Polymers for Space Applications Processed by Plasma Immersion Ion Implantation

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Protection of Components for Spacecrafts Orbiting LEO

Low Earth Orbit (LEO) environment (180-650 km): rich in atomic oxygen, degrades polymeric materials (like Kapton, Mylar or Teflon) used in satellites.

May erode certain polymers by over 2 µm in 90 days.

Oxygen resistant polymers could improve the lifetime of satellites and space stations and could find many applications in space, including huge fold-up antennas, inflatable mirrors & lenses, solar sails...

Kapton is extensively used in thermal blankets.

International Space Station orbiting LEO region (~450 km)
Oxidation protection: Thin layers of several metal oxides such as Al₂O₃, MgO, or SiO₂ are being studied as protective coatings for polymers in LEO

Thermal transients (-100° C to +100 ° C): Superior adhesion of the thin film is required

Plasma Immersion Ion Implantation and Deposition (PIII) of metal ions is ideal.

PIII in polymers: charging of the dielectric is proportional to plasma density

Typically for ~ 20 µm thick polymers:

- \( n \sim 10^{17} \text{ m}^{-3} \) \( \Delta V \sim 7\text{ kV} \) in 2µs
- \( n \sim 10^{15} \text{ m}^{-3} \) \( \Delta V \sim 700\text{ V} \) in 60µs
In metal plasmas generated by vacuum arcs: Magnetic field increases plasma density by two orders of magnitude.
Objectives

Aluminum implantation in Kapton® by three different methods

- Direct implantation in a magnetized Al plasma
- Direct implantation in an unmagnetized Al plasma
- Al deposition + implantation in nitrogen plasma (recoil implantation)

Resistance tests for space environment

- Oxygen degradation (oxygen plasmas)
- Thermal cycling
- Adhesion test
Direct Aluminum implantation

Experimental Set-up
Vacuum Arc:  Al cathode    Tungsten grid anode  
HV trigger : 10-13 kV

Vacuum chamber  \( \phi=0.22\text{m}, \ L=1.05\text{m} \)
Base pressure \( \sim 1\times10^{-4}\text{ Pa} \)
B field : 150G-7kG

Sample holder:  85cm from cathode

Straight magnetic filter:  not so good filtering but good plasma transport. Macroparticles avoided and deposition minimized by orienting samples parallel to plasma stream
Implantation Conditions

With $B = 125 \text{ G}$  $I_{arc} = 1 \text{kA}$
7$\mu$s pulses, 2.5 kV,
900 Hz (13-14 pulses / discharge)
100 discharges

With $B = 0$  $I_{arc} = 1 \text{kA}$
7$\mu$s pulses, 6 kV, 900 Hz
800 discharges
Recoil Aluminum implantation
200 Å, 500 Å and 2000 Å aluminum films deposited by electron beam on Kapton samples followed by

**Implantation** in **Nitrogen** (n ~ 10^{10} cm^{-3}, T_e < 10 eV) and **argon** plasmas.

**HV pulses:** 5 \mu s, 100Hz, 5 kV

**Treatment time** of 30 minutes
Analysis

Elemental composition and morphology
- RBS
- XPS
- SEM, EDS

Oxygen degradation
- Oxygen plasma: 40kHz parallel plate capacitive reactor
- 200 mTorr, 200W ($10^{10} \text{ cm}^{-3}$, 1-2 eV), ~ one hour exposure

Transmittance and Reflectance (Hitachi U-3501 spectrophotometer)

Thermal cycling
- 1 minute liquid nitrogen immersion (-196 °C)
- 1 minute pre-heated oven (100 °C)
- 15 cycles

Adhesion Test
- applying and removing a pressure sensitive tape + SEM
Results

**Oxygen Degradation**

![Graph showing oxygen degradation over exposure time. The graph plots mass (g) against exposure time (min). Three different materials are compared: Kapton untreated, Al + N₂, and Al B = 125G and Al B = 0. Each material shows a decrease in mass over time.](attachment:graph.png)
Direct Implantation in Magnetized Plasmas

RBS retained doses of $10^{16}$ atoms/cm$^2$, but mostly at the surface.
XPS ß formation of an ion mixing layer

Kapton + Al
HV=7kV
B=125Gauss

Atomic Concentration (%) vs. Sputtering Time (s)
SEM: morphology conserved after oxygen degradation, thermal cycling and adhesion tests

Pristine Kapton

After tests
Without treatment, after oxygen exposure
Transmittance decreases only by (5-15)%
Total reflectance increases

![Graph showing the total reflectance increases with wavelength for different samples. The graph plots Total Reflectance (diffuse) against Wavelength (nm). The y-axis ranges from 0.00 to 0.30, and the x-axis ranges from 200 to 800 nm. The samples compared are: B = 125 Gauss, Pristine Kapton, Kapton + Al + O, Kapton + Al + O, Kapton + Al + O, and Kapton + Al + O.]
Direct Implantation in Unmagnetized Plasmas

- Treatment time increased eightfold was not enough to compensate the plasma density decreased by two orders of magnitude without magnetic field. This resulted in **lack of uniformity**

- Treated samples had “good” and “bad” parts.

- “Good” parts behaved in the same way as samples treated in magnetized plasmas: no oxygen degradation revealed by conserved transparency, and conserved morphology after oxygen exposure, thermal cycling and adhesion tests.

- “Bad” parts behaved like untreated samples: “carpet” like morphology after oxygen exposure, loss of transparency.
Deposition and recoil implantation

- For 200 Å and 500 Å depositions (but not for 2000 Å films), nitrogen and argon implantation results in a cracked film.
Cracking of the deposited film is not caused by differences in thermal expansion since it does not occur after oven heating at 100 °C or even at 200 °C.

Immersion of the deposited samples in nitrogen or argon plasmas does not result in cracking, which occurs as soon as the high voltage pulses are turned on.

In direct implantation process, an aluminum film is also deposited without cracking, probably due to ion induced stress relief.

Cracking in recoil implantation could be related to the formation of a stressed aluminum nitride (with nitrogen plasmas) and a stressed aluminum dioxide (which occurs in argon plasmas, even with very low oxygen contamination) films, although ion induced stress relief would be expected in this case as well.

We have no conclusive explanation for the observed ion induced cracking.
Conclusions

- Kapton samples implanted with Al in a magnetized vacuum arc discharge resulted in excellent protection of the polymer against oxygen degradation.

- Retained doses of $10^{16}$ atoms/cm$^2$ was obtained, and although most of the atoms are concentrated on the surface, an intermediate ion mixing layer was formed.

- Adhesion test after thermal cycling shows good adhesion to the substrate.

- Implantation with Al in unmagnetized plasmas produces a protection layer as effective as in the magnetized case, but needs much longer treatment times, incompatible with present machine configuration.

- Al deposition by e-beam, followed by recoil implantation in nitrogen and argon plasmas resulted in a cracked film, induced by ion bombardment. No conclusive explanation has been found for this observation.