Study on the Atomic-Oxygen-Protection Film Preparation of Organic Silicon and Its Properties

Zheng-Kuohai, Yang-Shengsheng, Li-Zhonghua, and Zhao-Lin

Abstract—Materials used on exterior spacecraft surfaces are subjected to many environmental threats which can cause degradation, atomic oxygen is one of the most threats. We prepared organic silicon atomic-oxygen-protection film using method of polymerization. This paper presented the effects on the film structure and its durability of the preparation processing, and analyzed the polymerization theory, the film structure and composition of the film. At last, we tested the film in our ground based atomic oxygen simulator, and indicated that the film worked well.

Keywords—Atomic oxygen; siloxane; protection; plasma; polymerization.

I. INTRODUCTION

ATOMIC oxygen is formed in the low Earth orbital environment (LEO) by photo dissociation of diatomic oxygen. Short wavelength (<243nm) solar radiation has sufficient energy to break the 5.12eV O_2 diatomic bond [1] in an environment where the mean free path is sufficiently long (~ 10^8 meters) that the probability of reassociation or the formation of ozone (O_3) is small. As a spacecraft orbits the Earth at velocities on the order of 7.8 km/sec, the average impact energy of arriving atomic oxygen is 4.5eV±1eV（the ram direction）and the impact energy decreases with altitude. Atomic oxygen possesses sufficient energy to break most organic polymer bonds and sufficient flux to cause oxidative erosion of the spacecraft surface materials and the properties of thermal control materials will be influenced significantly. All these effects will affect the performance of the spacecraft and its life in orbit. The erosion of the spacecraft surface materials varies with the atomic oxygen fluence, however, the fluence is determined by the altitude、attitude、the inclination、the life and the solar activities. So it is necessary to study the interaction mechanism of atomic oxygen with spacecraft surface materials in LEO, especially for the long-life vehicles, thus, we can take effective mitigative measures.

II. SAMPLE PREPARATION AND TESTING

The atomic-oxygen-protective film was prepared by self-designed co-axis cylinder RF (radio frequency) plasma polymerization device. Work gases include

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hexamethyldisiloxane (HMDSO) monomer and oxygen without argon which is often is used as carrying gas. The ratio of the work gases flow was controlled by Mass Flow Controller (MFC,Sevenstar), and the work pressure by butterfly valve. The substrate is Kapton (Dupont) with Al flim on the single face. The research focused on the influence to the film structure and properties of the process parameters such as pressure, electric power, oxygen partial pressure and the monomer transfer rate.

X-ray photoelectron spectroscopy (XPS) and infrared spectrometry were used for atomic-oxygen-protective film analysis such as the chemical structure and the contents of different elements. At last, the film was tested in grounded atomic oxygen simulator with atomic oxygen flux 5.1×1015 atoms/cm2.s and fluence 3.05×1021 atoms/cm2. The test result indicated that the film worked well.

III. INFLUENCE ON THE FILM STRUCTURE OF POLYMERIZATION PARAMETERS
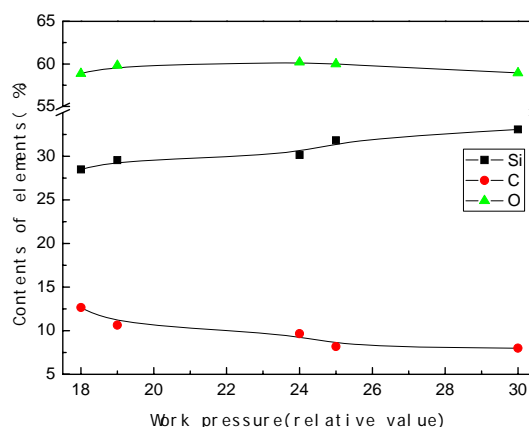

Fig. 1 Contents of elements related to work pressure

In the atomic oxygen resistant film polymerization process using HMDSO, the pressure increased in the first seconds and became stabile after that. This maybe because that the chemical bonds of the monomer were broken into various free radical, thus resulted the increased pressure; subsequently, the radicals combined into more large structure and deposited on the substrate, and the pressure decreased again, this is the so-called "pump effect"[2].

Fig. 1 gives the relation between the element contents and the pressure. From the figure, we can see that inorganic content (content of Si) of the film increased with pressure and organic content (content of C) decreased linearly, however, the content of oxygen almost keep constant. This means that the content of silicon complex such as and increases gradually with pressure.

But too high pressures maybe lead to failure of organic polymerization because of the formation of thermal plasma.
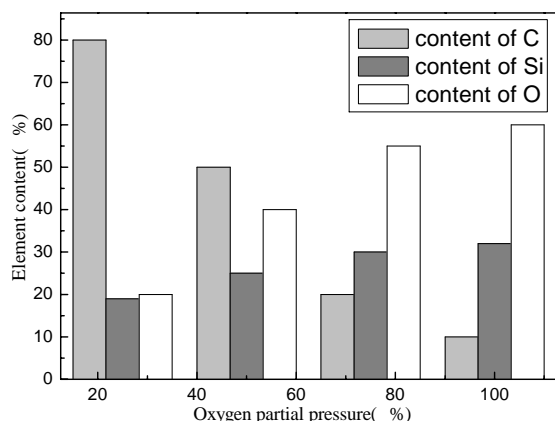

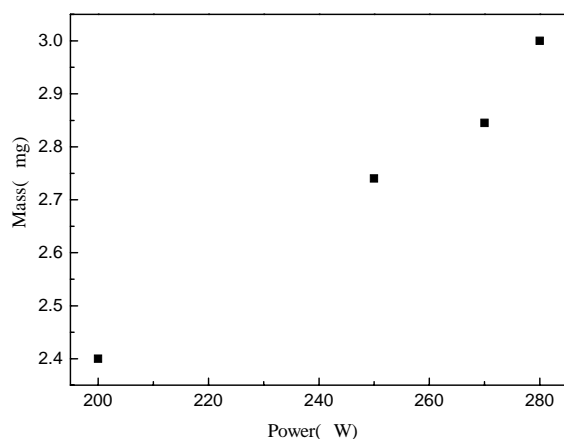Fig. 2 Element content related to oxygen partial pressure

Fig. 3 Rate of deposition related to power

As shown in Fig. 2, the organic content that is the carbon decreased rapidly with the oxygen partial pressure increase, the inorganic content that is silicon increased gradually. This is assumed that in the plasma, the monomer interacted with the oxygen plasma, and the carbon vaporized as various volatile matter, for example CO and CO_2; and the silicon retained as organic complex or SiOx (1<x<2) in the film. The deposition rate of the atomic oxygen resistant film increases linearly with the discharge power as shown in Fig. 3. The deposition time is 30 minutes.

It is reported that the plasma polymerization film is affected greatly by the temperature[3], the density at room temperature is 1.7g/cm3 and increases gradually with increasing substrate temperature, these high densities (1.98g/cm^3) indicate that when substrate temperature is above ~ 500℃, little "organic" content remain in the plasma polymers. Compared with the conventional silicon polymers (0.98g/cm^3), the plasma polymerization film is more glassy, colorless with smooth surface, lower pin hole/defect density (Fig. 4) and more chemical, mechanical and thermal stability. So by simply choosing the appropriate substrate temperature, the degree of inorganic structure can be controlled, this will be the focus of

our next work. This is also the reason we choose HMDSO as the monomer of atomic oxygen resistant film. Through the analysis, we get the polymerization parameters:

Plasma discharge power: 150~250W,

work pressure: 5~10Pa,

Polymerization time: 0.5~1 hour,

O_2/monomer: 1/3~1/1.

IV. ANALYSIS OF POLYMER FILM STRUCTURE/COMPOSITION

Fig. 5 is the structure of the HMDSO monomer. The process of the atomic oxygen resistant film is the process of the mixing of oxygen and the monomer, and the process of the radicals recombination on the substrates (Kapton) which are the pieces of the monomer in the plasma.
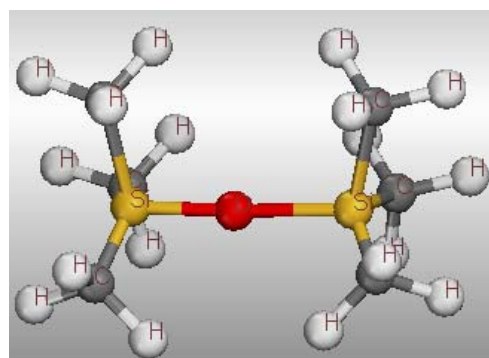

Fig. 5 Structure of HMDSO monomer

A. Infrared Spectra

The film chemical structures are documented by IR spectra (Fig. 6). As can see, there exist two absorption peak and one band:

1) 1260cm^{-1} absorption peak, attribute to the vibration of methyl group (-CH$_3$) on silicon atoms;

2) 1030cm^{-1} absorption peak, corresponding to methylene (-CH$_2$-) vibration in Si-（CH$_2$）1or2-Si groups, and overlap with Si-O-Si and Si-O-R, the result is the broaden peak;

3) 870—750cm^{-1} absorption band, attributed to -SiC- and -CH$_3$ vibrations in the silicane with different numbers of methyl groups[4]; the peak is similar with that of SiO_2.
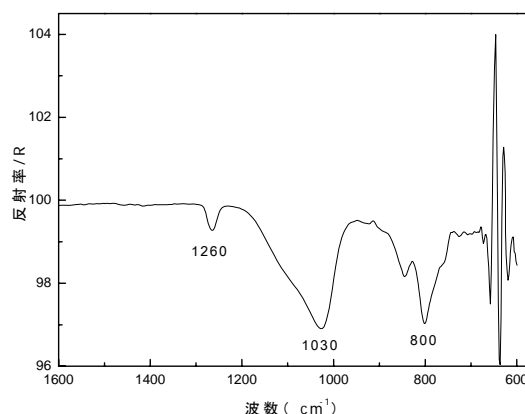

Fig. 6 IR spectra of the film

The peak at 1030cm^{-1} does not exist in the monomer, that is to say it is formed in the plasma by polymerization. And the process of polymerization is reported by A. M. Wrobel ect. as follows[3]:

$\equiv Si\text{-}CH_3 \rightarrow \equiv Si\text{-}CH_2\bullet + \bullet H$

（1）Hydrogen lost

$\equiv Si\text{-}CH_3 \rightarrow \equiv Si\bullet + \bullet\text{-}CH_3$

（2）Methyl lost

$\equiv Si\bullet + \bullet H \rightarrow \equiv Si\text{-}H$

（3）Hydrogen gathering

$\equiv Si\text{-}CH_2\bullet + \bullet Si\equiv \rightarrow \equiv Si\text{-}CH_2\text{-}Si\equiv$

（4）Polymerization

$2(\equiv Si\text{-}CH_2\bullet) \rightarrow \equiv Si\text{-}CH_2\text{-}CH_2\text{-}Si\equiv$
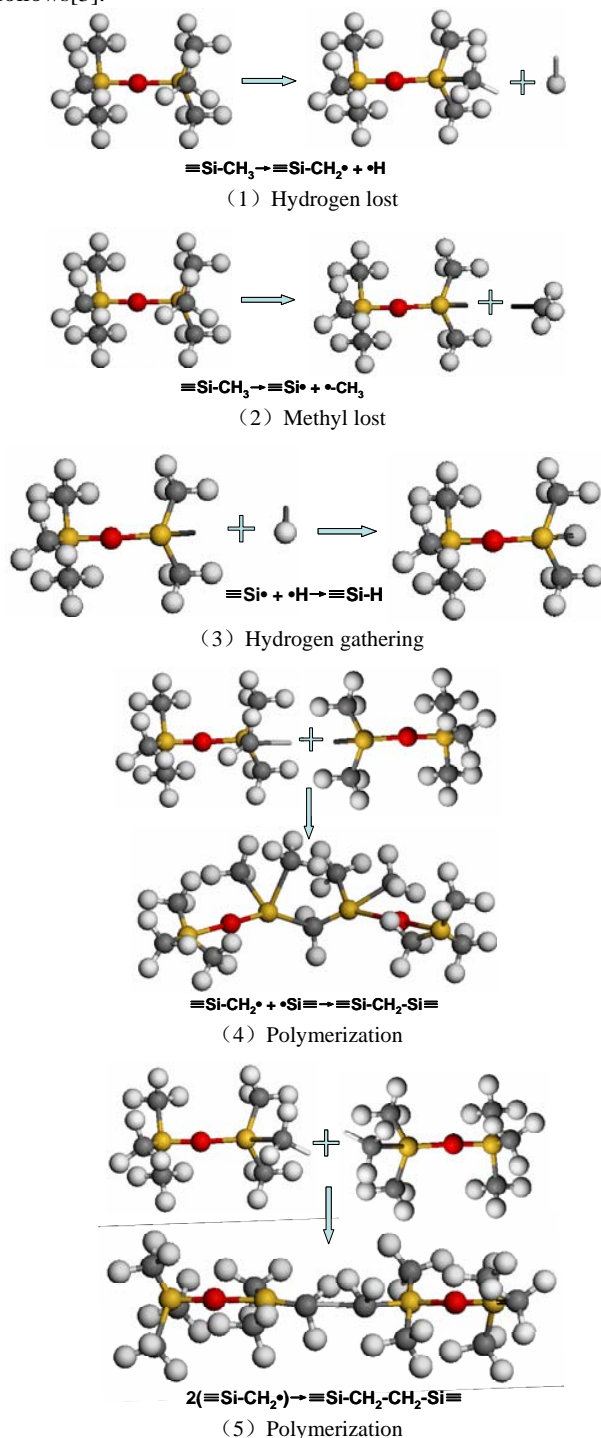
（5）Polymerization

Fig. 7 Illustration of polymerization

The Si content in the polymer film is higher than the monomer as can be inferred from Fig. 7; if oxygen flow is fed in the polymerization, the organic content would decrease obviously. In Fig. 6, absorption peak at 1030cm^{-1} become broadened and asymmetrical, all these are the characteristics of inorganic silicon complex. The asymmetry indicates that the polymers are cross-linking with high degree (Fig. 7 (4) and (5)). Although Fig. 7 (3) gives the reaction of hydrogen gathering, there is no peak of Si-H in Fig. 6, this may be due to its lower content or the poor sensitivity of the instrument.
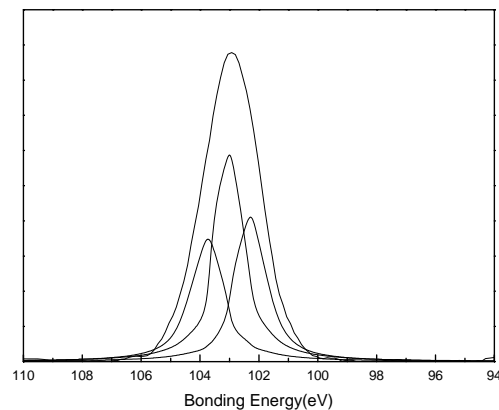
B. X-Ray Photoelectron Spectroscopy

Fig. 8 Si2P spectra of the HMDSO film

TABLE I
RESULT FROM THE SI2P SPECTRA

Si2P (eV) Binding energy	Functional group	FWHM	Peak area (%)
103.6	SiOx	1.25	33.4
102.7	$\left[Si\text{—}O\text{—}Si\right]_n$	1.03	41.3
101.7	$\text{—}CH_2\left[Si\text{—}O\text{—}Si\right]_n CH_2\text{—}$	0.84	25.3

As illustrated in Table I, there exist the functional groups such as SiOx、 $\left[Si\text{—}O\text{—}Si\right]_n$ and $\text{—}CH_2\left[Si\text{—}O\text{—}Si\right]_n CH_2\text{—}$, the inorganic content is much higher compared to the monomer, this is agreed with the result of IR spectra. The information of hydrogen can not be obtained by XPS, so the content of Si-H is uncertain.

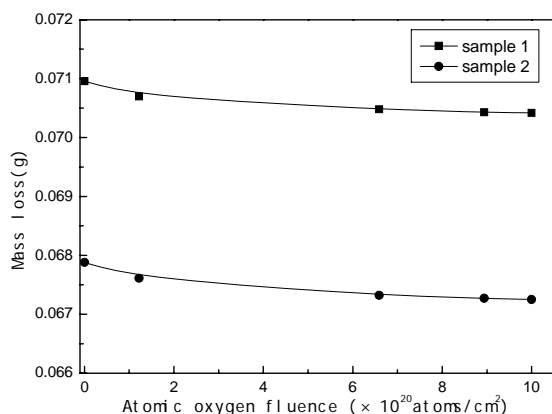V. Atomic Oxygen Testing of the Film

Fig. 9 Mass loss of the film related to atomic oxygen fluence

Fig. 9 gives the mass loss of the film in the grounded atomic oxygen environment. The thickness of sample 1 is 250nm, and sample 80nm. Like many other polymers, vacuum outgassing is the main reason of mass loss of the film in atomic oxygen environment at the first hours. The figure shows that the mass loss of sample 1 is 0.4 mg, and sample 2 is 0.6 mg; the different mass loss maybe attribute to the different thickness, sample 2 is much thiner, and the pin hole/defects density is much more higher. The control witness's mass loss is 0.4mg, this confirms that sample 1 does well in atomic oxygen environment. We can get the mass loss of uncoated Kapton using formula (1) with atomic oxygen fluence of 1×10^{21} O atoms/cm^2:

$$\Delta m = \phi \cdot A \cdot \tau \cdot d \cdot \eta$$

where：

Φ= atomic oxygen flux （atoms/cm^2.s）

A= exposure area， （cm^2）

τ= exposure time， （Sec）

d= density of the film， （g/cm^3）

η= erosion yield （cm^3/ atom）

Here, the density of Kapton is 1.42 g/cm^3, the exposure area 11.6 cm^2, and erosion yield 3.0×10^{-24} cm^3/atom. The calculating result indicates that mass loss of the uncoated Kapton will be as large as 6 mg with atomic oxygen fluence of 10^{20}O atoms/cm^2 which is much larger than mass loss of coated Kapton under atomic oxygen of 10^{21} O atoms/cm^2. This again means that the film made by polymerization as atomic oxygen resistant film is feasible.

As a normal thermal control material, Kapton is very sensitive to atomic oxygen, although the situation could be changed by cover it with resistant film, its thermal control properties should not be affected. Fig. 10 is the reflectivity of Kapton related to atomic oxygen fluence with HMDSO atomic oxygen resistant film. The reflectivity of the two samples keeps stabile. This owed to the glassy surface of various type of silicon complex.
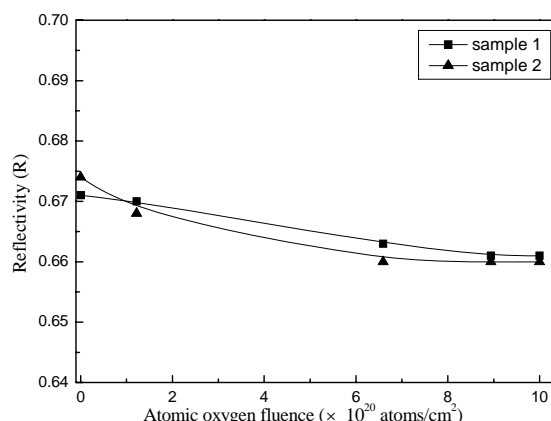

Fig. 10 Reflectivity of the film related to atomic oxygen fluence

Fig. 11 Kapton/Al (a)covered (b) uncovered

VI. Conclusion

We prepared atomic oxygen resistant film using method of plasma polymerization with the monomer HMDSO. The surface of the film is composed of SiOx, $\left[Si-O-Si\right]_n$ and $-CH_2\left[Si-O-Si\right]_nCH_2-$ which are the main reasons that the film could do well in atomic oxygen environment. The organic content increases with increasing oxygen partial pressure and discharge power. The prepared film is a good atomic oxygen resistant film with smooth, compact and almost perfect surface. Ground based atomic oxygen test indicates that the film has little affects on the optical properties of the substrates; and would be a good choice to use it as antiatomic-oxygen film.

References

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