

Specialty Coatings to Reduce Corrosion in Scrubber Components

Advanced Equipment Process and Materials

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Abstract—Scrubbers play an essential role in the safe manufacturing of semiconductor devices. However, metal parts degrade very quickly in the highly corrosive scrubber environment, and this poses an environmental and safety challenge. In this paper, we present data for specialty coatings that significantly reduce the corrosion rate of metal scrubber parts. The benefits are a reduction of heavy metals in the waste stream, a minimized exposure of employees to the corroded parts, a solid-waste reduction, and a lower cost in part replacements. In short, the quality of the semiconductor process is improved, and the cost reduced.

I. INTRODUCTION

The semiconductor industry continues to increase integration level. Lithography is no longer the principal driver. Instead, varieties of processes that use materials that can be toxic, corrosive, or both, have been incorporated into the manufacturing process. Since only a fraction of the chemicals used are consumed in the process, typically 30% or less¹, the remaining amount need to be removed before atmospheric exhaust. The abatement systems used in the semiconductor industry² are hybrid (wet and dry) and point-of-use (POU). This is because of the need to abate gases such as silane (SiH_4) and phosphine (PH_3) close to the point of origin; to provide the greatest flexibility in dealing with new effluents; and finally, to allow the measurement of emissions locally to ensure environmental compliance. Figure 1 shows a schematic representation of a hybrid, POU, scrubber used in the semiconductor industry.

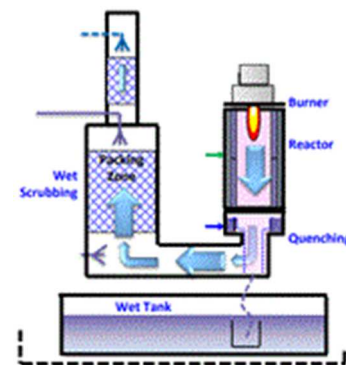


Figure 1. Schematic representation of a hybrid, point-of-use scrubber commonly used in the semiconductor industry.

Ni (nickel) and Cr (chromium) alloys³, such as Inconel™ are used to make scrubber parts to provide some resistance in the highly corrosive environment. Even these alloys perform poorly at the interface between the dry and wet portions of the scrubber, where parts are exposed to a corrosive environment, high moisture, and high temperature. As these metal parts corrode, heavy metal ions are incorporated into the fab waste stream and need to be removed to protect the environment. Additionally, corroded parts are contaminated and need to be discarded as corrosive solid waste. Finally, as corrosion progresses, the mechanical integrity of the part is degraded and may negatively affect the performance of the scrubber. In short, it is highly desirable to reduce the corrosion of scrubber parts to minimize its environmental impact.

II. CORROSION MECHANISM

There is a very large number of scrubbers in a high-volume semiconductor manufacturing facility because of the POU requirement. The effluents vary a great deal, depending on the chemistry of the deposition, etching or furnace tool. In some instances, the effluent variety and volume requires a redundant capacity, adding to the number of scrubbers.

A. STRESS-CORROSION CRACKING

We analyzed the parts that failed prematurely to establish a pareto distribution and focus on finding a solution for the most affected parts first. Using this list, we selected two metal scrubber parts made of Inconel™ that support CVD (Chemical Vapor Deposition) reactors in our wafer fab (part A and part B).

It is widely known that fluorine, F, in different forms, is frequently used in CVD processes⁴. Surprisingly, we did not find significant amounts of F by EDS (Electron-Dispersive X-ray Spectroscopy) in some of the corroded parts A and B. As we show in Figure 2, the parts consistently fail due to cracks in specific areas near a weld. A closer examination under an SEM (Scanning Electron Microscopy) shows a change in the grain structure near the cracks.

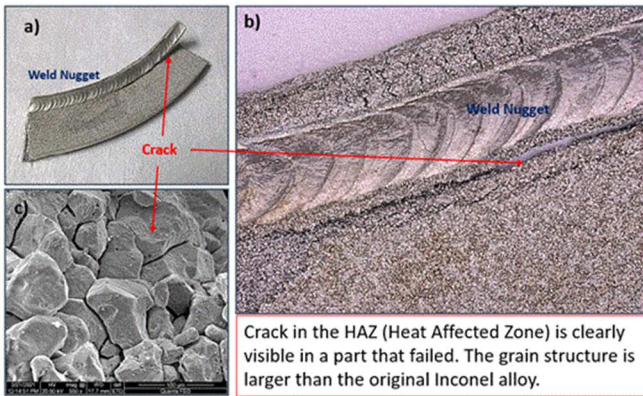


Figure 2. Clockwise, a) portion of a failed scrubber part shows the failure consistently takes place near a weld. b) A micrograph shows the crack in more detail. c) The SEM shows a larger grain structure in the crack area.

These observations are consistent with Stress-Corrosion Cracking⁵, SCC. The area under stress is the Heat Affected Zone, HAZ, from the weld, as shown in Figure 3.

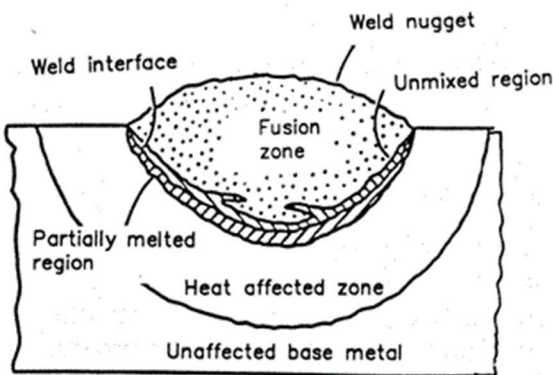


Figure 3. Schematic representation of a heterogeneous weld.

We confirmed that SCC was the main corrosion mechanism by careful examination of the parts. In Figure 4, we show that the HAZ becomes visible before the onset of corrosion. This implies that it is etching at a faster rate⁵.

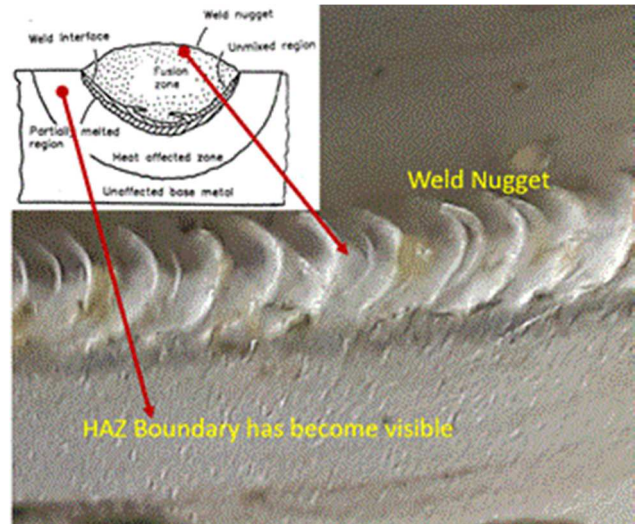


Figure 4. The Heat Affected Zone, HAZ, becomes visible just before the corrosion onset.

B. UNIFORM CORROSION

Scrubbers support tools running different chemistries. Failed Parts A and B from a scrubber (Figure 5) supporting a different process chemistry were also analyzed. These parts show a different failure signature. The corrosion takes place over the bottom 1/3 of the piece, in the very transition from the dry- to wet- portions of the scrubber, as shown in Figure 5 (Part B), and not preferentially along the HAZ.

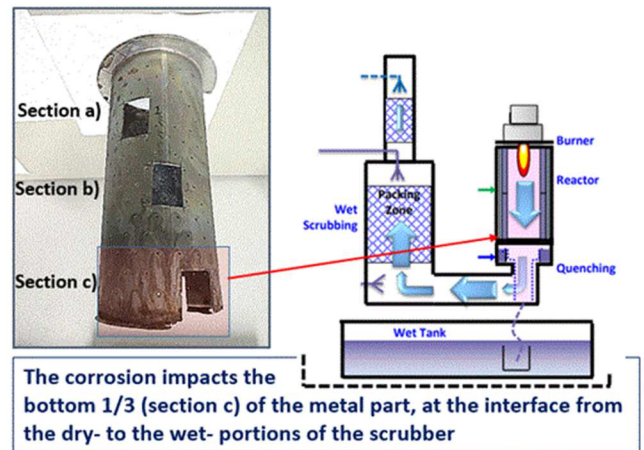


Figure 5. Corrosion of Part B. Coupons for analysis were taken from the sections labeled A) to C). Corrosion mainly takes part on the bottom 1/3, corresponding to Section C), the section at the very interface between the dry- and wet- portions of the scrubber.

Elemental analysis by EDS shows a drop in the Cr and Ni content. The sharpest drop is in Section C, where Ni has dropped from 75% down to 11%, and Cr from 16% down to 2%. This behavior better fits uniform corrosion, but at the interface between the dry- and wet-portions of the scrubbers.

Based on these two corrosion mechanisms, we looked for films that would protect the scrubber parts from corrosion. After considering several films, amorphous silicon (a-Si) and amorphous silicon-oxide nitride (a-SiON) were evaluated. Since both films are amorphous, the formula shown does not represent a stoichiometric composition.

III. FILM DEPOSITION AND CHARACTERIZATION

Industrial thermal chemical vapor deposition (CVD) is a robust and useful manufacturing platform.⁶ The process is scalable from small fittings to large vacuum chambers as well as being capable of coating simple geometries and complex geometries with high aspect ratios or high surface areas. The technique is compatible with most materials able to withstand the thermal requirements of the deposition. This includes stainless steel, aluminum and its alloys, titanium, super alloys (Hastelloy®, Inconel®, etc.), glass, and ceramics.

Components are placed into a vacuum chamber, heated under vacuum, and exposed to reactive source gases to deposit the coating layer or layers to achieve the desired coating thickness. Processing parameters are selected and controlled to sufficiently coat all pathways and surfaces of the component while limiting gas phase nucleation (which can lead to particulate contamination). While the coating can take several hours to construct an appropriate coating layer, the batch nature allows for multiple components to be coated during a single deposition.

The resulting coating layer is molecularly bound to the substrate. CVD coatings have shown improved adhesion strength over other coatings such as fluoropolymers and ceramics.⁷ Reductions in adhesion strength can also lead to fracture of the coating layer when the substrate is bent or flexed.

The coating described in the current work is a combination of silicon, oxygen, and nitrogen, which we describe as an amorphous, silicon-oxy-nitride coating. This has been verified by Fourier Transform Infrared Spectroscopy (FTIR), shown in Figure 6.

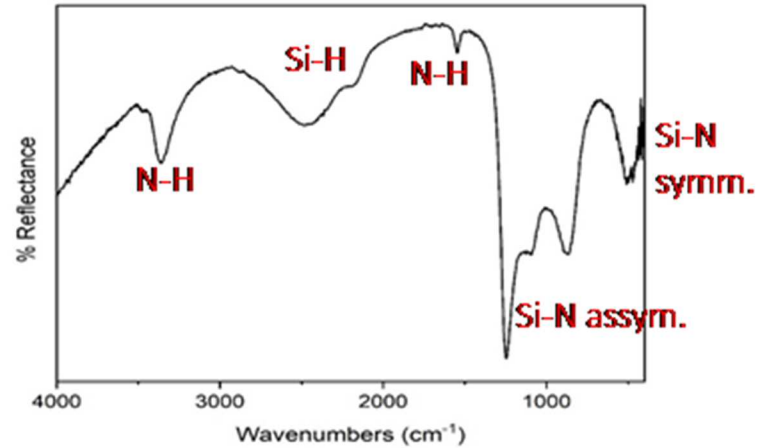


Figure 6. FTIR spectrum of the coating used in the present work.

We characterized the film by Energy Dispersive Spectroscopy (EDS) to verify the chemistry found by FTIR as shown in Table I.

TABLE I
EDS RESULTS

Element	Wt%	Error (σ)
Silicon (Si)	28.5	0.1
Nitrogen (N)	20.3	0.1
Oxygen (O)	6.3	0.0
Substrate (SST)	44.9	0.3

IV. EXPERIMENTAL RESULTS

Scrubber Parts A and B, made from an Inconel™ alloy, were coated with a SiON film. For Part B, an additional test was done with an a-Si film. Coated parts were installed in a scrubber. New, uncoated parts were installed as a control in another scrubber exposed to the same chemistry and in close proximity to each other. The coated and control parts were examined at frequent and regular intervals. The parts were weighed to measure mass loss from corrosion, and examined the parts for any changes likely sourced from the effects of corrosion. Finally, the process was documented with photographic images.

RESULTS FOR PART A

Figure 7 shows the mass loss as a function of wafers processed in the reactor chamber for Part A. Please note that the control part has been replaced twice. As of the writing of this paper, the 3rd quench sleeve has already lost 11% of its initial mass. Based on the previous two failures, we estimate that it is at 1/3 of its lifetime. By contrast, the coated part has not lost a significant amount of mass. Based on this data, we conclude that the a-SiON film extends the lifetime of Part A in this particular chemistry by at least 300%.

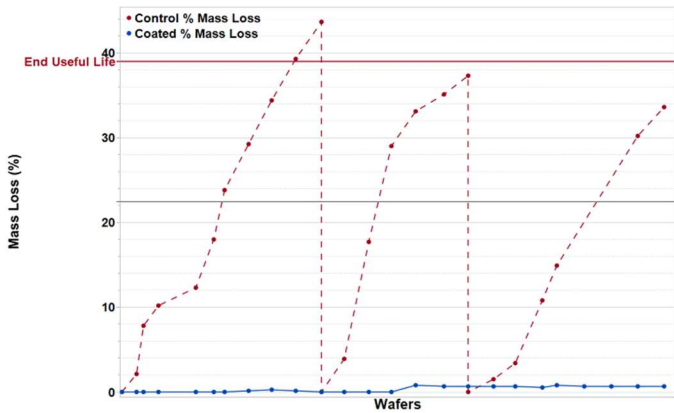


Figure 7. Mass loss as a % of the initial mass for part A as a function of wafers processed. The control had to be replaced 3 times. The coated part has lost less than 2% of its initial mass.

The set of images below compares the replaced control parts, and the a-SiON coated Part A undergoing testing, with a new one.

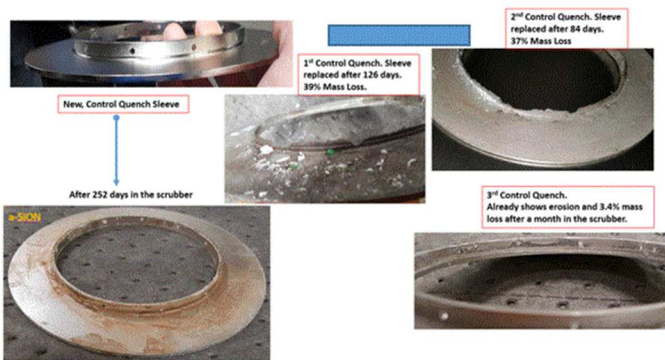


Figure 8. Photographic images of a new control part A and the 3 control parts that have been replaced. The part coated with the a-SiON film is shown in the bottom left corner.

We can clearly see the corrosion and loss of mechanical integrity in the first two control parts. We can also see the onset of corrosion near the weld, as the mechanism predicts, on the 3rd control part. By contrast, the a-SiON part has some stains but on a significant portion of its surface the initial sheen remains. Finally, there are no signs of corrosion in the HAZ, near the welds.

RESULTS FOR PART B

Part B is exposed to higher temperature than part A. For part B, an amorphous silicon, a-Si, was included in the test, in addition to the a-SiON coating. The long-term corrosion resistance is shown in Figure 9.

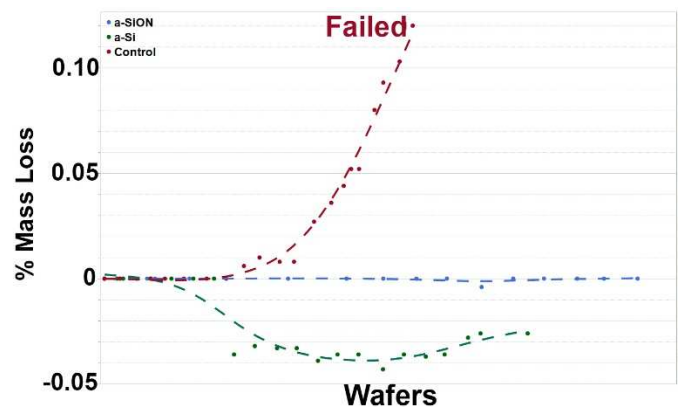


Figure 9. Mass loss as a % of the initial mass for Part B as a function of wafers processed. The control failed and was replaced. The part coated with the a-Si film underwent a mass gain and is now slowly losing mass. The part with the a-SiON film has lost no appreciable mass despite having processed a larger number of wafers.

The Part B coated with the a-Si film gained mass, probably because of oxygen uptake, forming SiO_2 . Although this film performs better than the control, the images in Figure 10 make it clear that the a-SiON film is the most desirable solution.



Figure 10. Photographic images of a new control Part B at the top-left of the graphic. Next, a Part B coated with SiON shows little corrosion. A failed, control Part B is shown at the top-right of the graphic. The failure mechanism is SCC (Stress Chemical Corrosion). By contrast, the failure mechanism of the control Part B shown at the bottom-right is bulk corrosion. The bar chart at the bottom-left shows the etch rate of the control is about two orders of magnitude higher than the control.

V. CONCLUSIONS

Two different coatings were tested to extend the lifetime of metal scrubber parts. The coated parts were exposed to 5 different chemistries. Two different corrosion mechanisms were elucidated from the failure analysis performed. It is possible, indeed likely, that additional corrosion mechanisms are at play

if all the possible process chemistries are taking into account. Although the a-Si coating performed better than the control, the coating of choice based on this study is an a-SiON.

Based on the reduced corrosion rate, at least 100 kg/year of heavy metals are no longer incorporated into the fab waste stream. The amount of corroded solid waste is reduced by an order of magnitude.

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