

# **Polymers for Space Applications Processed by Plasma Immersion Ion Implantation**

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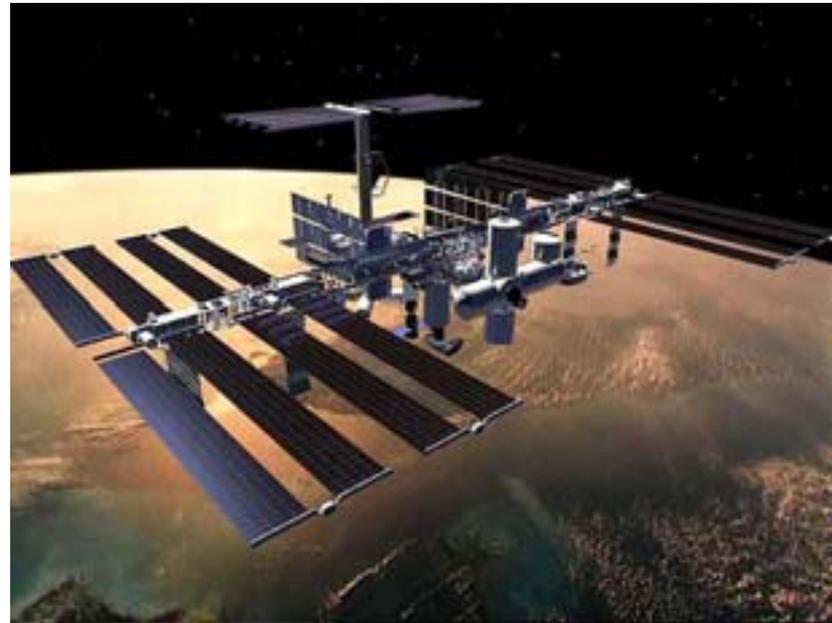
# Protection of Components for Spacecrafts Orbiting LEO

**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  $\mu\text{m}$  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  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ , or  $\text{SiO}_2$  are being studied as protective coatings for polymers in LEO

**Thermal transients** ( $-100^\circ\text{C}$  to  $+100^\circ\text{C}$ ): Superior adhesion of the thin film is required  $\emptyset$  **Plasma Immersion Ion Implantation and Deposition (PIII)** of metal ions is ideal.

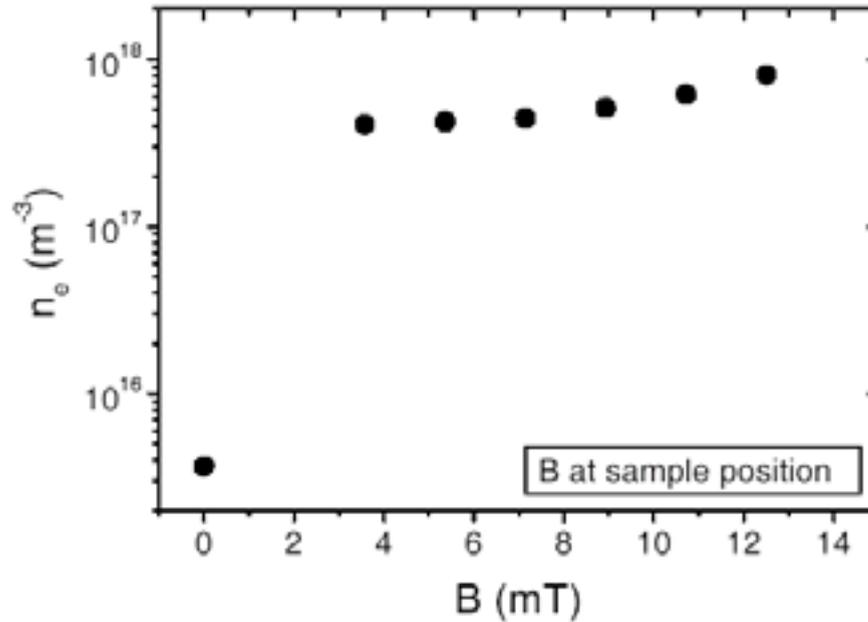
**PIII in polymers:** charging of the dielectric is proportional to plasma density

Typically for  $\sim 20\ \mu\text{m}$  thick polymers:

$n \sim 10^{17}\ \text{m}^{-3}$   $\emptyset$   $\Delta V \sim 7\text{kV}$  in  $2\ \mu\text{s}$

$n \sim 10^{15}\ \text{m}^{-3}$   $\emptyset$   $\Delta V \sim 700\text{V}$  in  $60\ \mu\text{s}$

**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**

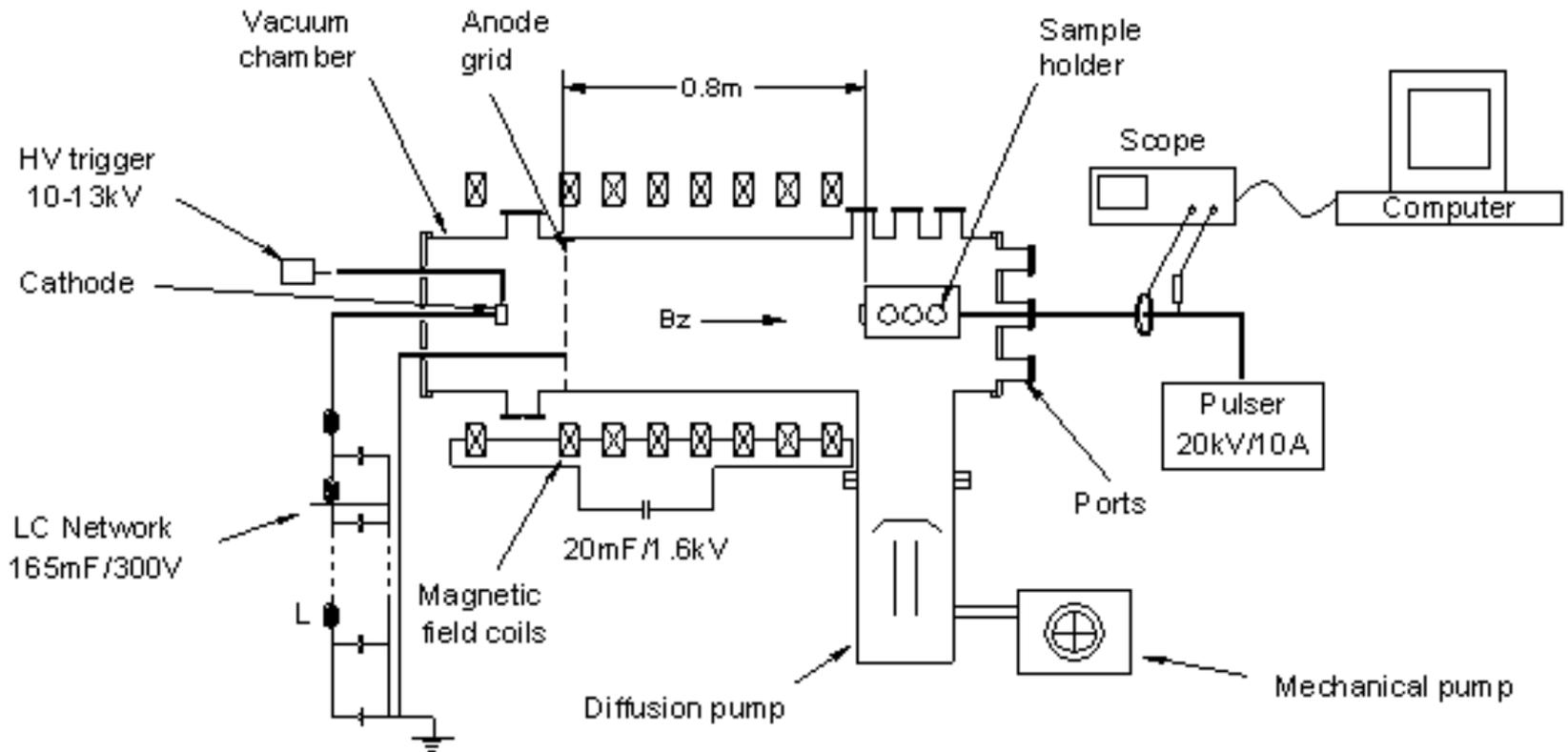
- Direct implantation in a magnetized Al plasma
- Direct implantation in an unmagnetized Al plasma
- Al deposition + implantation in nitrogen plasma (recoil implantation)

## **Resistance tests for space environment**

- Oxygen degradation (oxygen plasmas)
- Thermal cycling
- Adhesion test

# Direct Aluminum implantation

## Experimental Set-up



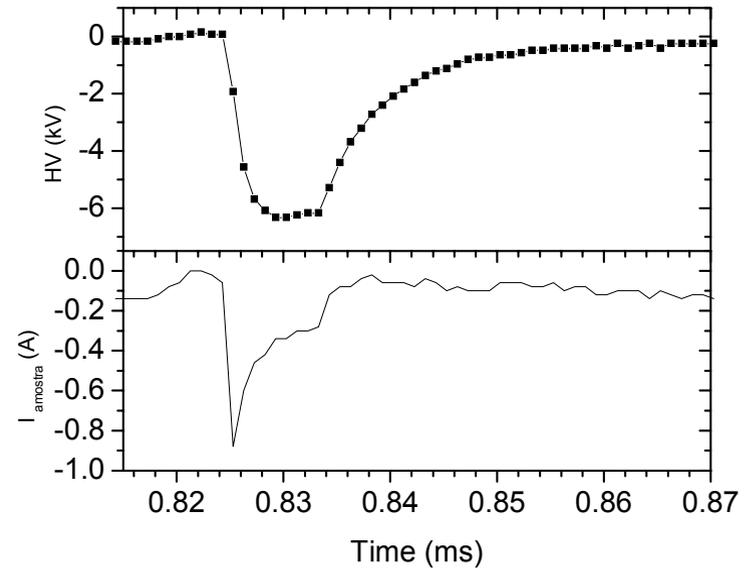
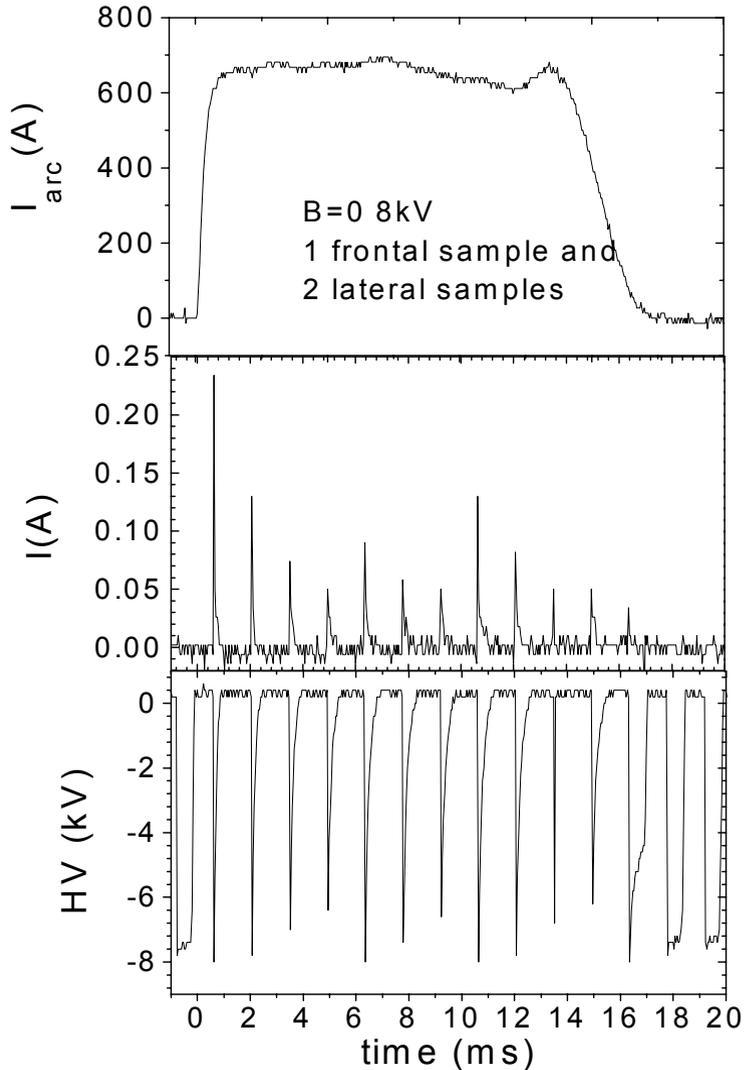
**Vacuum Arc:** Al cathode Tungsten grid anode  
HV trigger : 10-13 kV

**Vacuum chamber**  $\phi=0.22\text{m}$ ,  $L=1.05\text{m}$   
Base pressure  $\sim 1 \times 10^{-4}$  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**

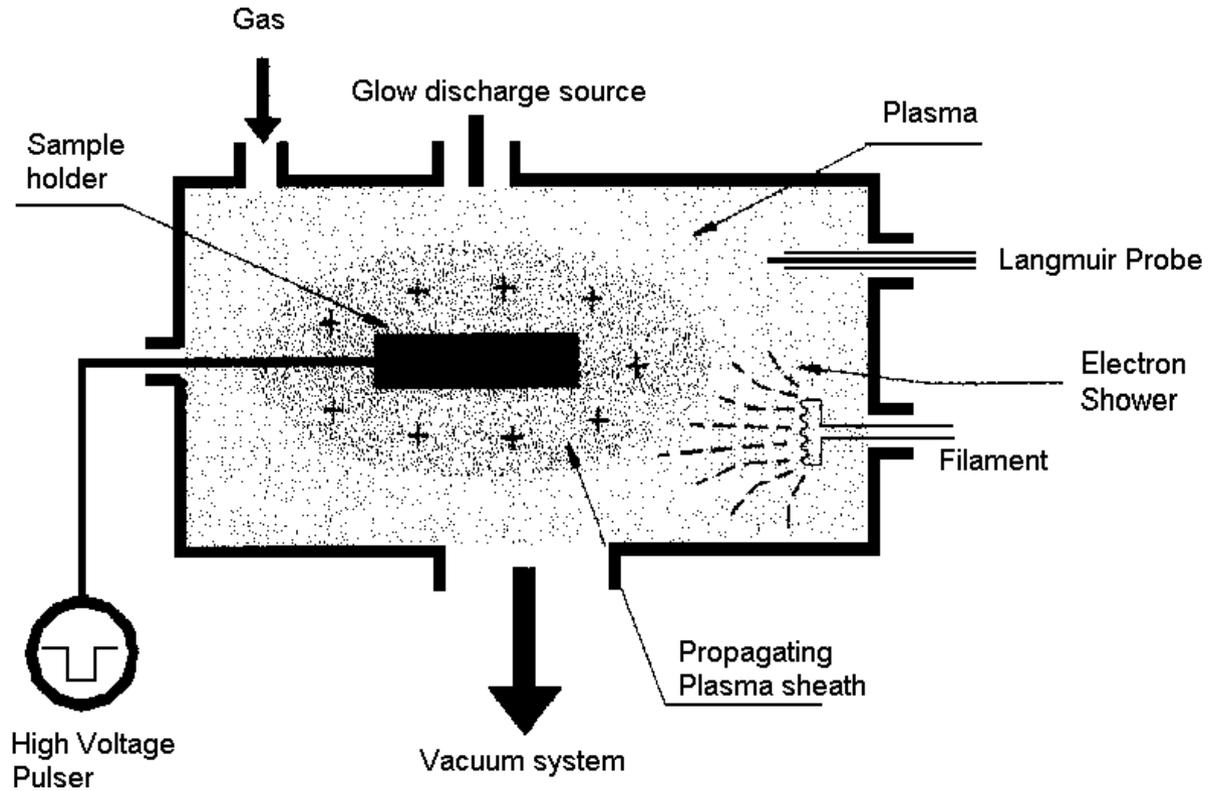
# Implantation Conditions



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

**With  $B = 0$**   $I_{\text{arc}} = 1 \text{ kA}$   
7  $\mu\text{s}$  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** ( $n \sim 10^{10} \text{ cm}^{-3}$ ,  $T_e < 10 \text{ eV}$ ) and **argon** plasmas.

**HV pulses:** 5  $\mu\text{s}$ , 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 ( $10^{10}$  cm<sup>-3</sup>, 1-2 eV), ~ one hour exposure

## Transmittance and Reflectance (Hitachi U-3501 spectrophotometer )

## Thermal cycling

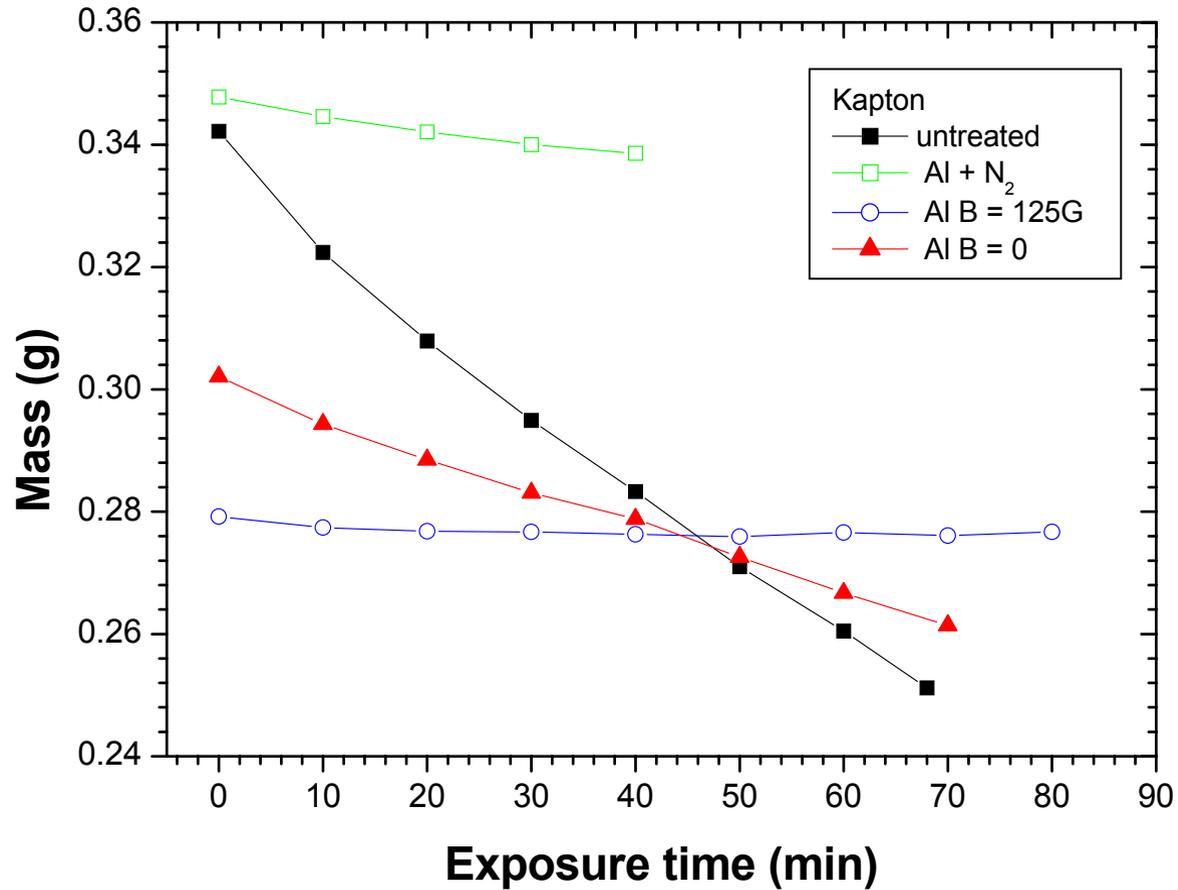
- 1 minute liquid nitrogen immersion (-196 °C )
- 1 minute pre-heated oven (100 °C)
- 15 cycles

## Adhesion Test

- applying and removing a pressure sensitive tape + SEM

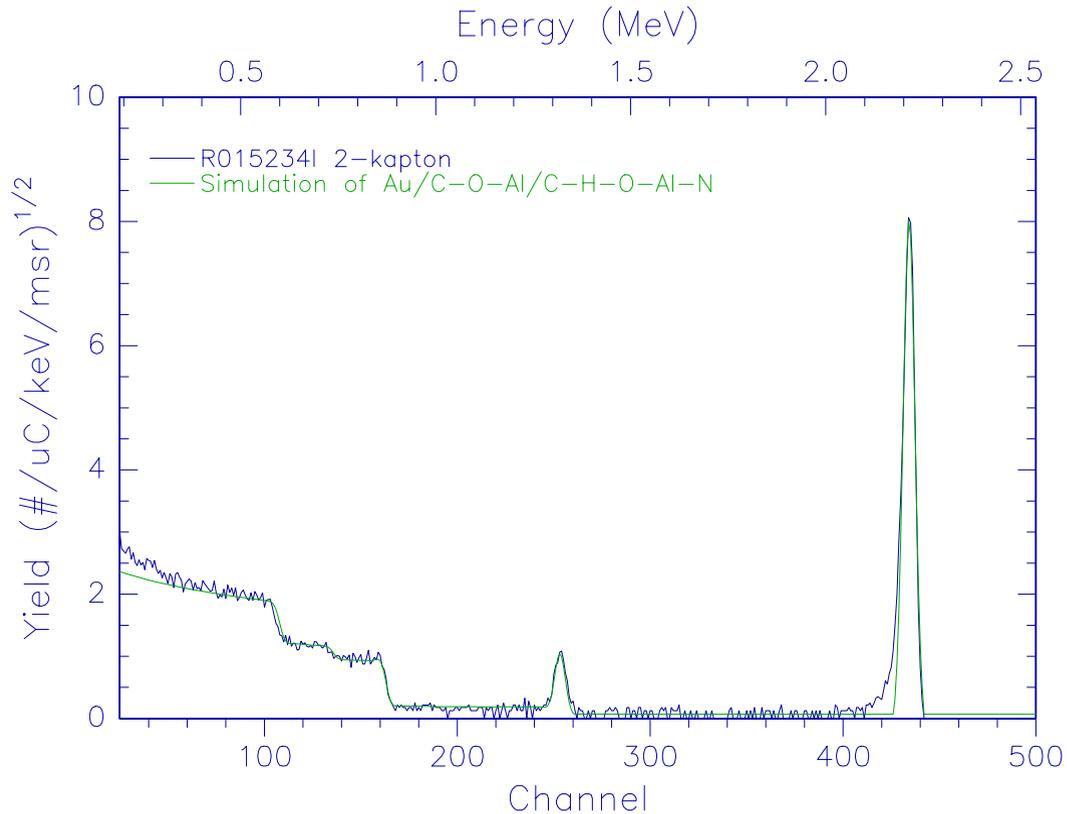
# Results

## Oxygen Degradation

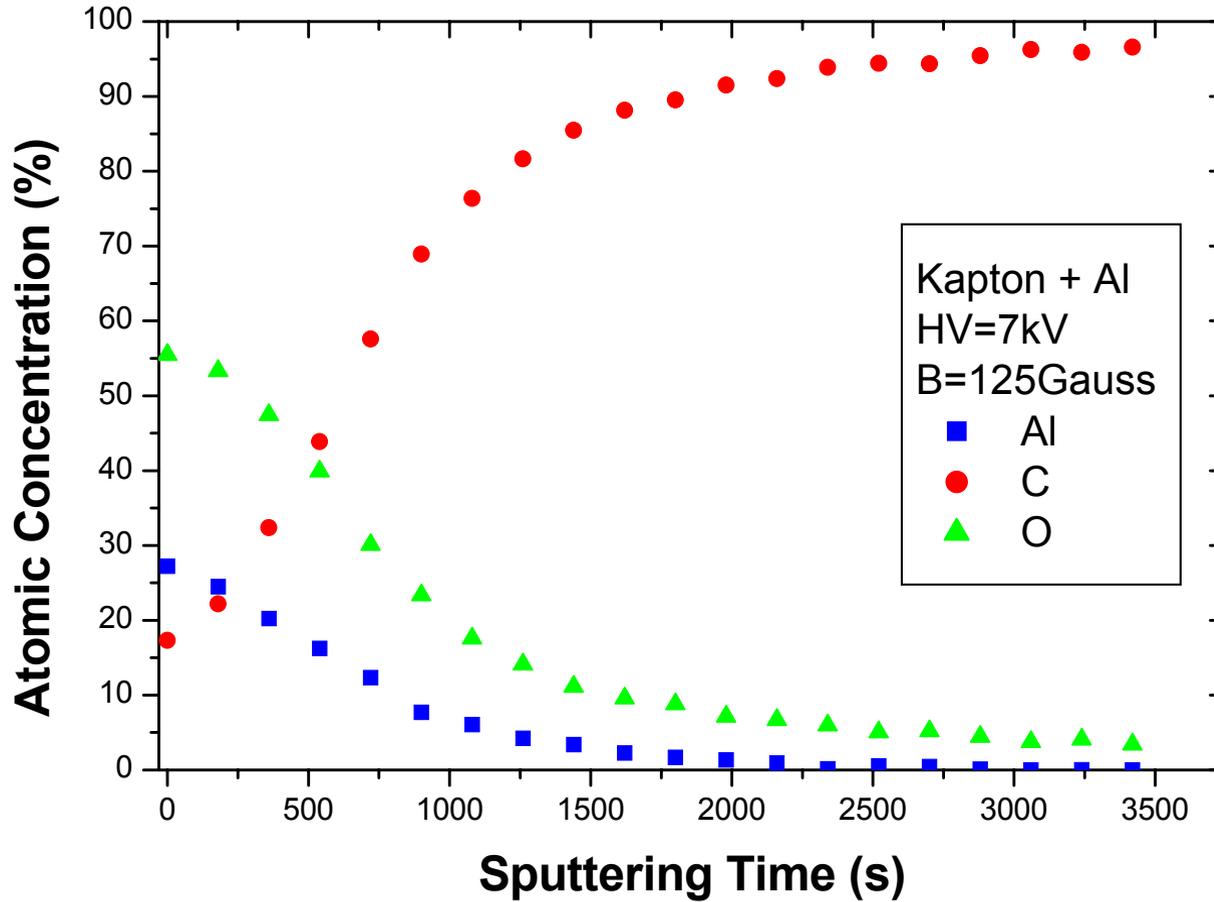


# Direct Implantation in Magnetized Plasmas

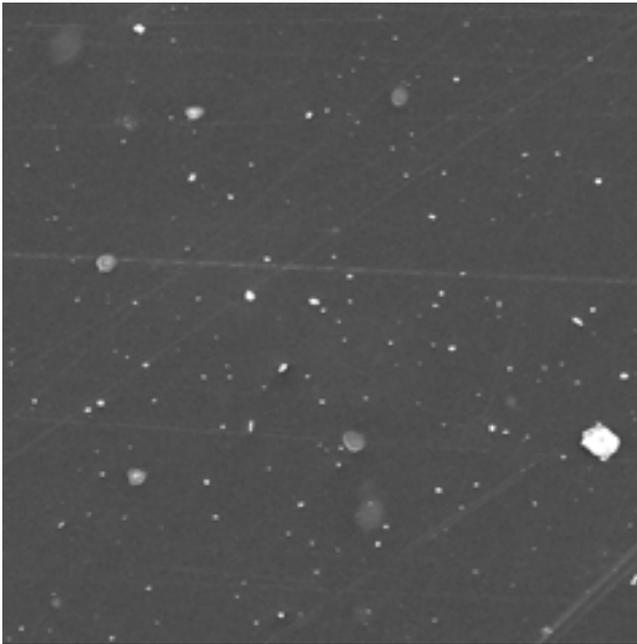
RBS  $\bar{A}$  retained doses of  $10^{16}$  atoms/cm<sup>2</sup>, but mostly at the surface



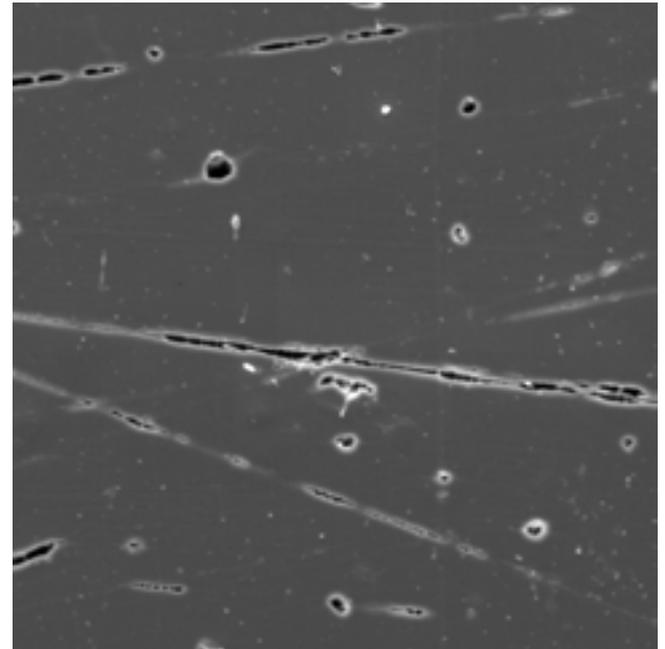
# XPS $\Delta$ formation of an ion mixing layer



**SEM : morphology conserved after oxygen degradation, thermal cycling and adhesion tests**

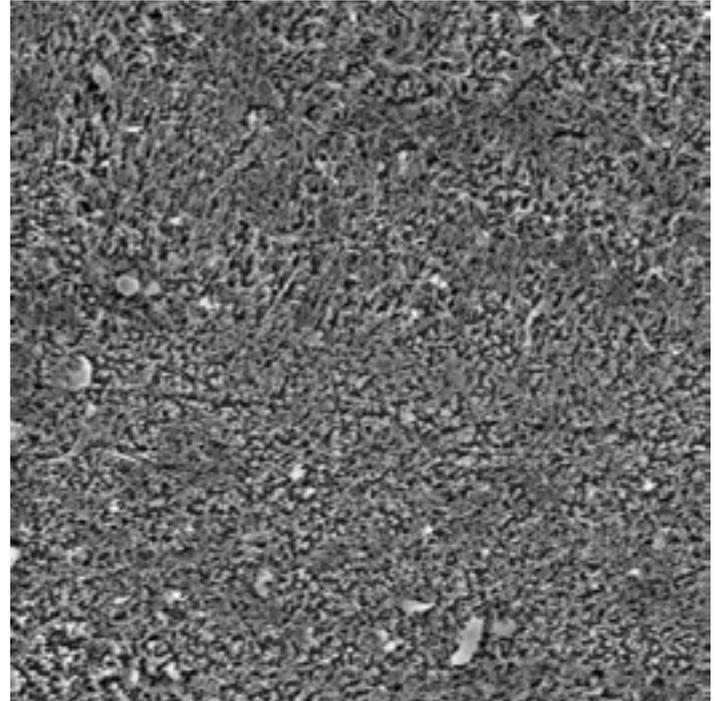


Pristine Kapton

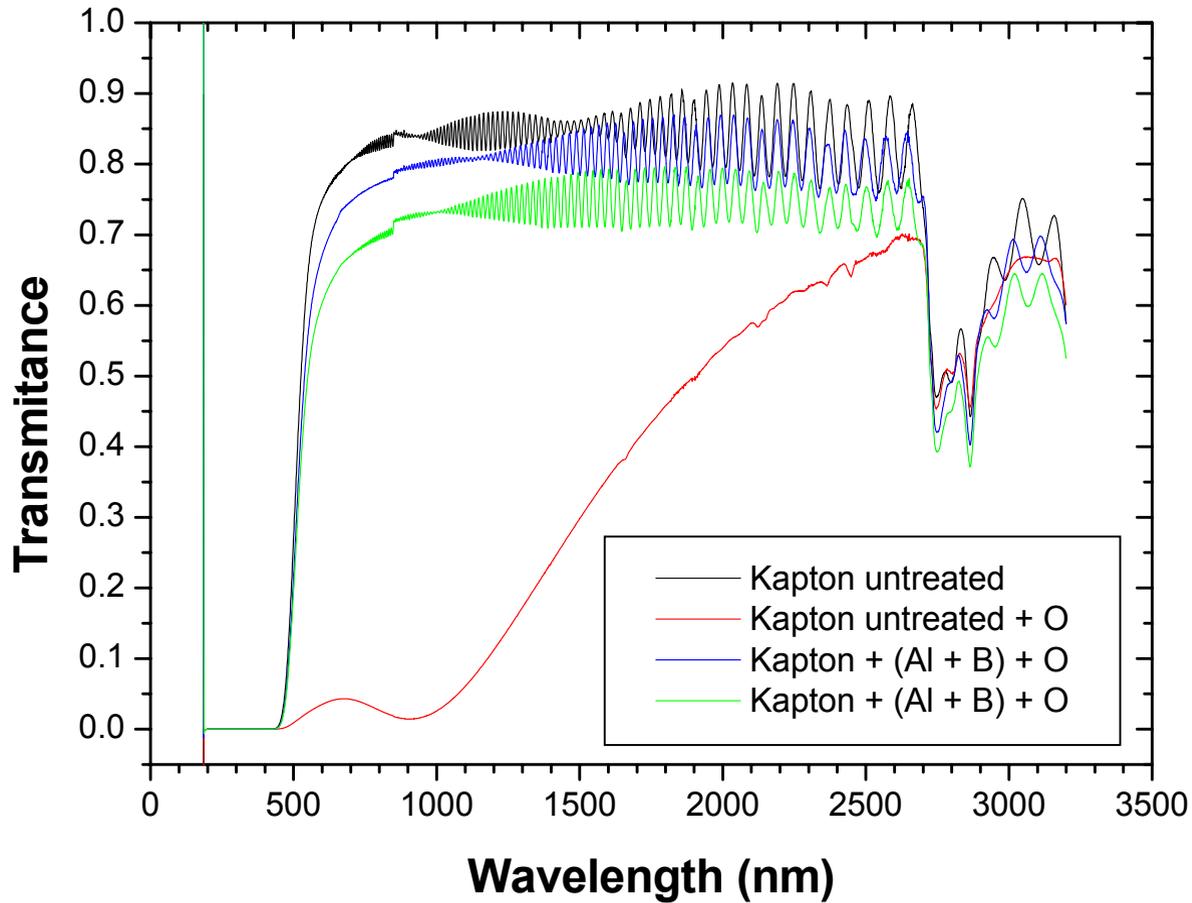


After tests

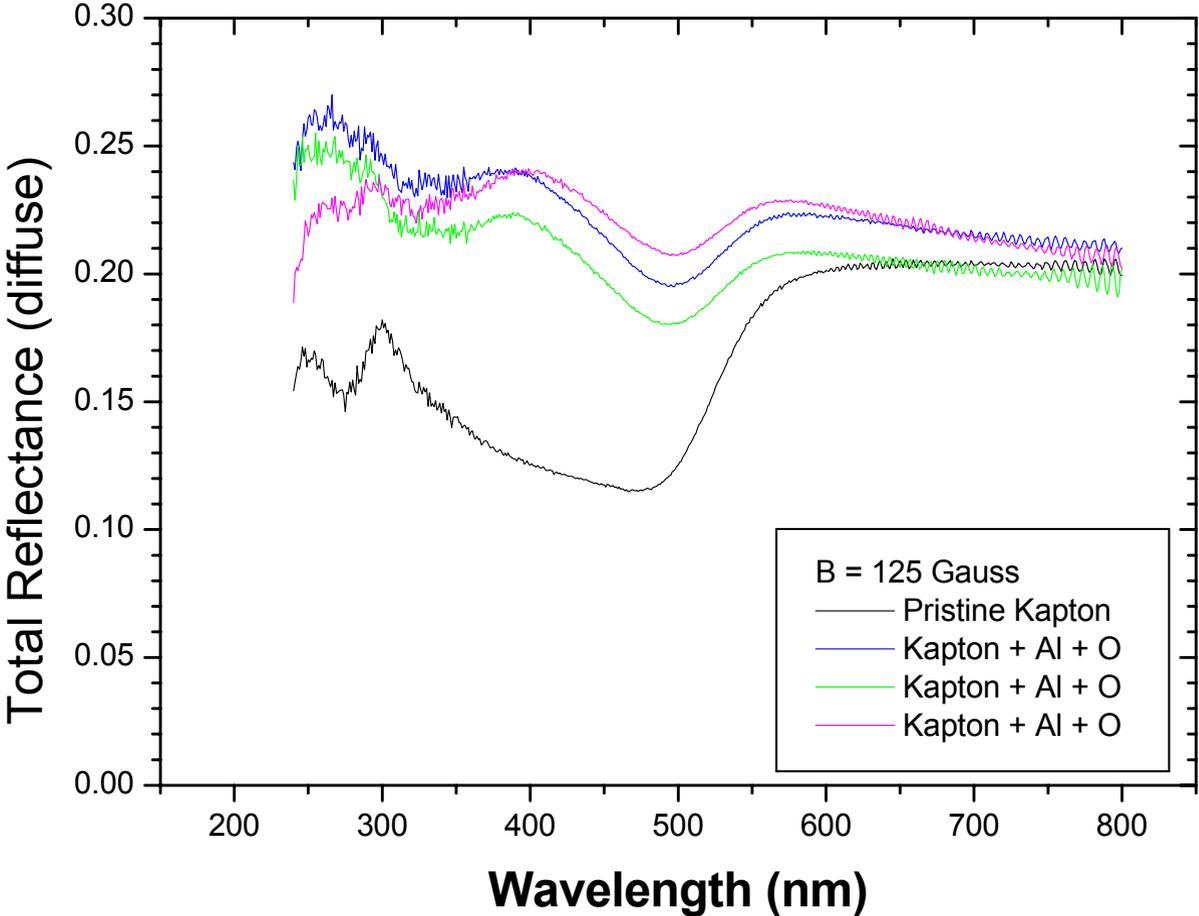
Without treatment,  
after oxygen exposure



# Transmittance decreases only by (5-15)%



# Total reflectance increases

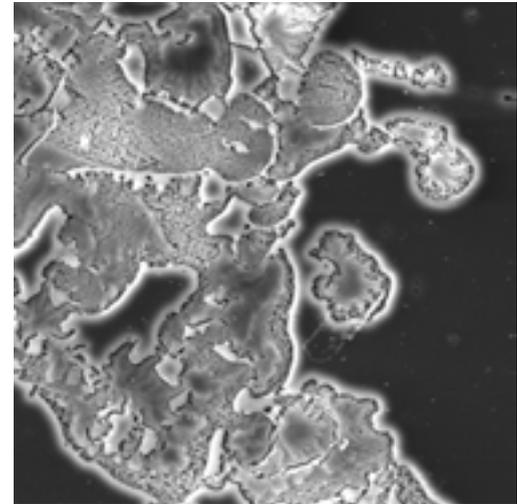
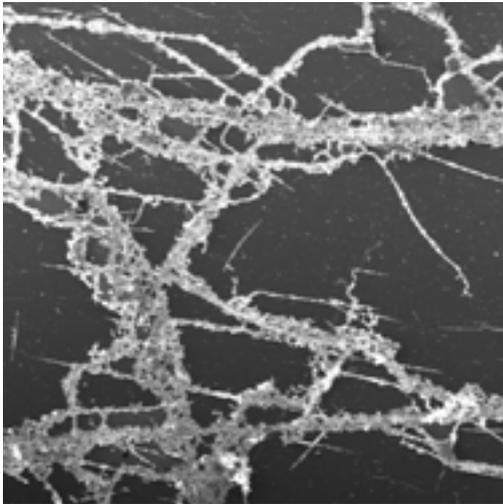


# Direct Implantation in Unmagnetized Plasmas

- 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<sup>2</sup> 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.