

Amorphous Silicon Coatings for Control of Corrosion and Metal Ion Contamination

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***Abstract*— As semiconductor devices become smaller and more complex, eliminating device-degrading contamination (i.e. metal ions, particulate, etc.) becomes more significant. At the same time, material removal (etch) has become increasingly important and has led to the introduction of more aggressive chemicals for both creation of the needed geometries and the need to maintain clean processing chambers. These chemicals require clean and inert pathways with minimal impact to the process. Amorphous silicon (a-Si:H) applied by a thermal chemical vapor deposition (CVD) process is an attractive candidate material for providing the necessary barrier between the corrosive process gases and the gas supply piping.**

***Keywords* – coatings, metal ion contamination, corrosion resistance, outgassing**

I. INTRODUCTION

With 3D NAND flash technology entering the mainstream, increased utilization of etching (staircase, hard mask, gate trench, channel hole, staircase contact, etc.) has created multiple challenges.¹ Several of these challenges are being addressed through innovative advances with etch equipment. Others have required increased dependence on aggressive etch chemistries to create the necessary chip geometries.^{2–5} Etch gas interacting with the gas delivery piping (often stainless steel) can lead to corrosion and corrosion byproducts (metal ions or particulate) reaching the wafer surface. Improving the corrosion resistance of the gas delivery system has become a higher priority.

Amorphous silicon coatings have been used extensively in gas chromatography applications to limit negative surface interactions where stainless steel surfaces can cause problems in complex gas analysis. The oil and gas industry was an early adopter of inert coating technology for the ease of use and accuracy it provides when measuring sulfur content in crude oil.⁶ Inertness, moisture control, and corrosion resistance properties can all be improved by coating the entirety of a sample or process flow path.^{7,8} These features can also provide benefit within semiconductor etch applications and other manufacturing processes such as atomic layer deposition, epitaxy, and ozone generation.

II. DISCUSSION

Numerous surface treatments exist which improve the material properties of bare metals such as stainless steel^{9,10}. Utilizing amorphous silicon films deposited by industrial thermal CVD can offer some unique advantages. The silicon layer acts as a barrier between interactions of the process gases and the metal tubing. This barrier reduces the opportunity for metal ions (iron, chromium, etc.) reaching the wafer surface with a common material which is, in many steps, being removed already. Industrial thermal CVD also does not suffer from line-of-sight limitations like spray-on coatings or physical vapor deposition (PVD) processes allowing for the coating of complicated three-dimensional geometries without issue. Components with tubing and bellows can also be coated and the amorphous nature of the silicon coating will allow an amount of flexing without the risk of fracture or delamination.

A. Chemical Vapor Deposition (CVD) Coating Process

Treating components with amorphous silicon coatings via industrial thermal CVD processing is a robust manufacturing platform. The process is scalable from small fittings and very high surface area parts (metal frits, filters, etc.) to very large fabricated parts (vacuum chambers, etc.). The focus of this paper is on stainless steel parts, but the industrial CVD process is compatible with coating any material able to withstand the thermal requirements (stable to about 500 °C). This will include aluminum and its alloys, titanium, super alloys (Hastelloy®, Inconel®, etc.), glass, and ceramics.

Components for coating are placed into a vacuum chamber, heated under vacuum, and exposed to reactive deposition gas in order to build the coating layer (this step is often repeated to achieve a specified thickness). Process parameters are selected so that the exposure time to the gas is sufficient to coat all pathways and orifi of the component while minimizing the production of particulate. The process can take upwards of several hours to build an appropriate layer, but the batch nature of the process reactor allows for per piece economies to be maintained.

The thermal CVD deposition creates a surface coating that is molecularly bound to the substrate. CVD coatings have also shown improved adhesive strength over other deposition

techniques¹¹. It has also been reported that adhesion issues with fluoropolymer coatings (PTFE or PFA) and ceramic coatings can lead to fracture of the coating if the substrate is bent or flexed¹². Many components used in semiconductor equipment require bending or flexing and the use of an amorphous coating with strong adhesion may offer a benefit.

B. Coating Composition

Depositing onto metal surfaces at high temperatures can create concerns of metal diffusion into the coating layer. As can be seen in the Auger Electron Spectroscopy (AES), metals are not detected within the bulk of the coating layer (Figure 1). The layer of a-Si:H is naturally inert to a variety of chemical compounds.

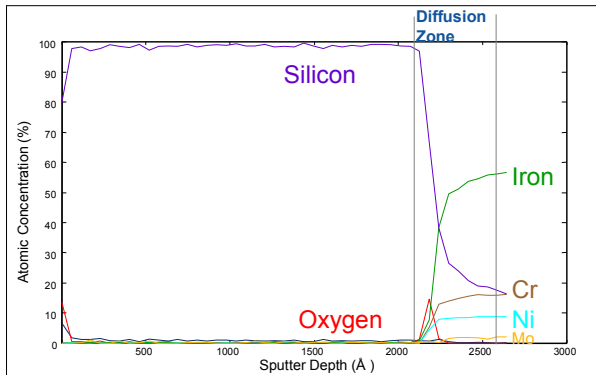


Figure 1: Auger depth profile of amorphous silicon (a-Si:H) coating on stainless steel substrate.

Deposition thicknesses may range from 200-2000 nm depending on the needs of the application. The deposited a-Si:H base layer provides flexibility for further processing as well. The layer can be treated to add non-polymeric, covalently bonded functionalization (C₂H₄ or similar) which can provide non-wetting, low stiction, or other surface properties specific to the application.¹³ The base coating layer is typically sufficient in semiconductor manufacturing applications and often preferred due to its inert silicon-only structure.

C. Coating Properties and Material Selection

Selection of coatings and surface treatments in semiconductor manufacturing applications is typically derived from a function of performance and process compatibility. High performance alloys such as Hastelloy® or Inconel® may provide superior corrosion protection in some environments but they are often prohibitively expensive and difficult to machine. Common surface treatments like PTFE or yttria-based coatings can be prone to physical damage that often leads to costly failures from particulate contamination. Besides the superalloy materials, other steel alloys or pure metals can succumb to aggressive etch chemistries and also present additional fabrication challenges.

The silicon coatings create molecular bonds to the substrate material (gas flow weldment, exhaust bellows, etc.). This coating provides a barrier between the process stream and the mechanical equipment to minimize or eliminate corrosion, metal ion contamination, and outgassing by reducing the ability for process gases (or vacuum) to react with free iron or other elements on the substrate. Amorphous silicon coatings deposited by industrial, thermal CVD improves surface properties without negatively affecting the mechanical properties or tolerances of the substrate materials or work pieces. This feature allows tool manufacturers to utilize the coating to derive benefits such as extending preventative maintenance (PM) intervals or increasing the mean time between failures without the need to redesign or reformat critical components. Table 1 compares some of the physical characteristics of common coating materials in etch applications.

Table 1: Physical Properties of common surface treatments used in semiconductor manufacturing

Property	a-Si ¹⁴	Yttria ^{15,16}	PTFE ¹⁴
Maximum temp.	1400° C	1800° C	260° C
Low pH limit	0	2	0
High pH limit	7	13	14
Thickness	0.5 μm	0.5 μm	25 μm
Adhesion/Flexibility ¹²	Very Good	Poor	Poor

A stainless steel surface coated with a-Si:H performs similarly to exotic alloys in several corrosive applications. Figure 2 illustrates the performance of amorphous silicon-coated 316L stainless steel in 6M HCl for 24 hours at room temperature compared to that of common high performance alloys. Dursan® is a methyl-silane functionalized silicon oxide coating deposited by MOCVD-like process. The coated stainless steel outperforms the more expensive Monel and Inconel materials.

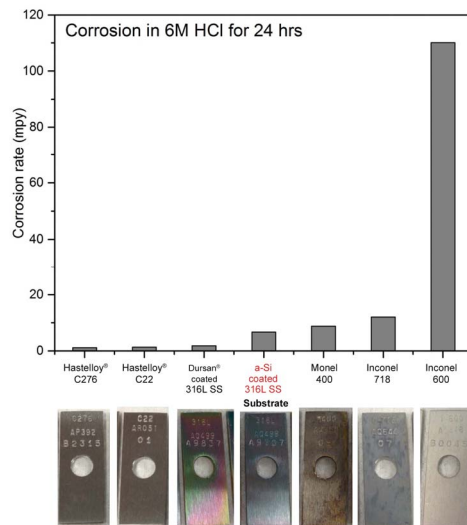


Figure 2: Comparative corrosion performance of high-performance alloys vs. coated 316L stainless steel

III. EXPERIMENTAL PROCEDURE

HCl Immersion (ASTM G31-12a)¹⁷

Corrosion coupons were immersed in hydrochloric acid (6 M, 18-20%) at room temperature for 24 hours. Additional coupons were subjected to similar, higher temperature exposure testing using 6 M acid at 50° C for 7 hours. Coupons were weighed prior to exposure to the acid solutions. Following exposure, coated and uncoated coupons (316L stainless steel) were removed from the solutions, rinsed and sonicated in DI water to remove corrosion by-products, dried, and weighed to obtain a mass loss which is used to calculate the corrosion rate in mils per year (mpy).

HBr Immersion (ASTM G31)¹⁷

Hydrobromic acid immersion was completed at room temperature in 6 M acid for 72 hours. As described above, 316L stainless steel corrosion coupons were massed and exposed to the acid. Following the same cleaning procedure, a post-exposure mass was obtained and the corrosion rate was calculated.

IV. RESULTS

Corrosion rates measured in material loss provide a reasonable approach for evaluating the corrosion resistance or expected lifetime of the material. These corrosion rates are calculated and compared for both a-Si:H coated and bare 316L stainless steel corrosion coupon samples exposed for 24 hours to a room temperature 6 M solution of HCl. Figure 5 (a) below shows the average corrosion rates and demonstrates a 30x improvement with the a-Si:H coating. The visual differences can be seen in Figure 5 (b).

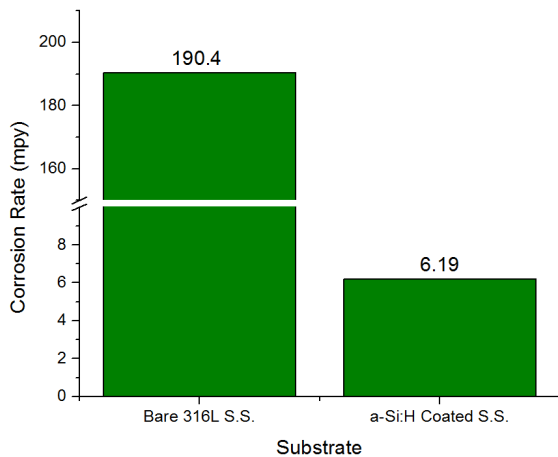


Figure 5(a): Corrosion rates of bare 316L and a-Si:H-coated 316L corrosion coupons after 24 hour exposure to 6 M HCl at room temperature.

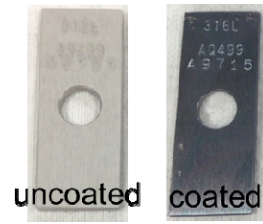


Figure 5(b): Visual degradation of 316L stainless steel sample coupons after 24 hour exposure to 6 M HCl at room temperature

Approximating the conditions of a plasma etch chamber is difficult at best. Using the ASTM G31 standard and looking at variants could provide a perspective with which to approximate the usefulness of coatings in the aggressive etch environment. Testing at elevated temperature (increasing the aggressiveness of the environment) demonstrates a continued improvement offered by the coating with exposure to 6 M HCl. Figure 6 displays a coated piece continuing to offer 30x better corrosion resistance than uncoated stainless steel. As the environment becomes more aggressive, the benefit of the coating begins to diminish. As the temperature goes from 50° C to 80° C, the corrosion rates continue to rise to a point where the bare stainless steel corrodes at a rate of about 2x as quickly as the a-Si:H coated steel.

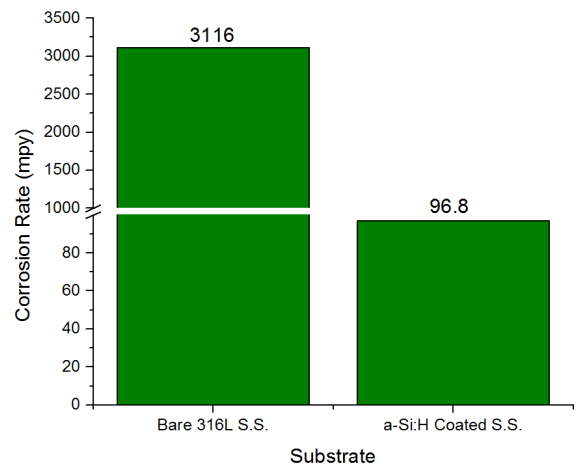


Figure 6: Corrosion rates of bare 316L and a-Si:H-coated 316L after 7 hour exposure to 6 M HCl at 50° C

Hydrogen bromide (HBr) is widely used in semiconductor etch processes. Using ASTM G31-type techniques as a way to approximate the usefulness of coatings in HBr applications can also be quite useful. Samples were measured after 72 hours of exposure to 6 M hydrobromic acid (HBr gas dissolved in water). The 316L stainless steel performed very well with only a 3.39 mpy corrosion rate while the a-Si:H coated samples performed better (0.67 mpy) which implies that corrosion products would be less likely to potentially contaminate process streams. Figures 7(a) and 7(b) illustrate

the a-SiH coating's performance compared to untreated 316L stainless steel.

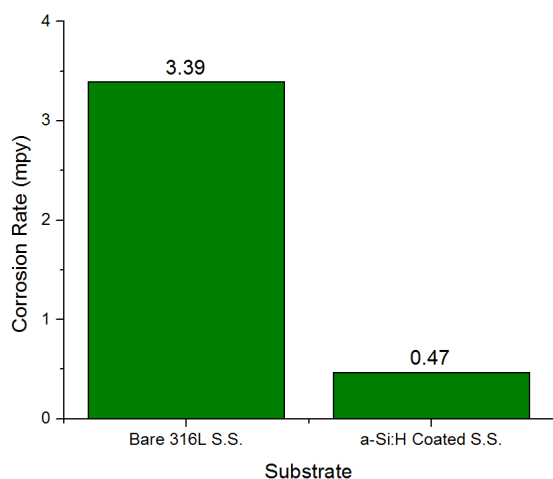


Figure 7(a) - Corrosion rate after 72 hour exposure to 6 M HBr at room temperature

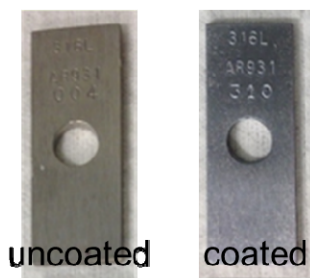


Figure 7(b) – 316L stainless steel sample coupons after 72 hour exposure to 6 M HBr at room temperature

If we assume, for example, that the corrosion rate of uncoated 316L stainless steel in HBr solution approximates 3000 RF hours of uptime, the a-Si:H coated part would allow over 23,000 RF hours before failure. While this may not be a perfect calculation, it is enough to suggest the a-Si:H would stop metal ion leeching over a wide range of conditions.

V. CONCLUSION

Coating critical process flow paths of semiconductor manufacturing equipment reduces failures related to corrosion and contamination which can lead to higher uptime and increased yields. As the industry continues scaling down to 10 nm and smaller nodes, inert, high-purity surfaces become an essential element of the production line. Thermal chemical vapor-deposited amorphous, hydrogenated silicon coatings provide a versatile material solution that inhibits corrosion and provides a higher degree of mechanical flexibility than alternative surface treatments while allowing equipment manufacturers to use preferred and affordable materials of construction.

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