EVALUATION OF PLASMA-DEPOSITED PROTECTIVE COATINGS FOR MULTIPURPOSE SPACE APPLICATIONS

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(Received March 24, 1989)

Summary

This paper reports evaluations of protective thin films applied to important polymers used on spacecraft, Kapton® polyimide and graphite–epoxy, that are attacked by atomic oxygen. These films, derived from volatile compounds through microwave glow discharge deposition, include amorphous silicon (a-Si:H) and inorganic silicon compounds (P-SiN and P-SiO$_2$). These materials are shown to provide excellent protection against atomic oxygen attack, as evidenced by the reduction in mass loss compared to unprotected specimens of the same materials after exposure to an atomic oxygen beam source. Scanning electron microscope photomicrographs are presented to confirm the lack of apparent attack of the surface. Results from high-energy (20 keV) electron beam bombardment show that these coatings reduce charge build-up which might otherwise result in electrostatic discharge phenomena. These materials provide promising candidates for coatings for exterior surfaces of spacecraft to protect the underlying materials from the deleterious effects of the space environment.

1. Introduction

Space systems operating in low Earth orbit (LEO) environment for long periods of time, such as the planned International Space Station, require materials which are stable in that environment. It is known from Shuttle flight experience that certain organic (*e.g.* polymeric) and metallic materials, used in structural and thermal protection applications, are attacked and eroded by atomic oxygen. Experience has shown that even a short-term exposure to this environment can have harmful effects on spacecraft surfaces, particularly if these are composed of or covered with organic materials [1 - 4].

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Organic polymers are important to the design of present and future genera-
tions of spacecraft, as they are used in advanced composites for structural
members, and for thermal protection in the form of films and coatings. When
organic materials are exposed to the highly oxidizing oxygen atoms, espe-
cially at the elevated velocities of spacecraft, the observed result is rapid
erosion (loss of mass) and surface roughening. This, in turn, leads to irre-
versible degradation of the physical characteristics (optical, electrical and
mechanical) for which the surface or structural members were designed.

At higher altitudes, charge build-up due to impinging electrons and ions
in the Van Allen Belts and solar wind (*e.g.* in geostationary orbit) has other
deleterious effects on insulating spacecraft materials such as organic poly-
mers. When charge build-up on an exterior surface reaches a certain critical
level, the result is surface discharge arcs or flashover, which can permanently
damage the polymer structure and integrity [5]. Furthermore, electrical
transients associated with these discharge events can perturb or destroy
electronic circuitry aboard the space vehicle. These events have been shown
to cause loss or near loss of spacecraft [6].

The present paper reports results of evaluations of thin protective
layers [7] applied to important polymers used on spacecraft: Kapton® poly-
imide and graphite–expoxy, which have been shown to be attacked by atomic
oxygen. These protective coatings, derived from volatile compounds through
microwave glow discharge, include amorphous hydrogenated silicon (a-Si:H),
and inorganic silicon compounds (silicon nitride, P-SiN; oxide, P-SiO$_2$; and
oxynitride, P-SiON). These microwave plasma-deposited coating materials
evaluated in this study provide an unique opportunity to tailor material
properties through the process parameters in the plasma reactor to meet
mission specific needs. These materials provide promising candidates for
coatings for exterior surfaces of spacecraft to protect the underlying materi-
als from the deleterious effects of the space environment.

2. Protective coatings for spacecraft materials

It is possible to apply very thin coatings onto the exposed surfaces of
organic spacecraft materials in order to protect these against the harmful
effects described above. Experiments with thin layers of polytetra-
fluoroethylene (PTFE, produced by plasma spraying) [2]; sputtered or vapour
deposited indium–tin oxide (ITO) [2]; and a SiO$_2$-polytetrafluoroethylene
(PTFE) mixture prepared by ion beam sputtering [8], have been reported by
other workers. It was found, in both ground-based laboratory and in-space
tests, that these thin protective coatings can act as barriers against oxidation
erosion of the underlying polymer.

The object of the present study was to evaluate the performance of thin
barrier coatings applied to spacecraft materials by low pressure plasma (glow
discharge) deposition (patents pending). Performance characteristics of vari-
ous coating materials were measured in a simulated space environment to

evaluate the resistance to atomic oxygen attack and electrostatic charging. Other performance characteristics including thermal radiative properties and flexibility are reported in refs. 7, 11 and 12.

The use of glow discharges for preparing thin solid films is well known [9 - 13]. A glow discharge is established in a reagent gas flow, which results in a plasma-chemical reaction leading to the desired thin film deposit. Various types of thin film coatings can be prepared, namely

(a) plasma polymers,
(b) inorganic insulating films,
(c) semiconducting and conducting materials.

In category (a), films may be derived from hydrocarbon, fluorocarbon, or organosilicon monomer compounds. Typical category (b) materials are silicon compounds such as plasma silicon dioxide (P-SiO$_2$), silicon nitride (P-SiN) or silicon oxynitride (P-SiON). These may be prepared by reacting silane (SiH$_4$) with an appropriate second gas (or mixture) such as N$_2$O, NH$_3$, N$_2$, etc. Films in category (c) include amorphous, hydrogenated silicon (a-Si:H) or germanium, prepared from SiH$_4$ and GeH$_4$ gas respectively, and metal films prepared from volatile organometallic compounds. Among the above-mentioned materials many can, in principle, provide suitable barriers except those prepared from hydrocarbon reagents which are not stable against oxygen atom attack. One of the most interesting of these materials is amorphous silicon. It has been shown that changes in the processing conditions, for example the addition of gaseous dopants like phosphine or diborane, reagent flow rate, substrate temperature, power density in the plasma and reactor pressure can very significantly alter the electrical conductivity of this material [9, 14].

A series of specimens from categories (a) to (c) was fabricated in this study. The materials, shown in Table 1, included silicon compounds, P-SiN, P-SiO$_2$, P-SiON and a-Si:H; and organosilicon (hexamethyldisiloxane, PP-HMDSO). As shown in ref. 10, all of these films can be prepared using the microwave plasma reactor as very thin, strongly adhering and pinhole-free

TABLE 1
Coatings on Kapton® polymide substrate

Specimen	Coating	Coating conditions[a]			
		T_s (°C)	SiH$_4$ (sccm)	Gas/Flow (sccm)	Thickness (μm)
1	SiO$_2$	250	8	N$_2$O/35	0.7
2	SiN	250	10	NH$_3$/35	0.5
3	a-Si:H	300	10	—	0.5
4	a-Si:H	300	8	He/35	0.5
5	a-Si:H	300	10	He/35	0.7
6	HMDSO	250	—	HMDSO/10	0.7

[a]Pressure, 100 m Torr; microwave power; 100 W.

over-coats on various substrate materials including the polymers used in the present study, as well as other polymers such as Mylar®.

A microwave plasma reactor was used to deposit the thin film materials onto Kapton® polyimide and graphite–epoxy composite specimens. Microwave power was coupled into the plasma chamber from a slow-wave applicator (periodic travelling wave structure) and the substrate holder was rotated to minimize any non-uniformities of thickness over the specimen. More details of the apparatus and the plasma coating procedures may be found in refs. 10 - 13.

3. Mass loss due to atomic oxygen exposure

Coated specimens of 13 μm aluminized Kapton® film were exposed in an atomic oxygen beam simulation facility described in detail in ref. 15. Briefly, this facility is comprised of three major components: a microwave induced plasma torch, a sampler-skimmer interface and a vacuum chamber with the associated support electronics. The plasma torch is used to generate a stream of essentially neutral oxygen atoms seeded in a helium gas carrier. The sampler–skimmer system strips off a portion of the lighter gas carrier from the plasma and produces a diverging atomic oxygen beam which is then directed into the connecting vacuum chamber. The vacuum chamber maintains candidate specimens at about 10^{-5} Torr to approximate LEO conditions. The input power to the plasma determines the energy level of the incoming atoms, which was held constant for these tests at 2.2 eV. Flux at the specimen location is determined by both input flow rate and specimen position. The flux used in these tests was approximately 8×10^{16} atoms $(cm^2 s)^{-1}$ which provides a slight acceleration factor on test time over that experienced in a nominal Shuttle orbit.

Each specimen was subjected to a fluence of approximately 3×10^{20} atoms cm^{-2}, although a second specimen coated with SiO_2 was also subjected

TABLE 2
Mass loss measurements

Specimen	Coating	Coating thickness (μm)	Fluence (atoms cm^{-2})	Mass loss (μg)
1	SiO_2	0.7	3×10^{21}	0.00 ± 0.02
1a	SiO_2	0.7	3×10^{20}	0.01 ± 0.02
2	SiN	0.5	3×10^{20}	0.02 ± 0.02
3	a-Si:H	0.5	3×10^{20}	0.00 ± 0.02
4	a-Si:H	0.5	3×10^{20}	0.04 ± 0.02
5	a-Si:H	0.7	3×10^{20}	0.04 ± 0.02
6	HMDSO	0.7	3×10^{20}	0.00 ± 0.02
Kapton® (ref)	—	—	3×10^{20}	0.43 ± 0.02

Flux $= 8 \times 10^{16}$ atoms $(cm^2 s)^{-1}$.

to a higher fluence of 3×10^{21} atoms cm^{-2}. Duplicate specimens were located inside the vacuum chamber but protected from the oxygen beam to be used as reference for mass loss measurements. Also, specimens were kept in a desiccator for 24 h prior to initial measurements. As expected, the unprotected Kapton® used as a comparative standard to flight experiment data, showed significant mass loss and visible surface change. In fact, for the 13 μm thick material used, the material over a 1 cm diameter circle in the centre of the beam was completely removed leaving only the aluminum coating on the back. However, the materials covered with all of the candidate protective coatings showed no visible signs of attack by the atomic oxygen beam. Mass loss measurements made using an electronic balance are shown in Table 2. No meaningful loss of mass was measured for any of the coating materials after exposure.

4. Surface analysis

Detailed examinations were made of the coated surfaces both before and after oxygen beam exposure using a scanning electron microscope (SEM). Photomicrographs of the surface before and after oxygen beam exposure are shown in Figs. 1, and 2 for coatings of two material types investigated.
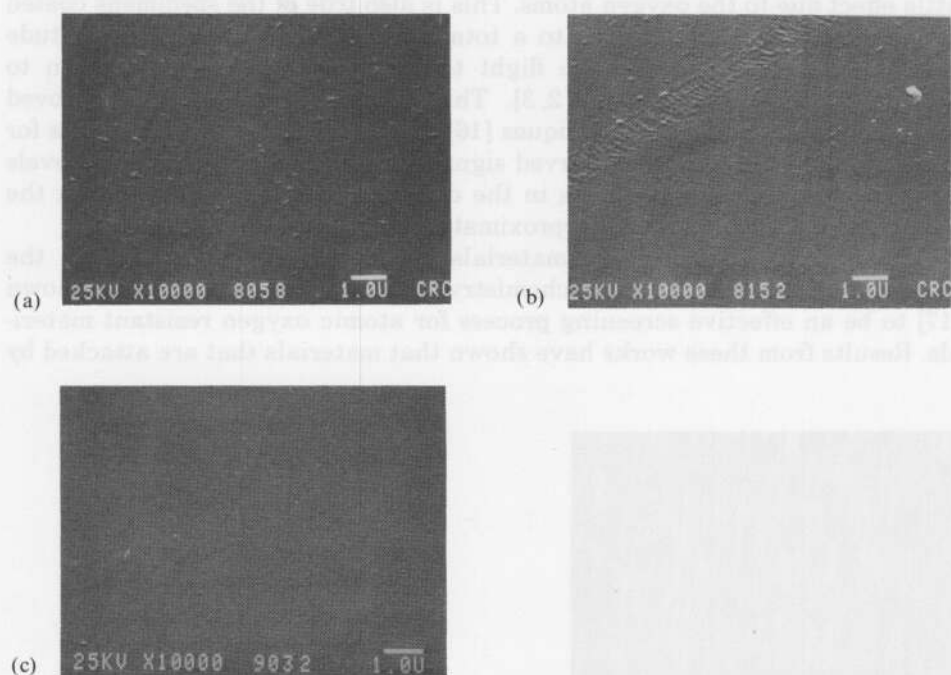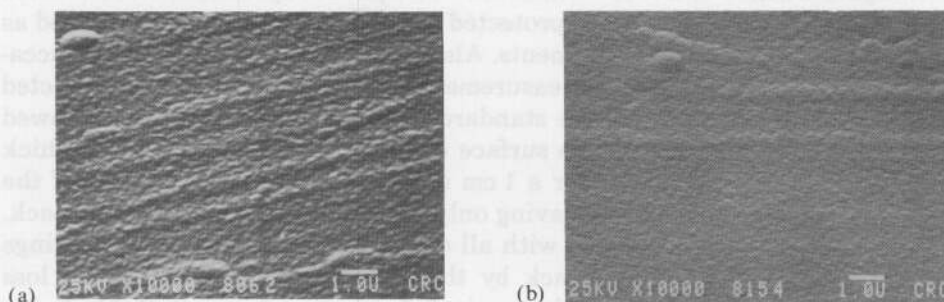

Fig. 1. SEM photomicrographs of P-SiO$_2$ coating on Kapton® before and after oxygen exposure. (a) Before oxygen beam exposure; (b) after oxygen beam exposure (3×10^{20} atoms cm^{-2}); (c) after oxygen beam exposure (3×10^{21} atoms cm^{-2}).

Fig. 2. SEM photomicrographs of PP-HMDSO coating on Kapton® before and after oxygen exposure. (a) Before oxygen beam exposure; (b) after oxygen beam exposure (3×10^{20} atoms cm^{-2}).

Photomicrographs of other materials evaluated were similar. For comparative purposes, a photomicrograph of bare Kapton® exposed in the same facility is shown in Fig. 3. As would be expected from the results of mass loss measurements, no distinguishing features were apparent that would indicate significant erosion of the surface of any of the coating materials. Rather, the surfaces before and after exposure were very similar in appearance indicating little effect due to the oxygen atoms. This is also true of the specimens coated with SiO_2 which were exposed to a total fluence of an order of magnitude greater than most past Shuttle flight test data that have been shown to severely erode this material [2, 3]. This confirms significantly improved results over other coating techniques [16] that have reported good results for lower levels of fluence but observed signs of erosion at higher fluence levels due to the presence of pin-holes in the coating. It should be noted that the thickness of the coating was approximately 0.5 - 1 μm.

The removal of organic materials by oxygen plasma is among the earliest applications of plasma chemistry. This process has also been shown [17] to be an effective screening process for atomic oxygen resistant materials. Results from these works have shown that materials that are attacked by
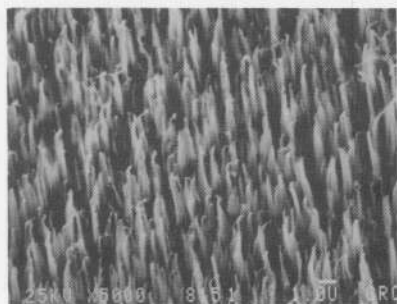

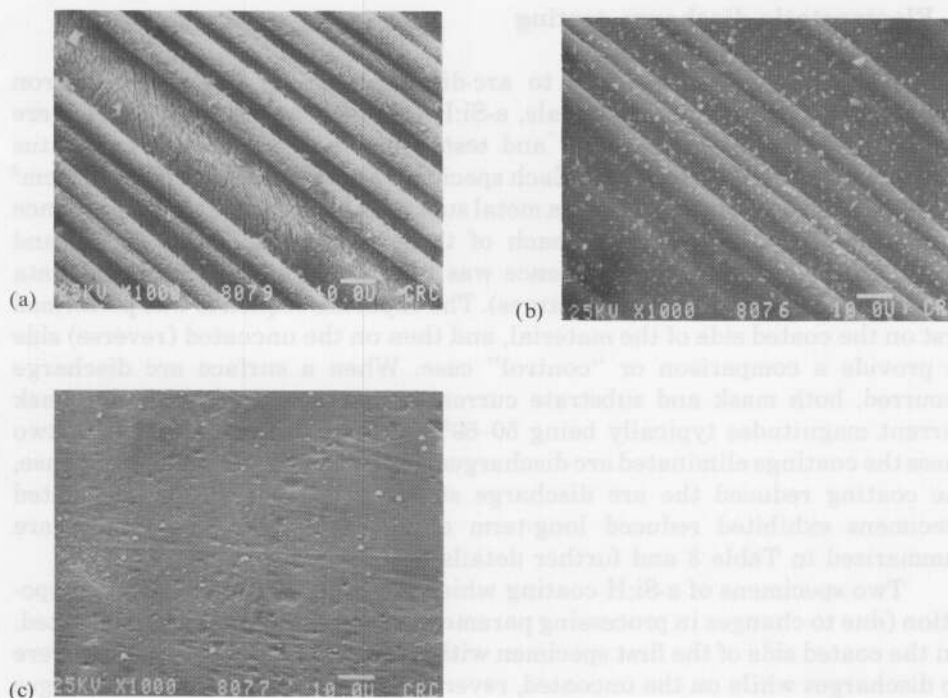Fig. 3. SEM photomicrograph of uncoated Kapton® after oxygen exposure.

(a) 25KU X1000   8079   10.0U CRC

(b) 25KU X1000   8076   10.0U CRC

(c) 25KU X1000   8077   10.0U CRC

Fig. 4. SEM photomicrographs of graphite–epoxy with and without a-Si:H coating. (a) True space exposure from STS 41-G (3×10^{20} atoms cm^{-2}) (without protective coating); (b) after oxygen plasma exposure (without protective coating); (c) after oxygen plasma exposure (with protective coating).

atomic oxygen in Shuttle flight experience, are also attacked by an oxygen plasma. Such an approach was used to evaluate a-Si:H coating for graphite–epoxy. Examinations were made of the coated surfaces both before and after oxygen plasma exposure. The latter treatment occurred in the reactor of ref. 13 using the methodology described in the same reference. SEM photomicrographs taken after oxygen plasma exposure of the surface of graphite–epoxy with and without protective coating are shown in Fig. 4 and compared to bare graphite–epoxy material exposed in space during Shuttle mission STS 41-G as part of the Advanced Composite Materials Exposure to Space Experiment (ACOMEX) [2]. The bare material from both the true space exposure (ACOMEX) and the oxygen plasma erosion are remarkably similar in appearance. The initially "smooth" epoxy surface has been eroded exposing the fibers in a "corduroy" fashion although the apparent attack on the fibers by the oxygen plasma is not as marked. Nevertheless the images confirm the use of an oxygen plasma as a screening method. In contrast, the specimen coated with a-Si:H shows no attack of the original surface of the epoxy verifying the effectiveness of the protective coating.

5. Electrostatic discharge testing

To evaluate the tendency to arc-discharge in an energetic electron environment, two coating materials, a-Si:H (two specimens) and P-SiN, were applied to 51 μm thick Kapton® and tested in an electron-beam apparatus employing 20 keV electrons [18]. Each specimen was mounted behind a 15.9 cm² aperture in a metal mask and over a metal substrate. The experimental sequence involved a 20 min exposure at each of three current densities 25, 50 and 100 nA cm⁻². This exposure sequence was terminated early if sufficient data were acquired (four or more discharges). The exposure sequence was performed first on the coated side of the material, and then on the uncoated (reverse) side to provide a comparison or "control" case. When a surface arc discharge occurred, both mask and substrate currents were measured, with the mask current magnitudes typically being 50–80% of the substrate current. In two cases the coatings eliminated arc discharges completely, while in the third case, the coating reduced the arc discharge strength by 50%. Also, the coated specimens exhibited reduced long-term charge retention. The results are summarized in Table 3 and further details are described below.

Two specimens of a-Si:H coating which were slightly different in composition (due to changes in processing parameters) and thickness were evaluated. On the coated side of the first specimen with a coating 1.0 μm thick, there were no discharges while on the uncoated, reverse side there were three discharges averaging 175 A peak substrate current. For the second specimen with an a-Si:H coating 1.5 μm thick, there were five discharges averaging 85 A when exposed on the coated side, while on the uncoated, reverse side there were six larger discharges averaging 183 A. Furthermore, the arc patterns on the uncoated side were observed to cover the entire dielectric surface exposed to the electron beam, producing the very strong arcs measured. The coated specimens tended to flatten out under the electron beam due to electrostatic attraction suggesting that some charging was occurring. However, they did not stick to the substrate upon removal from the vacuum, whereas all uncoated specimens stuck to the substrate, indicating long-term charge retention.

TABLE 3
Electrostatic discharge results

Specimen[a]	Coating	Coating thickness (μm)	Discharges	Substrate current (A)
1	a-Si:H	1.0	0	—
	reverse side	—	3	175
2	a-Si:H	1.5	5	85
	reverse side	—	6	183
3	P-SiN	0.5	0	—
	reverse side	—	4	—

[a]Kapton® substrate.

One specimen with a P-SiN coating 0.5 μm thick was tested. There were no discharges on the coated side, while on the uncoated, reverse side there were four discharges measured. Of these, peak currents over 53 A were recorded for two discharges. The coated side of the specimen exhibited a faint luminescence and tended to flatten against the substrate under the electron beam, indicating slight charging. After removal from the vacuum, the coated material showed no remaining electrostatic attraction and did not stick to the metal substrate.

6. Conclusions

Evaluation of thin barrier coatings applied to typical spacecraft polymeric materials using a microwave plasma reactor have been conducted. The coating materials have been shown to be resistant to attack by atomic oxygen while also acting to prevent charge build-up that might lead to harmful electrostatic discharge. SEM photomicrographs of the coated surfaces before and after exposure to an atomic oxygen beam source confirm that the surfaces were not attacked by the beam. In conclusion, these materials provide promising candidates for protective coatings for exterior surfaces of spacecraft to protect the underlying materials from the deleterious effects of the space environment.

Acknowledgments

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