

# Plasma Polymerization: For Industrial Production

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Film thickness

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## ABSTRACT

Environmental protection laws these days require industries to reduce or eliminate volatile organic compounds (VOCs), which are the byproduct of curing liquid topcoats. Keeping this need in mind, an in chamber topcoat process is developed for sputter coated aluminium headlight reflectors which meets performance specifications of the automotive manufacturers.

Gaseous vapors of liquid hexamethyldisiloxane (HMDSO) are introduced into a vacuum chamber for plasma polymerization. A 40 kHz power supply is used to generate plasma. The process is optimized for system pressure, pumping speed, system configuration, substrate fixturing, size of electrodes, substrate preparation etc.

Corrosion testing was done with 1% potassium hydroxide solution. Other tests performed include 240 hrs humidity test and 24 hrs water immersion test. X-ray photoelectron spectroscopic (XPS) analysis of polymerized film showed presence of silicon, carbon and oxygen in ratios different from the monomer confirming the cross linking.

The plasma polymerized organo-silicon films are hydrophobic and relatively pinhole free. They provide a good functional coating on any vacuum metallized surface without the environmental concerns of VOCs.

## INTRODUCTION

Plasma polymerized organic films were considered undesirable byproducts in the 1930s [1] but have gained much popularity since then. Silicone resins are commonly used as starting materials to produce such solid films for various applications [2].

Silicone is a general term used for a wide class of high molecular weight compounds containing silicon-oxygen network with various organic groups attached to the silicon atom. The carbon to silicon and oxygen to silicon ratios in a silicone determine the mechanical and barrier properties of the cured film [3-4]. Polymerization in a chemical vapor deposition process (CVD) requires a high substrate temperature as temperature is the source of energy to carry out chemical reactions. For polymer substrates which have low heat resistance,

plasma enhanced chemical vapor deposition (PECVD) is the desirable low temperature growth technique [5-8]. Silicone based polymer films deposited by PECVD have shown good adhesion to polymer substrates.

In PECVD, the vapors of desired ingredient are transported through glow discharge plasma, which activates the neutral atoms or molecules. The energetic electrons either ionize or excite atoms or fragment the molecules into radicals. These active species can reflect, reevaporate after a residence time, condense or nucleate on the surface in their path. They also might move on the surface before condensing depending upon energy of impinging atoms, surface temperature or binding energy between two atoms. Nucleation on the other hand, depends on surface morphology and presence of foreign atoms in surface. Nucleation can be modified by change in surface roughness, or by depositing a adhesive layer first. Growth can be vertical or lateral and on polymer substrates, due to low substrate temperature, can leave voids. The growth morphology and residual stress in the film determines its density and porosity, which in turn affects its mechanical properties and corrosion protection capability, respectively.

Last year we reported [9] a plasma polymerization process, which did not meet required end product specifications, but the process reported here gives good barrier films to specifications. Thus, an in chamber topcoat process for automobile reflectors is developed which exceeds performance requirements of manufacturers.

## EXPERIMENTAL DETAILS

Experiments were carried out in a 30" diameter cylindrical vacuum chamber. The pumping configuration included a rotary vane pump with blower for roughing and a diffusion pump for high vacuum. The chamber was pumped down to a base pressure of  $2 \times 10^{-4}$  Torr before filling up with HMDSO vapors. HMDSO was preheated to about 130°F and only vapors were drawn into the chamber. Two aluminium electrodes, one-inch diameter rods, were connected to the vacuum chamber via high voltage feedthroughs. The power for the processing was supplied by a 40 kHz AC power supply. Processing for topcoat was done through rough pumping only and the chamber pressure was monitored with compact full range gauge.

Experiments were done on both glass slides and polycarbonate plaques. Experiments were also done on automobile reflector parts, which were vacuum metallized with aluminium before in chamber topcoat. Thickness measurements were done on a profilometer and film characterization was done by XPS analysis.

Hardness testing was done using ASTM pencil scratch test and corrosion testing was done by submerging the part in 1% potassium hydroxide solution at 70°F. 2% and 10% sodium hydroxide solutions were tried also. A 24 hrs water immersion test was performed with adhesion testing at the end with ASTM tape test. A 240-hrs humidity test was also performed.

## RESULTS AND DISCUSSION

Various system configurations and processing conditions were used to optimize the present day process. Our specifications also changed from developing an in chamber protective hard clear coat to anti corrosive barrier coat.

One of the system configurations tried involved use of inductively coupled plasma (ICP) generator. ICP experiments used reactive gas nitrogen or oxygen together with HMDSO vapors. Nitrogen-ICP films were hydrophobic in nature but oxygen-ICP films were hydrophilic. Deposition rates with oxygen were lower than with nitrogen but the films did not pass either hardness or corrosion test specifications.

Another configuration involved use of rectangular copper rod electrodes. Polymer films with copper electrodes gave good results but copper electrodes got hot in continuous processing and powder deposits showed on and around the electrodes which might be due to charge concentration at corners of rectangular rods. Therefore the present day round aluminium rod electrodes were tried and results are presented in this paper.

### System Configuration

Success of PECVD applications depends greatly on reactor geometry and gas flow patterns amongst other process variables [10].

In these experiments, system configuration was optimized for monomer inlet, pumping outlet, electrode size, pumping speed, electrode placement etc. to meet coating specifications.

Pumping speed was a critical parameter in depositing a useful coating as only 10 to 50% of the monomer is utilized in a glow discharge polymerization [10, 11], the rest of the material goes down the pump. Processing was done through a mechanical pump for the same reason, as the diffusion pump will lose its efficiency if insulating material condensed on its inside walls.

Monomer inlet placed in front of the parts to be coated gave good results. The parts were rotated between capacitively coupled aluminium electrodes.

AC power input was used to eliminate frequent foil changes on electrodes, which is needed with DC processes due to non-conducting film build up on electrodes. The electrodes were used for several hours without cleaning.

Electrodes were mounted at various positions inside the vacuum chamber and deposition rate and film quality was monitored. When both electrodes were placed along the back wall, close to the diffusion pump port, the glow was mainly in the port and corrosion test done on samples was inferior. The most useful precipitation seems to be concentrated between the electrodes and the parts coated by rotating on only one side of the electrodes did not stand up to the required specifications.

Different sizes of aluminium rods were tried for electrodes (Table 1). Thinner electrodes had the glow concentrated in close proximity. The 0.75" electrodes gave brighter glow in the chamber as compared to 0.5" which is also reflected in the film thickness measurements. Distance between the two electrodes was optimized to fit the parts as electrodes too far apart gave lower deposition rates.

Table 1: Effect of electrode size on film deposition

Rod electrode diameter	0.5"	0.75"	1.0"	1.5"
Film Thickness	120 Å	150 Å	135 Å	165 Å

### Processing Conditions

Effects of process parameters on organosilicone PECVD are reported in literature [7]. Intensity of plasma depends on process pressure, discharge power, distance between electrodes, surface area of electrodes, total volume of chamber etc. Most of the precipitation or polymer film formation takes place in glow region, therefore the parts to be coated, need to be immersed in the glow.

Processing conditions for optimum corrosion protection also vary with the shape and size of part involved. Lower process pressures were needed for the monomer cloud to reach inside the parabola in a part but if process pressures were too low, the glow shifted behind the electrodes, away from the parts. Good coverage was obtained when parabola was no more than about 1.5 times deeper than its width.

Orientation of parts with respect to rotation of the fixture in the chamber made a difference in coverage also as the inside circle of the rotation travels the least distance. A low spindle speed gave a film with better corrosion protection as the part

spent more time in the glow than outside the glow. Adhesion test done after 24 hrs water immersion improved greatly with the application of an in chamber basecoat before vacuum metallizing and the topcoat.

Since polymerization is proportional to current density in space between electrodes, the power input and distance between electrodes were adjusted with respect to total volume of the chamber. The strength of electric field determines the energy content of electrons as higher energy electrons give higher fractionation, hence higher polymerization.

In these experiments the processing time of 30 to 60s produced a barrier film that met customer specified corrosion tests. Longer processing at higher HMDSO pressures produced rainbow colors in the film.

### Substrate Location

Slides were mounted facing the electric flux lines between electrodes and parallel to the flux lines. When slides were perpendicular to flux lines, they were either facing the door of the vacuum chamber or the back wall.

Slides were mounted on a fixture representing spokes of a wheel or on a disc fixture which divided the vacuum chamber in two halves. In all these configurations, film thickness was measured and corrosion testing with potassium hydroxide was done to determine optimum location and orientation of substrate.

The results showed that orientation of slides with respect to flux lines did not matter but the type of fixture used did. Also since the monomer inlet was located close to the door, slides facing door gave better results than the slides facing back wall. These results are listed in Table 2.

Table 2: Effect of substrate location on film thickness

	Facing chamber door		Facing back wall	
	Thickness	KOH tolerance	Thickness	KOH tolerance
Plate fixture	160 Å	8 min	50 Å	3 min
Spokes fixture	320 Å	10 min	200 Å	7 min

### Characterization of Films

The films were characterized for corrosion protection, chemical nature and elemental concentrations. The methods used were submerging the parts in 1% potassium hydroxide solution, 24 hrs water immersion test, 240 hrs humidity test and

XPS analysis. One or more of these tests are used by auto manufacturers as performance requirements for aluminized reflectors.

The parts were submerged in a container of 1% potassium hydroxide solution after processing and loss of aluminium was observed after 10 min. Various parts showed no loss from 15 min to 3 days.

For water immersion test (ASTM D870-97), the parts were soaked in deionized water for 24 hours and then adhesion of coating was tested by tape test (ASTM D3359-97). The water immersion test was improved by applying a plasma polymerized basecoat on parts. Plasma polymerized basecoat, just like lacquer, promotes adhesion of metal. It is reported [5] to improve the quality of sputtered aluminium also, may be by blocking outgassing from substrate. Various parts showed no loss to total loss of adhesion after 24 hrs immersion.

Samples were sent to an independent laboratory for 240 hrs humidity test and ASTM D1735-99 was followed. The chamber was set at 38° +/- 2°C, source water pH was 7 and water collection rate was set at 1 to 2 ml/hour. The results of the test on various parts are as follows:

- #1 Polycarbonate part with Al showed total loss in 24 hrs
- #2 Polycarbonate part with Al + in chamber topcoat showed about 5% loss in 240 hrs
- #3 Polycarbonate part with in chamber basecoat + Al + in chamber topcoat showed about 5% loss in 240 hrs
- #4 Polycarbonate part with lacquer basecoat + Al + in chamber topcoat showed no loss in 240 hrs

Thus, the in chamber topcoat provides adequate protection of aluminium from humidity in the environment.

The XPS analysis of the polymer film gave the following results. Samples were sputter cleaned at 1 kV Argon ion voltage and sputter etched at 5 kV argon to establish film properties at various depths. The sample showed the presence of silicon, carbon, and oxygen only throughout the film (Table 3). In our previous experiments with stainless steel magnetron, XPS analysis showed presence of Fe, Ni, Cr etc. together with Si, C, and O.

Table 3: XPS analysis of polymer film

Sputter time	Si	C	O
As received	27.8%	43.1%	29.1%
17 m	32.6%	29.8%	37.6%
27 m	34.1%	27.4%	38.5%

The plasma polymerized film seem to have an empirical formula of  $\text{SiC}_{0.8}\text{O}_{1.1}$  as compared to the empirical formula of monomer which is  $\text{SiC}_3\text{O}_{0.5}$ . The lower than one, carbon to silicon ratio, indicates some cross-linking between the monomer units, as some of the hydrocarbon groups attached to silicon may be lost during processing. The polymer film, though remains a silicon containing hydrocarbon in nature.

The peak energies in XPS spectra of the polymer film (Figure 1) also indicate it to be a silicone compound. The peak at 533 eV for oxygen is characteristic of Si-O bonds, as  $\text{SiO}_2$  has a peak at 532.9 eV, the C-peak is characteristic of  $\text{CH}_3$ -group (284 eV) and Si peak at 102.1 eV represent energies for R-Si-O type silicones, higher than 101.3 eV energy of dimethyl silicone,  $[(\text{CH}_3)_2\text{SiO}]_n$ , and lower than the 103.4 eV peak for  $\text{SiO}_2$ . During polymerization it seems that silicon preferentially attaches to oxygen and some hydrocarbon groups disintegrate.

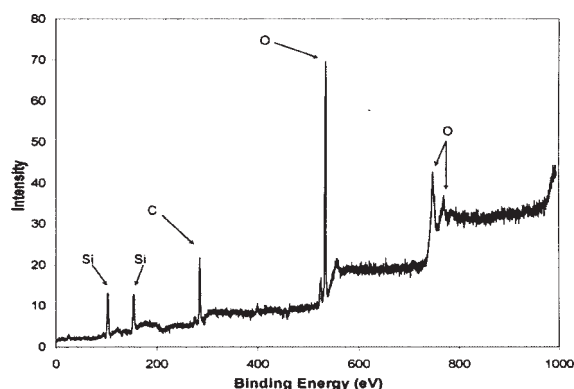


Figure 1: XPS spectra of polymer film

## CONCLUSIONS

An in chamber topcoat process is developed for automotive reflectors to provide barrier coating and corrosion protection. A production friendly compound HMDSO was used as the starting material to produce plasma polymerized films on Aluminium. Capacitively coupled electrodes were used to generate highly cross linked clear films. The films were not hard to pencil scratch test but probably, softness of film was coming from substrate. The process parameters and success of corrosion test depended on system configuration, geometry of the part and fixturing of the part. Typically 100 Å of film thickness was measured for 10 sec of processing. The parts showed no loss of aluminium in 1% potassium hydroxide solution for 15 min to 3 days. In chamber basecoat improved 24 hrs water immersion adhesion test results. XPS analysis showed that final product was not completely inorganic in nature but had some loss of hydrocarbon groups as opposed to the monomer and some Si-O bonds were formed. This in chamber topcoat process provides an environmentally friendly alternative for protection of vacuum metallized parts from corrosion.

## ACKNOWLEDGEMENT

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