Surface Structure Analysis of Atomic Oxygen Protective Coating Film

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Explore to Realize

Introduction

- We have researched Silsesquioxane (RSiO3/2) coating as an Atomic Oxygen (AO) protective technology for spacecraft and this topic was presented at the last CCMPP in 2015, The title is “Development of a New Photocurable Silsesquioxane-coated polyimide films for Atomic Oxygen (AO) Protection”.
- Typical conventional protective-coating materials include indium tin oxide (ITO), SiO_2, germanium (Ge), and silicone. However, the defects associated with these coating materials render them insufficient to protect from the impact of AO.
- The AO resistance characteristics is believed to be due to the oxide layer formed by AO irradiation on the outermost surface of silsesquioxane (SiO_2). To elucidate formative process of a protective coating (SiO_2) by this analysis, Si spectral analyses by X-ray photoelectron spectroscopy (XPS) was performed and the details of the oxidation state of the protective coating layer were analyzed.

Contents

- Background
- Test Plan
- XPS Analysis
- TEM Observation
- (Flight demonstration experiment result)
- (Another some evaluation test results)
- Conclusion

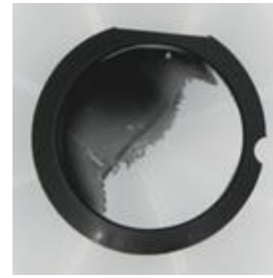
Examples of materials degradation by Atomic Oxygen (AO)

Space material exposure experiment on ISS

JEM/MPAC&SEED

ISS 259 days(8.5 months) Exposure

Ref. “Protection of Materials and Structures from Space Environment”, edited by Jacob I. Kleiman, Masahito Tagawa, Yugo Kimoto, Astrophysics and Space Science Proceedings Vol.32, 2009.

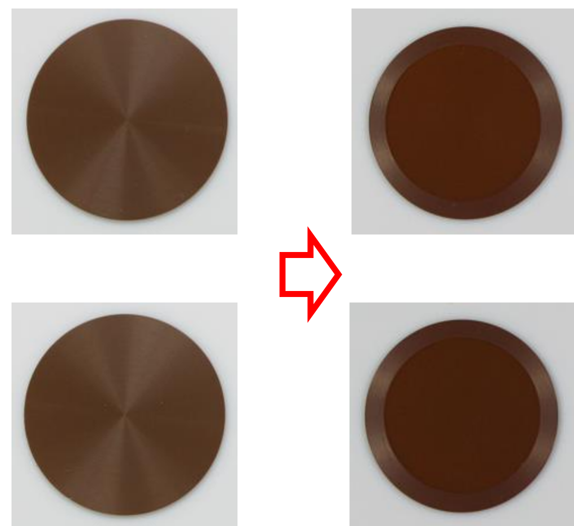


Black Kapton

Before flight After flight

VESL-J-A1

VESL-J-B1



10mm

VESPEL for the AO monitoring sample

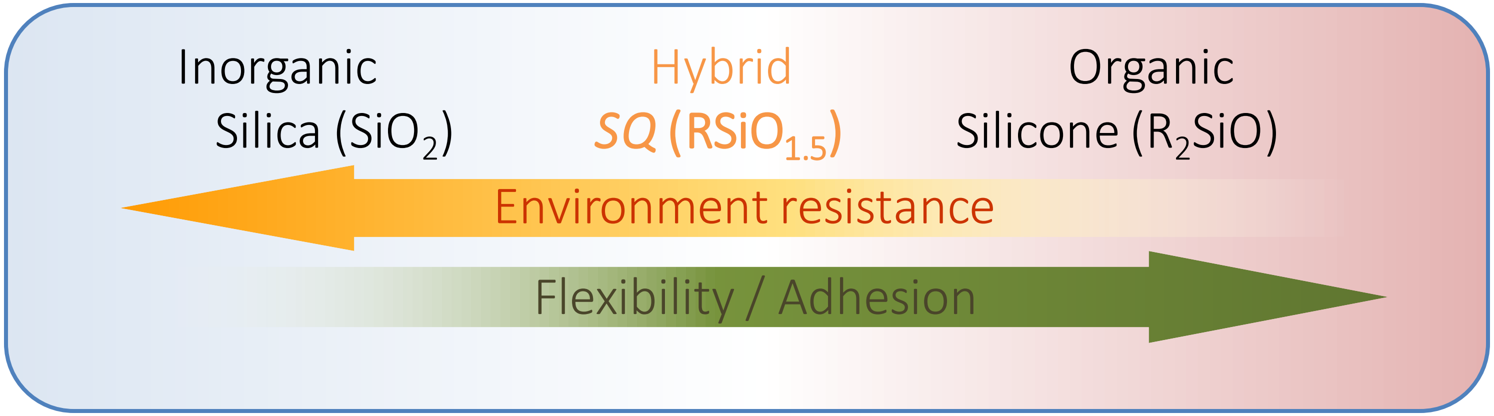
For AO protection

Effective : Coating to protect surface

Practical coatings have some issues・・・.

Coating technologies and their limitations inhibiting the use in polyimide film

Coating technologies	Limitations
Metal oxides, for example, ITO, SiO_2, and Al_2O_3.	-Easily damaged during handling -Difficulties associated with quality management
Germanium	-Colored -Gradually disappears in a humid environment
Silicone	- Colored by UV, high outgassing



Past AO resistance tests :

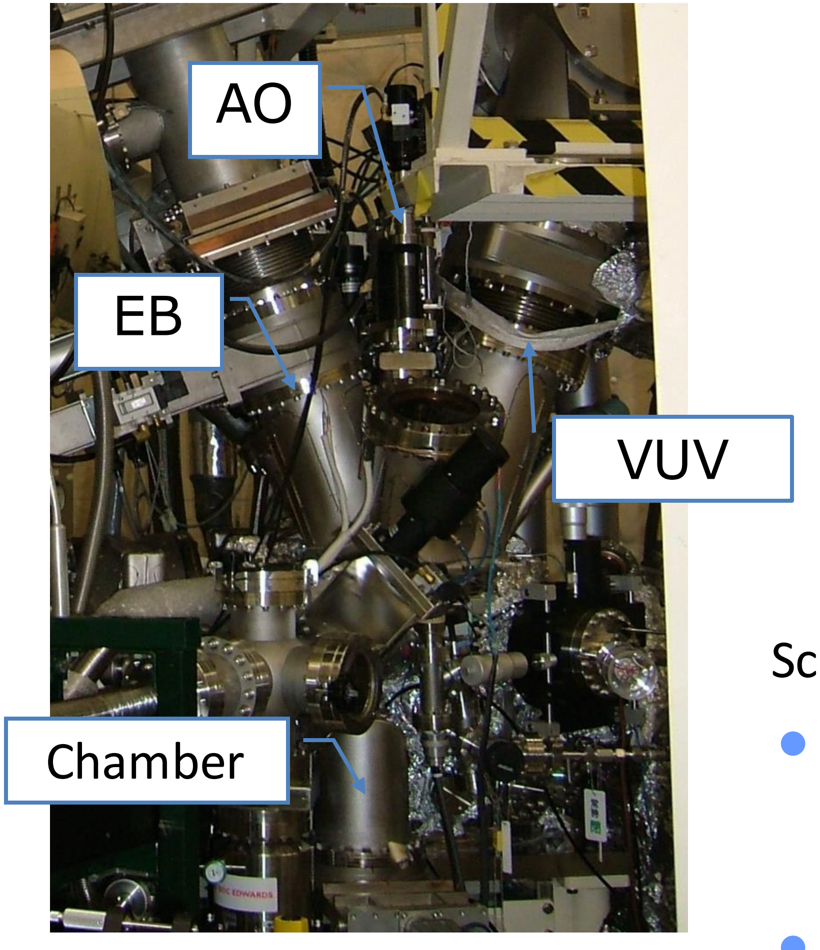
- *SQ* coating showed excellent resistance to AO.
- On the surface of *SQ* coating after AO irradiation, an oxide layer which is regarded as SiO_2 has been confirmed.
- It is inferred that this oxide layer protects materials from AO.

This presentation :

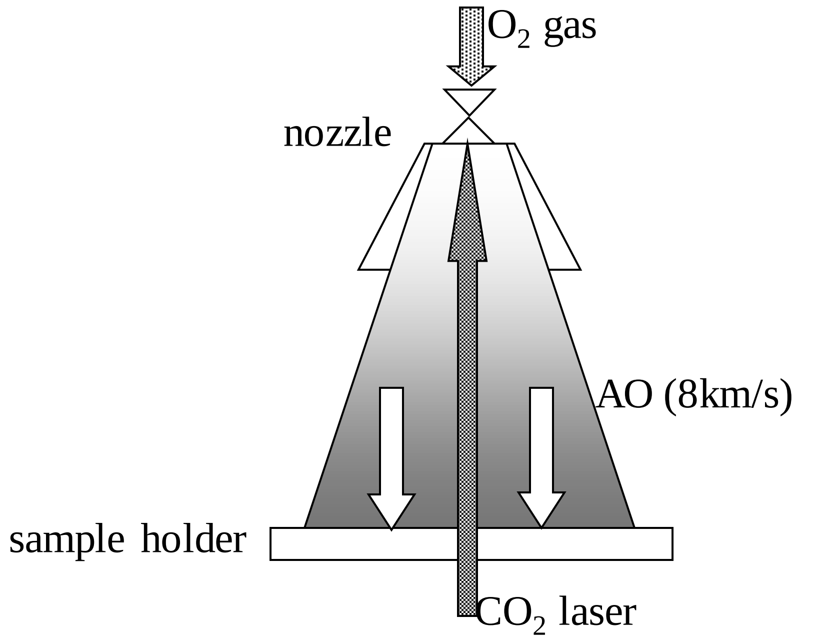
The observation and analysis results of the SiO_2 oxide layer are reported.

Ref. Yugo Kimoto, Takeshi Fujita, Naomasa Furuta, Akinori Kitamura, Hiroshi Suzuki,"Development of Space-Qualified Photocurable-Silsesquioxane-Coated Polyimide Films", Journal of Spacecraft and Rockets, Volume 53, Issue 6, November 2016, pp.1028-1034.

Test plan
AO irradiation test



The Combined Space Effects Test Facility in TKSC, JAXA

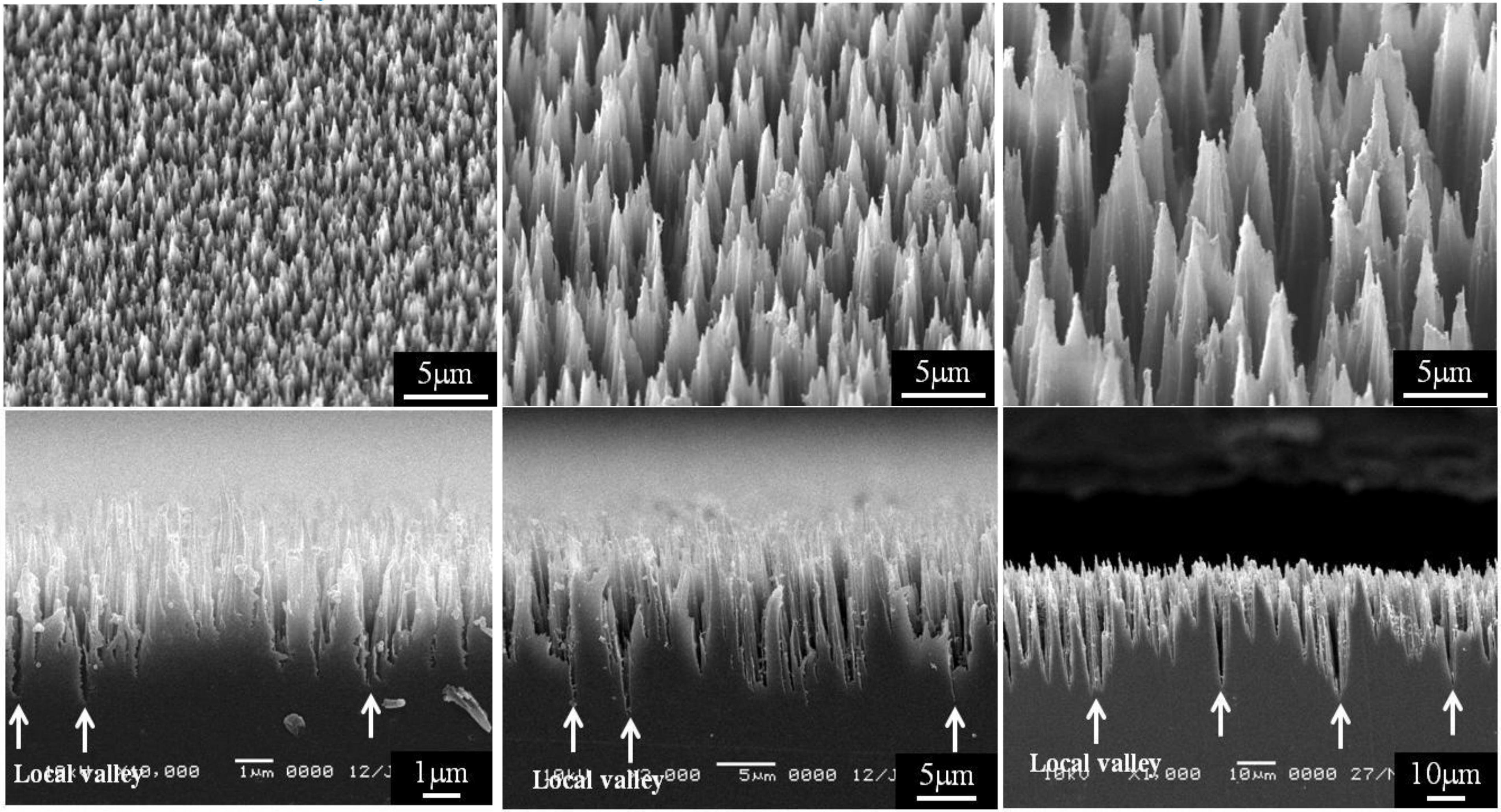


Schematic of AO beam generation

- A pulsed CO_2 laser is then used to break down the O_2 with the subsequent laser supported detonation (LSD) wave creating AO.
- The AO expands down to the nozzle as a blast wave (8km/sec) to sample holder.

Examples of top surface structure attacked by AO

AO-PI 0.3 E21 atoms/cm^2	AO-PI 1.3 E21 atoms/cm^2	AO-PI 3.0 E21 atoms/cm^2



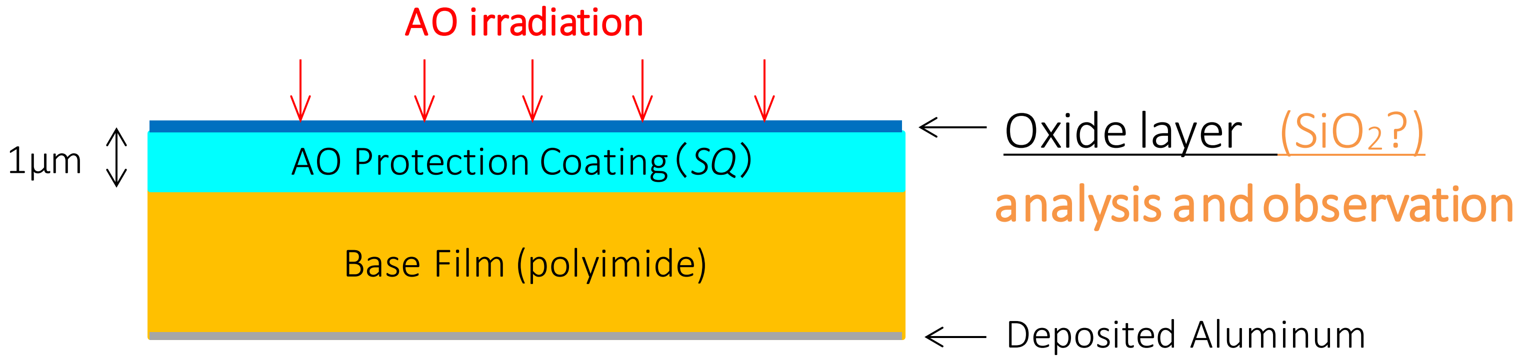
Ref. Hiroyuki Shimamura, Takashi Nakamura, Investigation of Degradation Mechanisms in Mechanical Properties of Polyimide Films Exposed to a Low Earth Orbit, Polymer Degradation and Stability, Vol. 95, pp. 21–33.2010

Test plan

Samples of this presentation

***SQ* coating Al deposited polyimide film :**

- Silsesquioxane derivative "photocurable *SQ* series" (*SQ*) manufactured by Toagosei Co., Ltd. was applied.



AO irradiation amount

ID	AO fluence [atoms/cm^2]	Base film	Test
34	-	UPILEX	XPS
AO-34-1	1.010E+21		
L-1	-	Apical	TEM・EDX
L-1	9.79E+19		
0-1	-	Apical	TEM・EDX
1-1	1.039E+20		XPS
1-2			TEM・EDX
2-1	5.507E+20		XPS
3-1	1.033E+21		XPS
4-1	2.107E+21		XPS
4-2			TEM・EDX

XPS **Analysis results**

- Surface composition

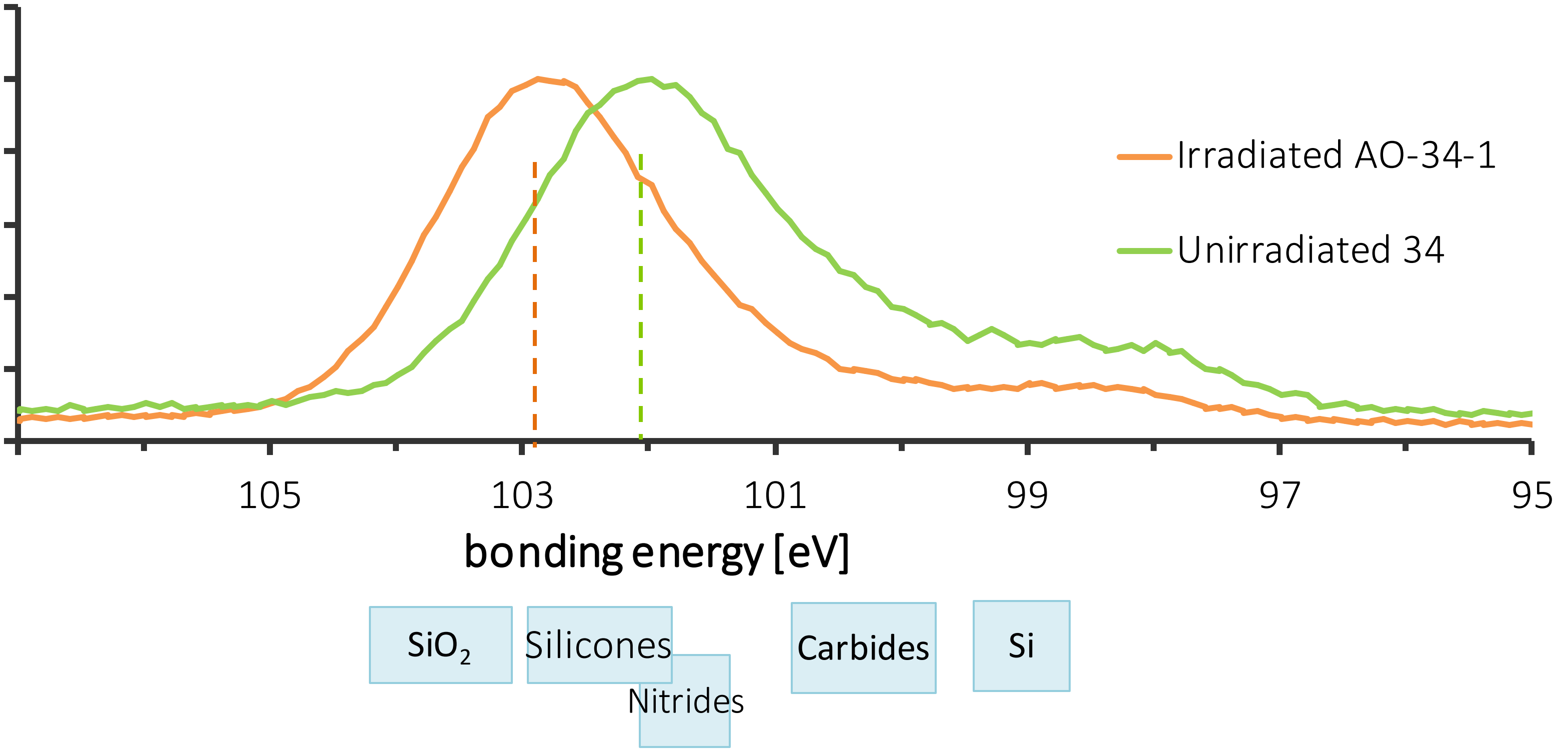
Surface composition(%)

	Si2p	C1s	N1s	O1s
Unirradiation ID:34	21.6	52.5	0.0	25.8
Irradiation ID:AO-34-1	33.6	7.1	0.0	59.3

- There was no difference in the types of the detected elements between unirradiation and AO irradiation.
- In the AO irradiation film, **Si** and **O** increased, while **C** decreased significantly.
- These changes indicate the possibility that *SQ* ($RSiO_{1.5}$) oxidized by AO irradiation and became Silica (SiO_2).

$$2RSiO_{1.5} + O \rightarrow 2SiO_2 + 2R$$

SQ AO Oxide Organic group



irradiated 34 :

i peak is around 102 eV

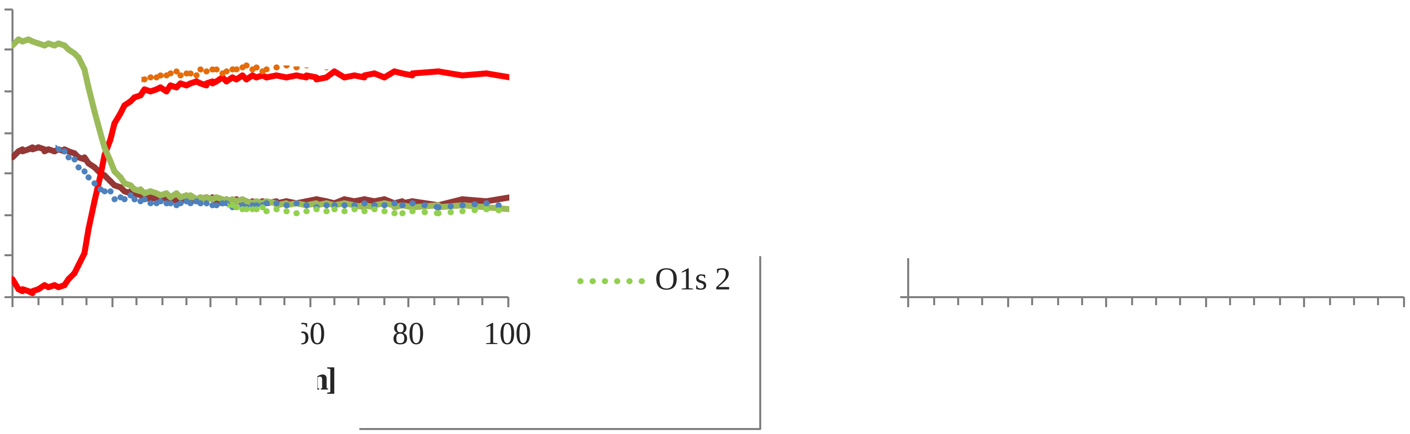
egion shows silicone

$SiO_{1.5}$) is detected

Irradiated AO-34-1 :

- The apex of **Si** peak shifts to around 103 eV
- It is close to the energy region of SiO_2

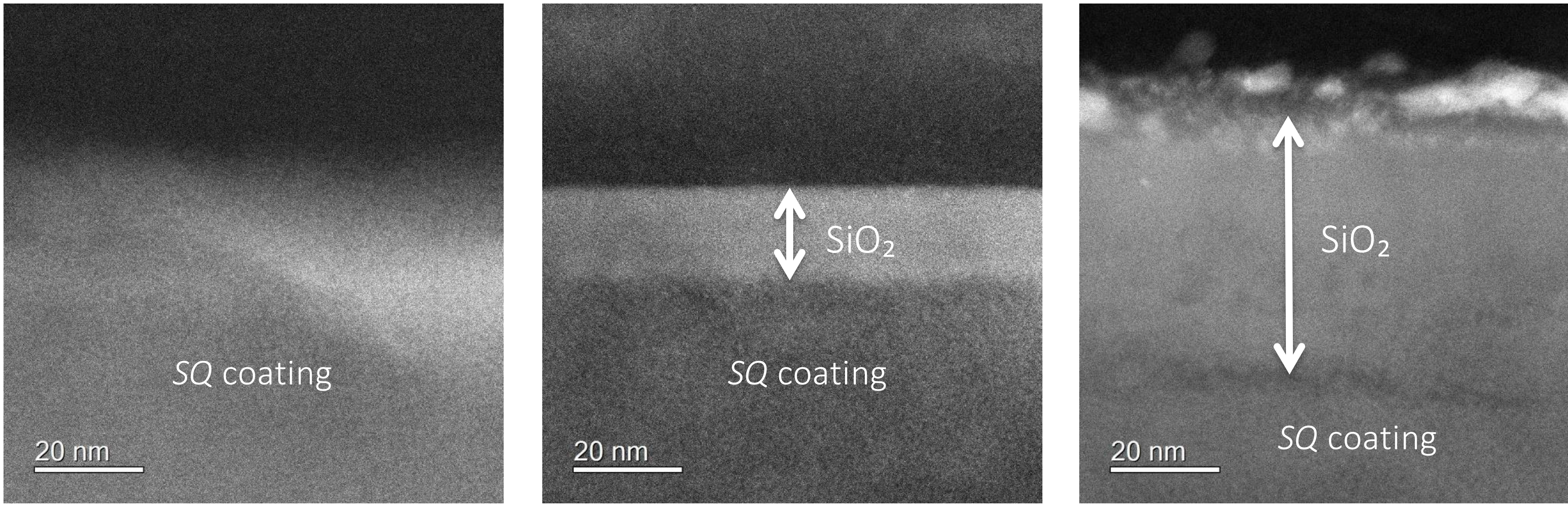
→ **Shift to the bonding energy of Si via the formation of SiO_2**



60
80
100
O1s 2

STEM/EDX
- STEM images

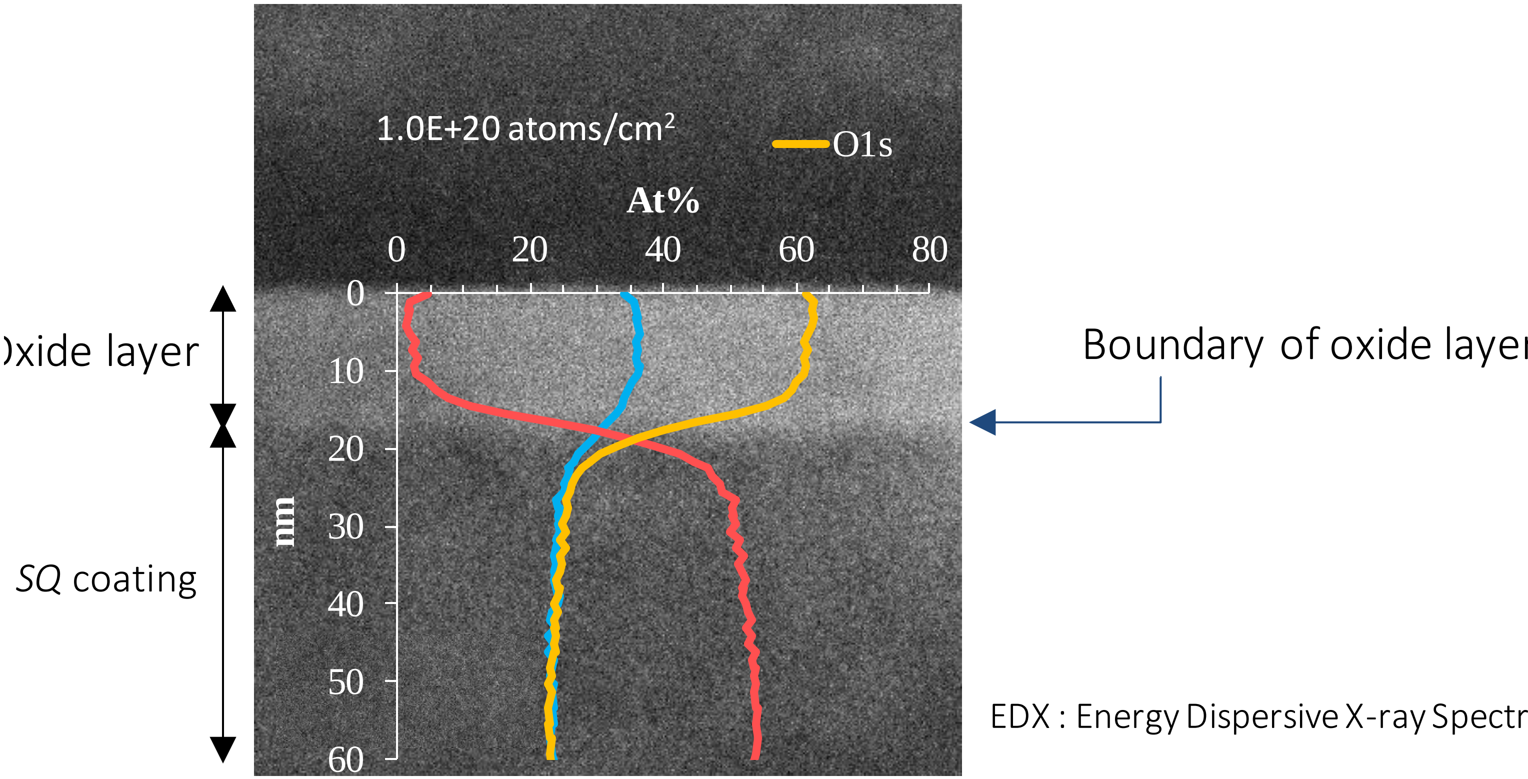
Unirradiation | 1.0E+20 [atoms/cm^2] | 2.1E+21 [atoms/cm^2]



STEM : Scanning Transmission Electron Microscope (A heavier element reflects more brightly)

- In unirradiated film, there is no structure peculiar to the sample surface.
- In AO irradiated film, a layer of several tens of nm (regarded as SiO_2) was confirmed.
- Given the large amount of irradiation, the SiO_2 thickness also becomes thicker.

- Line analysis

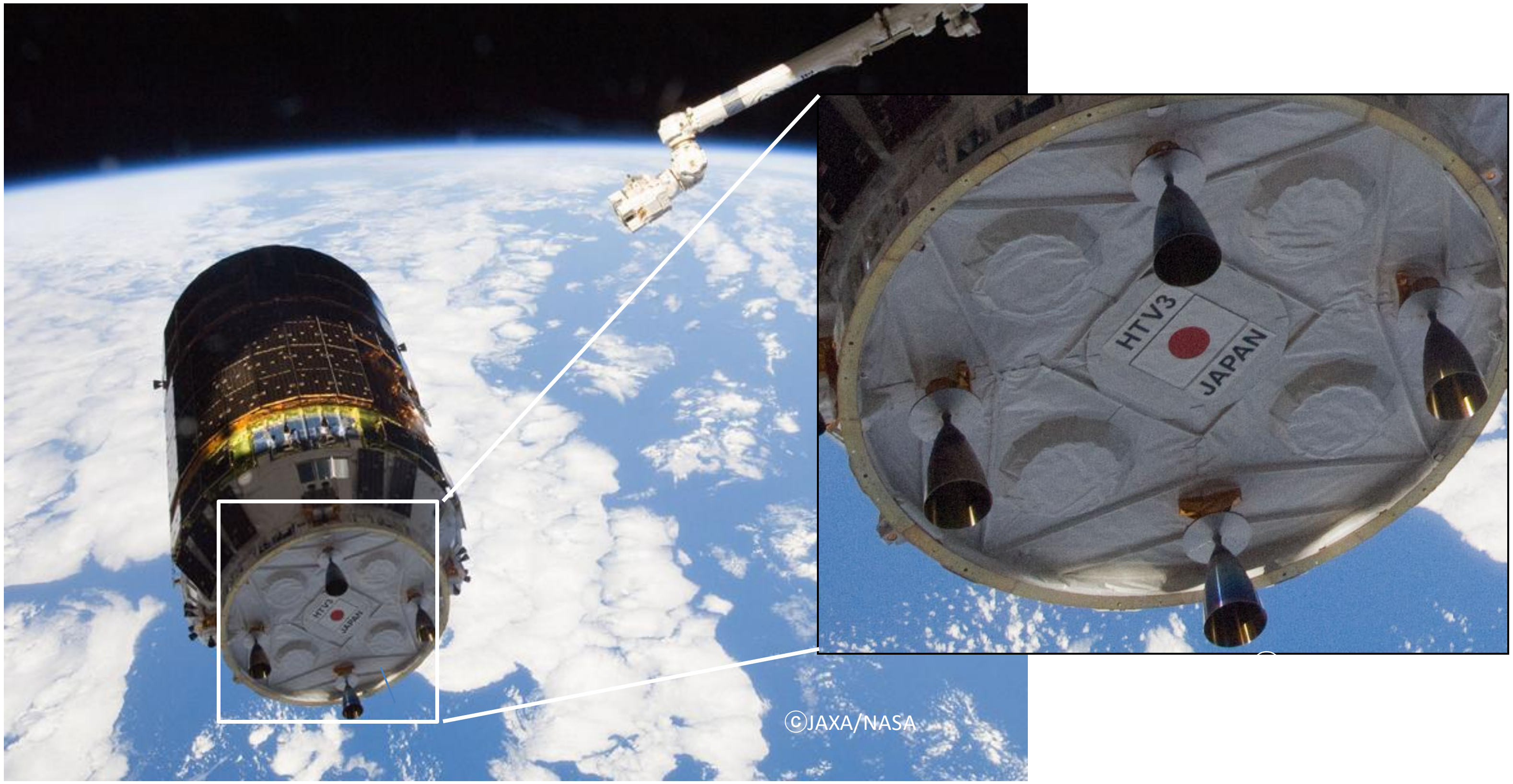


EDX : Energy Dispersive X-ray Spectroscopy

- The element distribution changed significantly at the boundary of the oxide layer.
- Similar changes could be confirmed with other AO fluence.
- The oxide layer has almost no **C**, and mainly consists of **Si** and **O**.
- The abundance ratio of Si and O in the oxide layer is 1 : 2.

Application of SQ coating
HTV 3 launched in July 21th, 2012

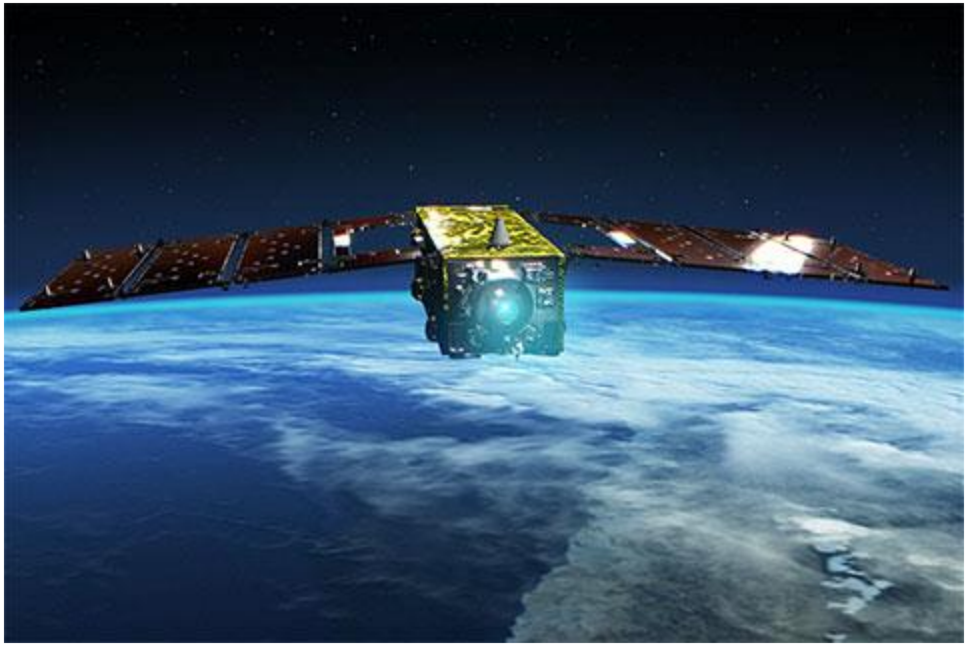
To protect a logo paint from AO



Propulsion Module

Ref. Junichiro Ishizawa, Yugo Kimoto, Takashi Tamura, Naomasa Furuta, Akinori Kitamura, Hiroshi Suzuki, "Photocurable Silsesquioxane for Atomic Oxygen Protective Coatings", Proc. '12th Int. Symp. on Materials in Space Environment' Noordwijk, The Netherlands (ESA SP-705, February 2013)

Space Demonstration experiment of SQ coating Super Low Altitude Test Satellite "TSUBAME" (SLATS) (under development)

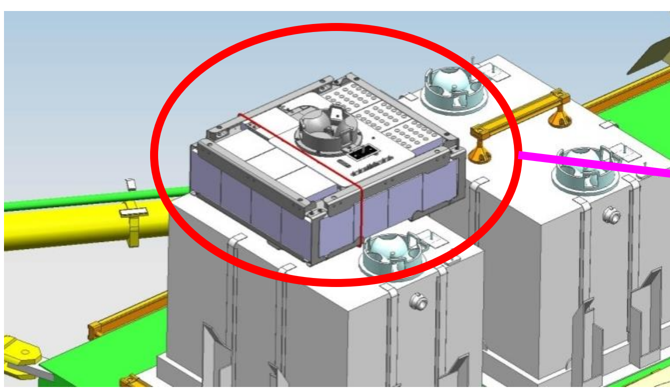


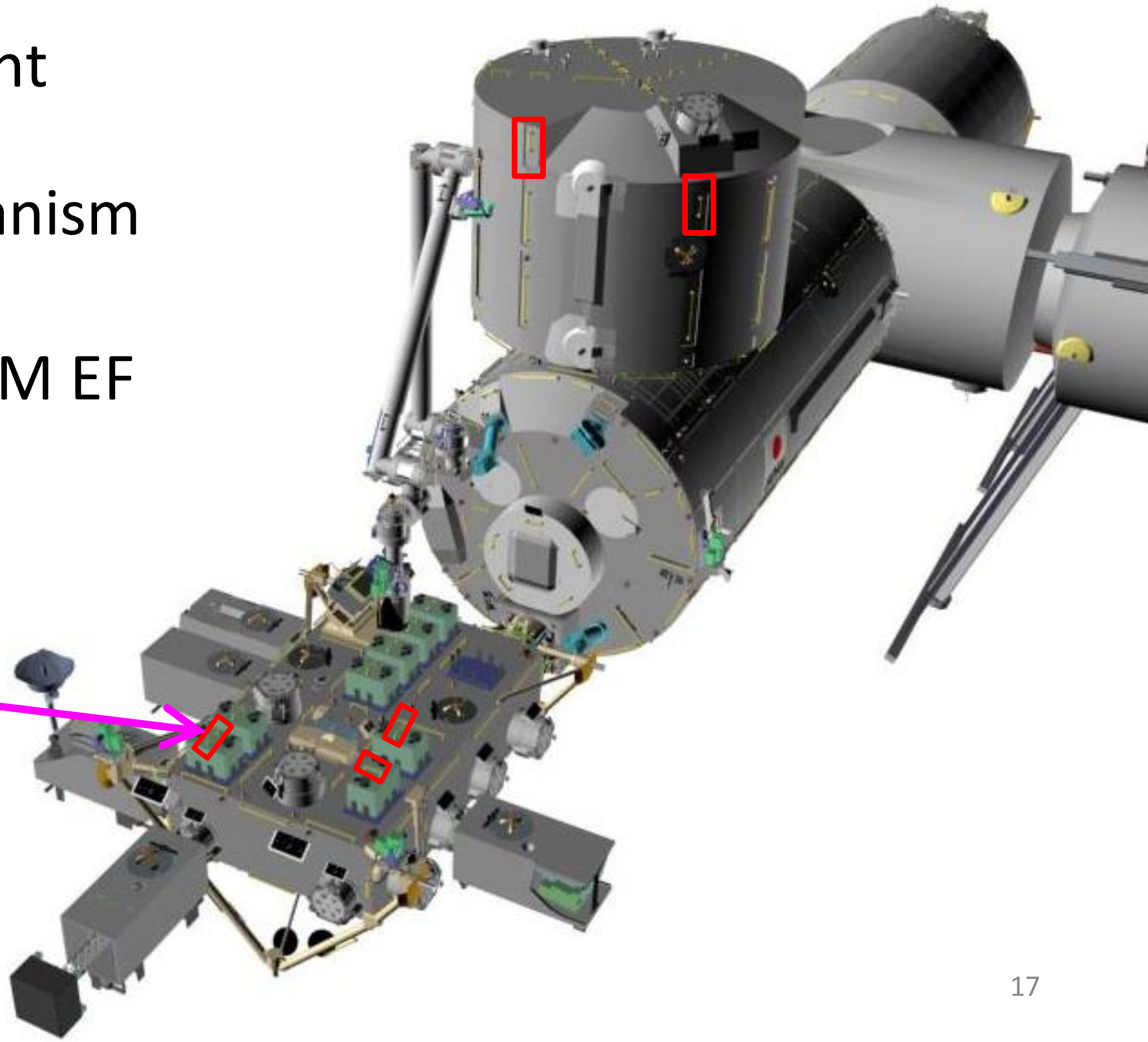
- The Super Low Altitude Test Satellite "TSUBAME" (SLATS) is the first Earth observation satellite to use a super low orbit. A "super low orbit" refers to an orbit with an altitude lower than 300 km.
- This orbit is an undeveloped region and it has yet to be fully utilized by satellites. Satellites in a super low orbit will bring benefits such as high resolution observations for optical imagers, low power transmissions for active sensors, and cost reductions for satellite manufacturing and launches.

http://global.jaxa.jp/projects/sat/slats/

SQ-coating
Space Environment Exposure Experiment on ISS

- Exposed Experiment Handrail Attachment Mechanism (ExHAM)
- Deployed on ISS JEM EF

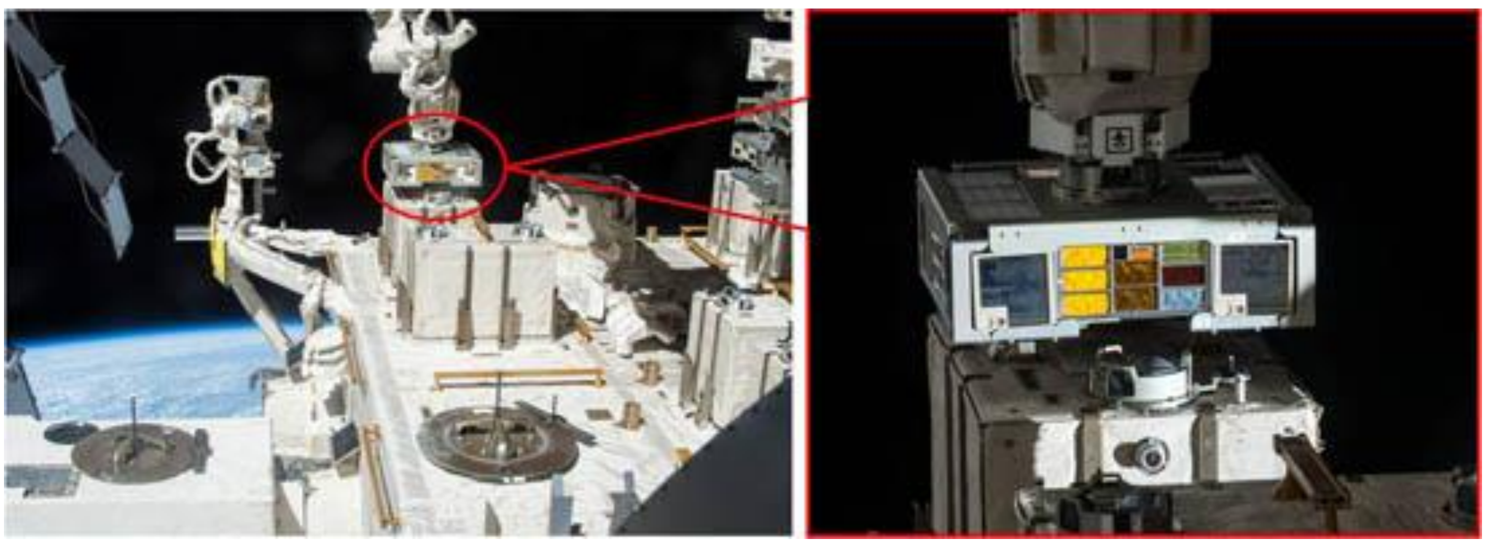




Space Environment Exposure Experiment

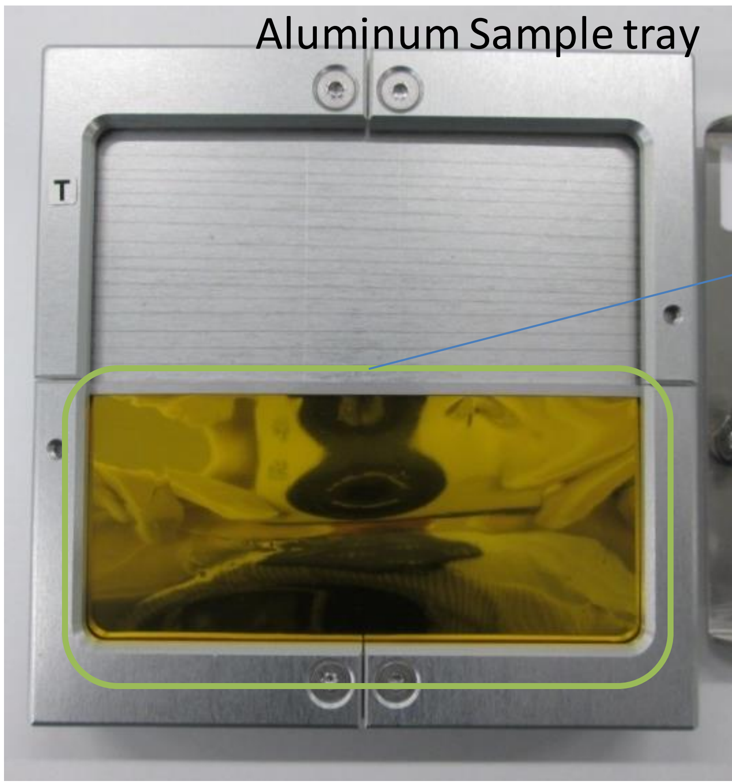
- 3 sets of SQ coated polyimide film samples are mounted on Exposed Experiment Handrail Attachment Mechanism (ExHAM).
- The 1st sample was retrieved. Change of exposed sample properties were analyzed on ground.

Sample	Deployment	Retrieval
#1	2015 May 16	2016 June 13
(#2)	2015 May 16	2017 June (TBD)
(#3)	2015 Nov. 11	2017 Mar 13

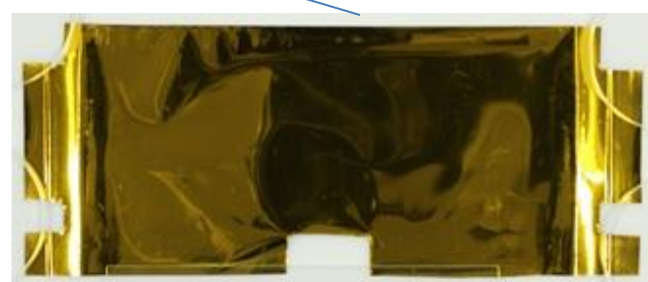


Space Environment Exposure Experiment -Visual inspection-

- The SQ coated film was set on the 10 cm x 10 cm sample tray (The SQ coated film is a half of the size).
- Retrieved sample tray discolored.
- The SQ coated film was no damage.



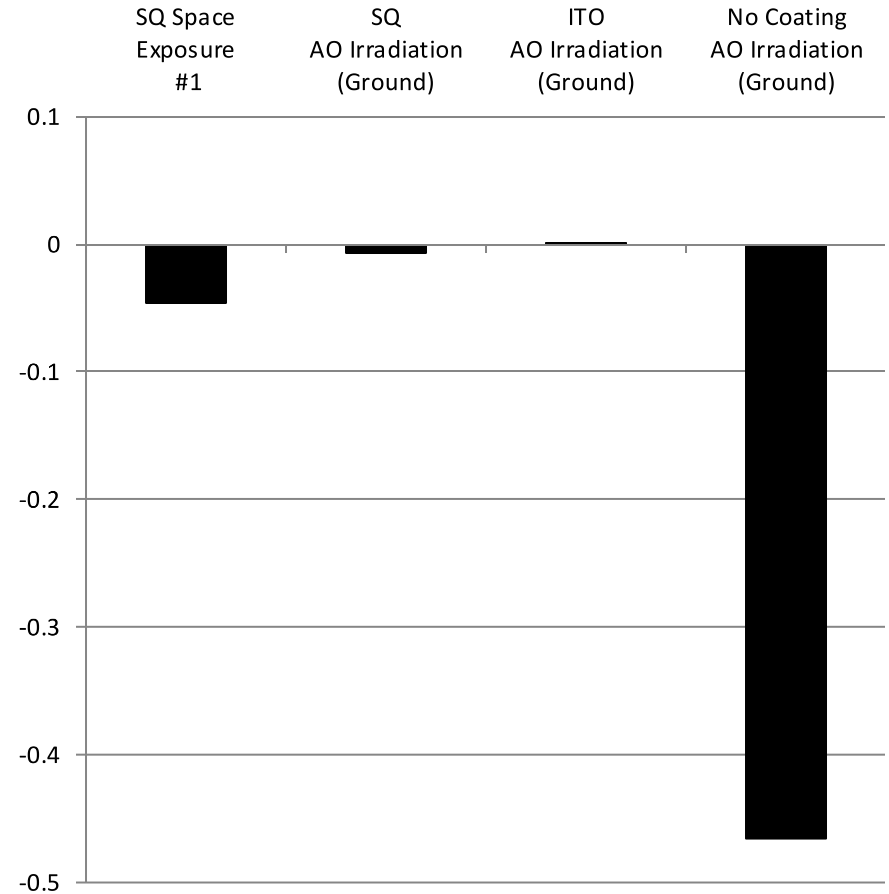
SQ coated film



1cm

Space Environment Exposure Experiment -Mass Loss-

- Measured mass loss was 0.046mg/cm^2. It includes loss caused by sample handling ex. folding, taping, cleaning.
- Predicted mass loss due to chemical transformation from Silsesquioxane to SiOx was 0.06 mg/cm^2. it was calculated using SiOx layer thickness observed by TEM.



International Standard Proposal of Atomic Oxygen Protective Coating on polyimide film

Contents

Conclusions

- After AO irradiation, *SQ* is oxidized to form a SiO_2 layer
- In AO irradiated film, a layer of several tens of nm (regarded as SiO_2) was confirmed.
- Given the large amount of irradiation, the SiO_2 thickness also becomes thicker.
- Change of retrieved sample which was exposed in ISS environment were analyzed on ground.
- Excellent AO protection properties has demonstrated in Space.
- International Standard Proposal of Atomic Oxygen Protective Coating on polyimide film