

# Anti-Fouling CVD Coatings and Surface Modifications for Industrial Applications

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## ABSTRACT

Academia has witnessed a surge in novel coating materials and methods to control the behavior of surfaces in a variety of applications, specifically where non-stick properties (low surface energy) are desired. However, few of these innovative technologies have been adapted by industry, either due to scale, performance, or cost.

This paper will introduce a fluoro-functionalized surface modification that is applied by thermal chemical vapor deposition, or CVD [1,2]. This surface modification can be applied directly to substrates including stainless steel, aluminum, glass, ceramics, brass, diamond-like carbon (DLC), and more. In addition, this paper will demonstrate how the same modification can be applied as a functionalization layer onto an existing silicon, oxygen, carbon coating which is also applied by CVD. By using a vacuum thermal process instead of dip, spray, or line-of-sight methods, the CVD surface treatment lends itself to ease of processing, high volume scale-up, and uniform deposition onto complex components with narrow internal cavities, high aspect ratio features, and blind holes. Unlike solvent-based or polymeric treatments, the molecularly-bonded CVD treatment can be flexed without risk of flaking or damage.

After an introduction to the surface modification and coating's compositions and deposition process, data will be presented to illustrate their performance. Real-world applications will be discussed and comparisons will be made to other low-energy surfaces and coatings.

**Keywords:** coatings, hydrophobicity, oleophobicity, surface energy

## 1 INTRODUCTION

Surface fouling is problematic in many applications. For example, the adhesion of carbon - a phenomenon known as "coking" - onto fuel injectors prevents efficient distribution of gasoline for optimal combustion, hindering performance, efficiency, and increasing maintenance costs. Other applications for low energy surfaces include sampling of bio matter, trace-level analysis of reactive process pollutants, or other scenarios where material that is stuck to the substrate causes downtime for cleaning and/or system re-calibration purposes.

Although substrates like stainless steel and aluminum alloys are highly favorable materials of construction in many industries, both are prone to these undesired adsorption effects. Coupled with an all-embracing demand

for less maintenance, higher efficiency, and more uptime, there is now an overwhelming need for anti-fouling technology that improves how substrate materials behave in the presence of highly reactive or otherwise challenging media. As is always the case with coatings and surface treatments in general, a single solution is difficult to find. However, pairing the performance of a low energy coating with the scalability and flexibility of a CVD process provides favorable surface performance while meeting production demands.

## 2 DISCUSSION

Numerous options exist for low energy surface treatments, but there are distinct advantages to utilizing fluorocarbon-functionalized films applied via CVD. This material composition offers omniphobic properties while the deposition process is ideal for treating parts with complex geometries and narrow passageways, an especially useful feature in automotive or process instrumentation applications.

### 2.1 Coating Composition

The deposition process entails a thermal decomposition and reaction of gas-phase precursors to form the base coating layer of elemental silicon, oxygen, and carbon, which is naturally inert to a variety of chemical compounds. Further tailoring, i.e. functionalization, of the layer significantly lowers the energy at the surface such that bulk material is much less likely to be retained by the coated substrate. Instead, the material beads and does not stick to the surface.

Through secondary ion mass spectroscopy (SIMS), Figure 1 illustrates a typical depth profile of the amorphous silicon, oxygen, and carbon base layer deposition.

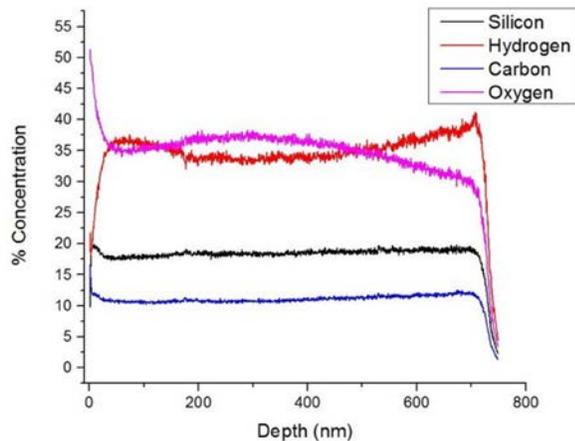


Figure 1: Secondary Ion Mass Spectroscopy (SIMS) depth profile of amorphous silicon, oxygen, and carbon coating base layer

Typical deposition thicknesses may range from 200-1000 nm; the example in Figure 1 has a surface depth of 750 nm. The elemental ratios are relatively consistent throughout the layer at 3:3:1.5:1 for Si:H:O:C. The deposited base layer is further treated to add a non-polymeric, covalently bonded fluorocarbon functionalization which provides significantly hydrophobic and oleophobic surface properties. Grazing angle FT-IR spectroscopy confirms the presence of functional C-F moieties with a strong peak at  $1250\text{cm}^{-1}$ .

It is worth noting the fundamental differences between a chemical vapor-deposited coating comprised of elemental materials and alternatives such as fluoropolymers. A compositional comparison is listed in Table 1.

Coating	Composition
PTFE or PFA	100% polytetrafluoroethylene or perfluoroalkoxyacetyl
Siloxane	polydimethylsiloxane
a-Si	amorphous silicon
a-SiOC-R; R=(C-F)	fluorocarbon-functionalized amorphous silicon

Table 1: Common commercial coatings and compositions

## 2.2 Selection of Coatings

Selection of low energy materials is most always derived from a function of performance and cost. In extreme applications such as petrochemical, the non-wetting properties of the surface are less critical than the physical capabilities; coatings must often survive temperatures in excess of  $300^\circ\text{C}$ . For more benign applications such as those in analytical laboratories, a much greater emphasis is placed on the hydrophobic and

oleophobic properties of the surface. Table 2 summarizes physical characteristics for common coatings.

Property	SiOC-R	a-Si	Siloxane	PTFE or PFA
Maximum Temp.	$450^\circ\text{C}$	$1400^\circ\text{C}$	$250^\circ\text{C}$	$260^\circ\text{C}$
10W40 Oil Contact Angle*	$96^\circ$	$15^\circ$	$20^\circ$	$49^\circ$
DI Water Contact Angle	$163^\circ$	$49^\circ$	$90^\circ$	$110^\circ$
Useable pH Range	0-14	0-7	2-7	0-14
Thickness	$1\mu\text{m}$	$1\mu\text{m}$	$1\mu\text{m}$	$25\mu\text{m}$
Adhesion	Very Good	Very Good	Good	Poor

Table 2: Physical properties of coatings  
\*120 grit; 58 rms ( $\mu\text{in.}$ ) 316 SS coupons.

Fluorocarbon-functionalized amorphous silicon coatings provide the most versatile performance and physical properties with regards to low energy surface applications. Table 3 briefly summarizes some of these typical applications and the various treatments' compatibility. This varies based on the specific application, but compatibility here considers temperature, surface energy requirements, and chemical exposure.

Coating	Auto. (Fuel Injection)	Analytical Sampling	Refining Process	Bio Diagnostics
PTFE or PFA	X	X		X
Siloxane		X	X	
a-Si		X	X	
a-SiOC-R; R=(C-F)	X	X	X	X

Table 3: Compatibility of coatings in common low surface energy applications

It is clear, then, that the specific surface energy requirements for the application must be strongly considered, but selection of materials is primarily constrained by the coating's ability to survive temperature and other physical requirements. Still, the coating/treatment deposition is a critical factor for commercial and industrial uses of low energy surfaces..

## 2.3 Chemical Vapor Deposition (CVD) Process

Treating components with amorphous silicon-based coatings via thermal CVD processing is a highly scalable and reproducible process. Parts that receive CVD coating treatment are often made from stainless steel, but the process is compatible with several other substrates, including aluminum alloys, titanium, exotic or “super” alloys, glass, brass, ceramics, and other high temperature materials.

Components are placed into a vacuum chamber which is connected to a gas source and heat source. Once vacuum is pulled, gas begins to flood the entirety of the chamber, penetrating all pathways, cavities, and holes, and depositing silicon homogeneously across the surface of the parts inside. This takes several hours and, depending on the process, will reach temperatures as high as 450° C. One version of direct substrate functionalization will not exceed 300C.

Aside from the non-line-of-sight advantages to CVD processing, the deposition creates a surface coating that is molecularly bound to the substrate. Unlike fluoropolymers such as PTFE or PFA, the coating can be bent or flexed without risk of flaking. This is a critical feature in many industrial applications, such as those under high pressures.

### 3 EXPERIMENTAL

The performance of the functionalized amorphous silicon coating deposition confirms a low energy surface with high water (avg. 115°) and hexadecane (avg. 68°) contact angles on smooth 304 SS coupons (contact angles are improved on rougher surfaces).

#### 3.1 Thermal Stability

In order to measure the stability and robustness of this surface, its resistance to thermal oxidation was examined. Coated 304 stainless steel coupons with a smooth mirror finish were placed in a chamber and heated in the presence of process gases for set periods of time. The coupons were then cooled, and contact angles were tested to measure any oxidative reduction in hydrophobicity or oleophobicity.

Figure 2 illustrates the variation of hydrophobicity after total thermal oxidative exposure periods of 30, 60, and 90 minutes at two different temperatures (350° C and 450° C).

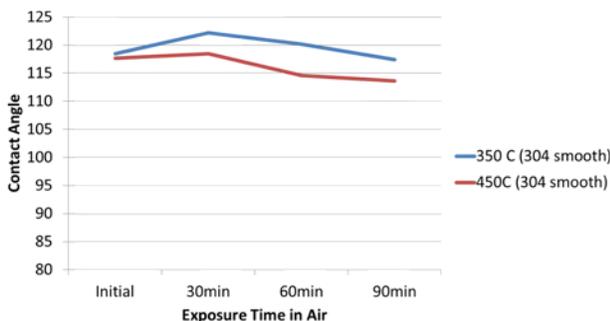


Figure 2: Thermal oxidative stability of fluorocarbon-functionalized amorphous silicon-based coating measured via water contact angle

Figure 3 illustrates the same coated coupons, but tested for oleophobicity via hexadecane contact angle. The short-term thermal oxidative stability is well illustrated in these figures i.e. the surface is highly stable at 350° C, but shows degradation at 450° C via a decrease in hexadecane contact angle after 30 minutes of exposure.

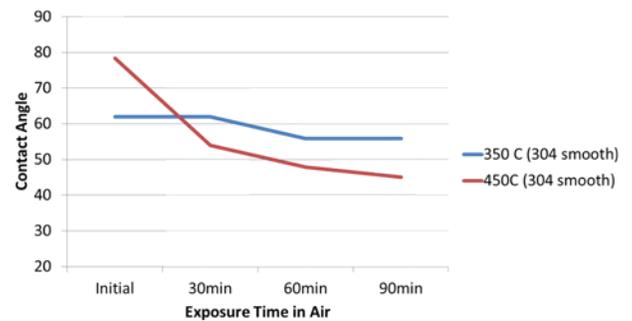


Figure 3: Thermal oxidative stability of fluorocarbon-functionalized amorphous silicon-based coating measured via hexadecane contact angle

Figure 4 highlights a longer-term evaluation of the coating’s stability at high temperatures. Both the DI water and hexadecane contact angles remain extremely stable over 20 hours at 300° C in air.

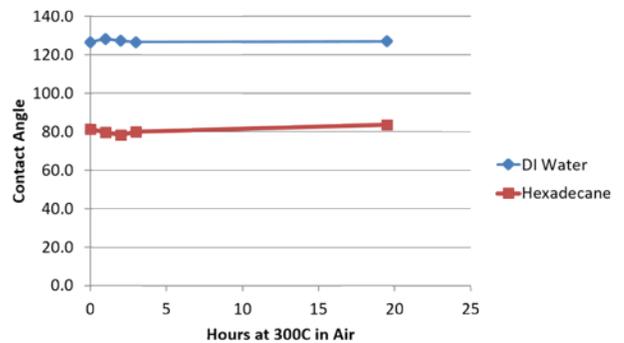


Figure 3: Thermal oxidative stability of fluorocarbon-functionalized amorphous silicon-based coating over 20 hours at 300° C in air

The nature of this thermal-only CVD process well-lends itself to bulk processing and scale-up as the uniform distribution of thermal energy is a simpler task than for that of plasma energy. This has been demonstrated by processing several three dimensional parts simultaneously in one reaction vessel. A drawback to this approach is that

the relatively high processing temperatures (450° C maximum) eliminates the use of substrates such as plastics, fabrics, polymers and other low melting or outgassing materials.

## 4 CONCLUSION

Today, coatings and other surface treatments are well-accepted means of improving the anti-fouling properties of stainless steel, aluminum, and several other materials in a variety of applications. While basic substrate selection may suffice in some instances, the demand for low surface energy materials is growing as more and more learn about the benefits these treatments can offer.

Many solutions exist for low energy surfaces, but depositing fluorocarbon-functionalized and silicon-based coatings onto industrial and laboratory componentry via chemical vapor deposition (CVD) combines advanced processing capabilities with high performance surface characteristics. The CVD process is highly robust, reproducible and scalable based on commercial requirements.

## REFERENCES

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