples were held in a vice and subjected to 300 passes (back and forth = 1 pass) with abrasive cleaning pads. A constant force was applied to the pads during the cleaning process. Scotch-Brite™ pads # 07448 fine silicon carbide and # 07445 aluminum silicate cleaning pads were used in these trials.

Upon completion of the simulated cleaning process, the integrity of the anodized coatings was evaluated with the HCl bubble test.

RESULTS AND DISCUSSION

A) Corrosion Resistance Performance

It is instructive to compare collectively the HCl bubble test images for the different anodized coatings. Figures 1 to 5 show representative elapsed time images taken during the HCl bubble tests on the 5 different sample coatings investigated. It is clearly apparent that the corrosion resistance performance of the coatings are quite different. From Figures 1 and 2, the current anodization shows clear evidence of bubble formation within a few hours of immersion in the HCl solution. This indicates an earlier onset of coating failure compared to the Advanced Anodize I and II coating results shown in Figures 3 and 4, respectively. Both of these coatings did not show any degradation until many hours of testing had elapsed. As presented in Figure 5, the Advanced Anodize III coatings also withstood many hours of testing. However, early random formation of bubbles close to the start of the test may suggest that failure may be already occurring.

The short time scale to failure, measured in hours, of all these coatings is due to the aggressive nature of the accelerated life test. For reference, uncoated aluminum samples fail within seconds under these test conditions. In real time application of these coatings in plasma etch reactors, the typical expected coating life would be on the order of months to years.

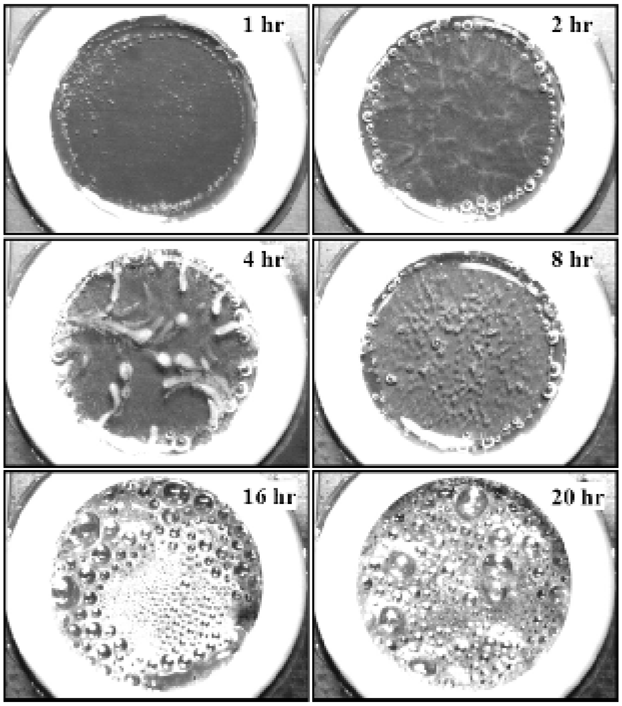

Figure 1. Typical HCl bubble test image sequence for Current Anodize coating recorded at the times indicated (Sample group A).

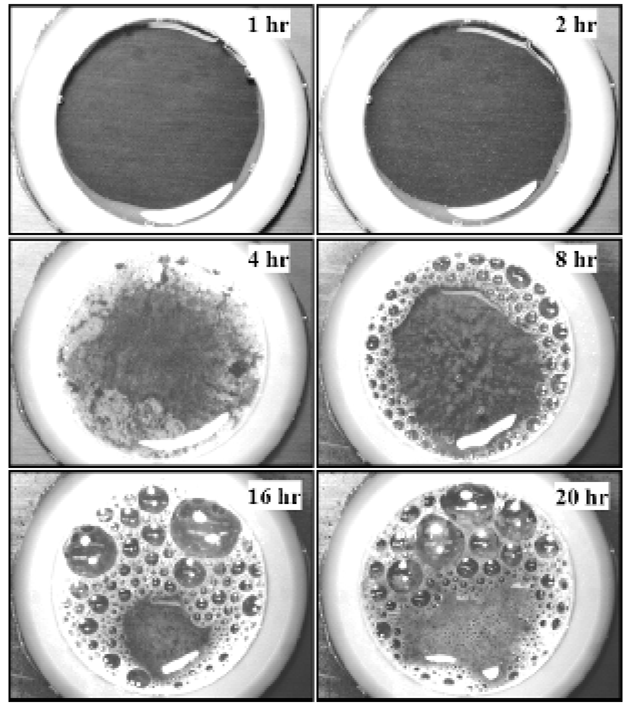

Figure 2. Typical HCl bubble test image sequence for Current Anodize coating recorded at the times indicated (Sample group B).

To rank the corrosion performance of the coatings required a more in-depth analysis of the recorded video images. The onset of failure was used to rank the performance. This was defined as the time that the first continuous stream of bubbles was observed. Table II summarizes the corrosion resistance performance results for the five different anodized coatings evaluated. Also shown in the table are the times at which excessive bubble formation occurs from multiple sites on the coating. This is defined as catastrophic coating failure. The failure times shown in the table are the minimum and maximum values obtained from the analysis of 3 to 5 data sets for each coating type. Variations in coating quality and nature of the experimental technique are responsible for the larger differences in failure times obtained for some coatings.

TABLE II
CORROSION RESISTANCE RANKINGS BASED ON ONSET TIME

Rank	Group (Coating)	Failure Onset Time (hr.)	Catastrophic Failure (hr.)
1	D (Advanced Anodize II)	11.7 - 15	15.6 -19
2	C (Advanced Anodize I)	6.8 – 9.9	10 – 13.4
3	E (Advanced Anodize III)	4.8 - 6	13.9 – 17.6
4	A (Current Anodize)	0.9 – 1.3	2.1 – 3.7
4	B (Current Anodize)	3.0 – 3.4	3.6 – 3.9

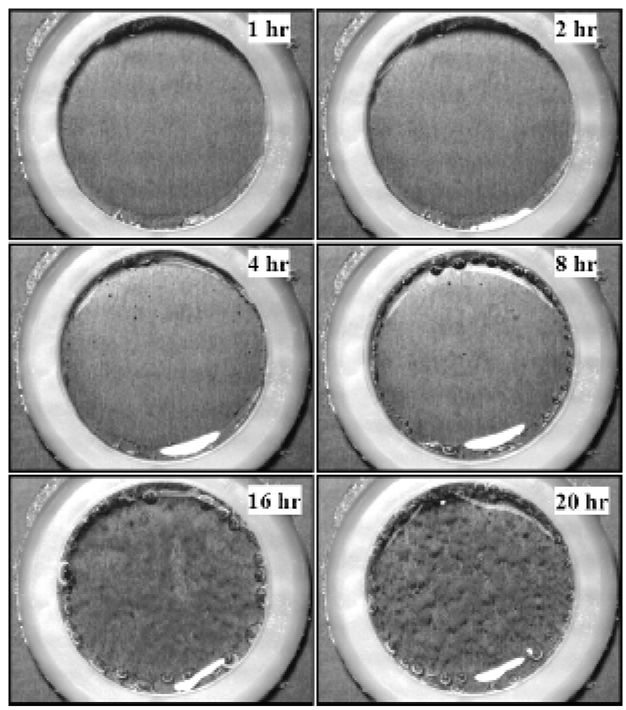

Figure 3. Typical HCl bubble test image sequence for Advanced Anodize I coating recorded at the times indicated (Sample group C).

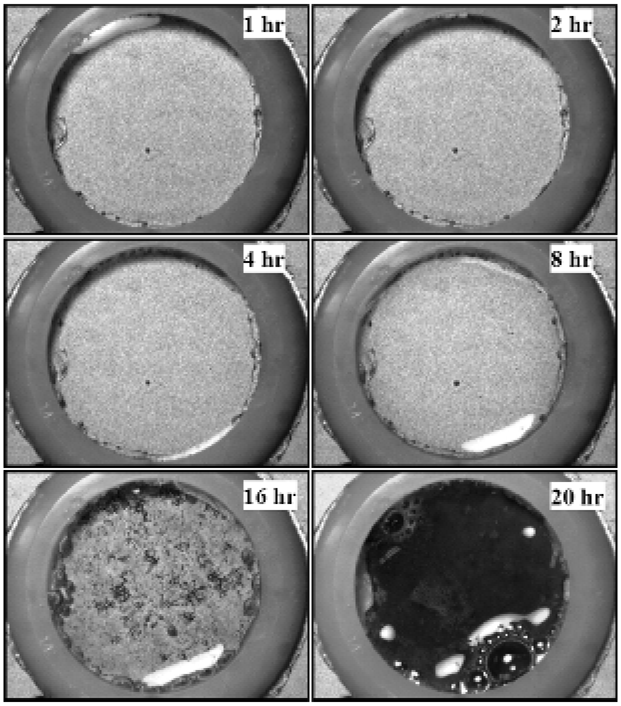

Figure 4. Typical HCl bubble test image sequence for Advanced Anodize II coating recorded at the times indicated (Sample group D).

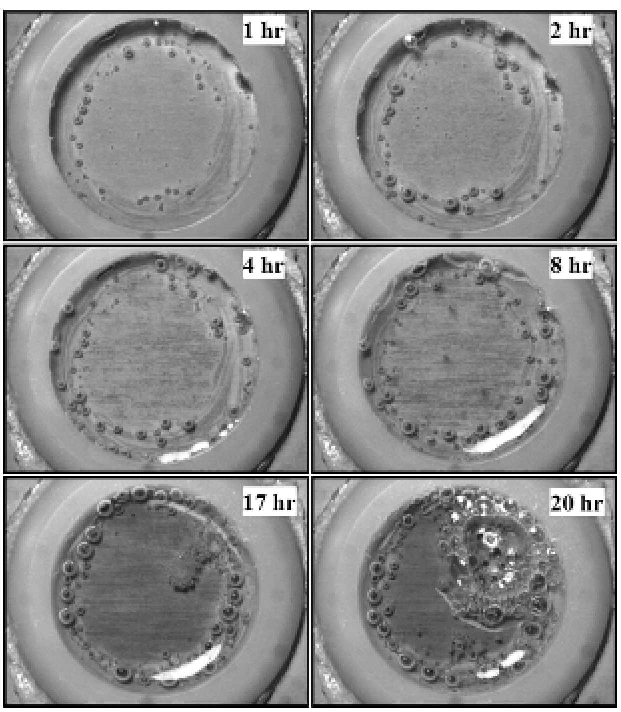

Figure 5. Typical HCl bubble test image sequence for Advanced Anodize III coating recorded at the times indicated (Sample group E).

B) Cleaning Performance

The lifetime of all coatings was reduced by at least 10% and in some cases up to 35% compared to the as-received coatings when subjected to either abrasive cleans.

CONCLUSIONS

The principal conclusions from this work are:

1. There are distinct differences in the corrosion resistance properties of the variety of coatings investigated.

2. Current anodize coating shows overall the weakest corrosion resistance.

3. Advanced Anodize II coating followed by Anodize I show the best overall corrosion resistance.

4. Anodize III coating withstood many hours of testing. However, there may be some evidence of early premature failure occurring.

5. Cleaning procedures adopted are critical to maintain the integrity of the anodized coating.

6. It is recommended that abrasive cleaning materials should never be used in the preventative cleaning procedure. From field trials on plasma etch reactors, implementation of an improved non-mechanical cleaning technique significantly prolongs the lifetime of the anodized components.

FUTURE WORK

From a technical aspect, the Advanced Anodize II or I are the best candidates for protective coatings for a plasma reactor. These are also the most expensive coatings evaluated. The next stage of this work will include a cost-benefit analysis of all the coatings explored. Future work will include evaluating the Advanced Anodize II and I coatings in a plasma reactor.

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