Effect of environment on 157nm soft pellicle durability

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Table of Contents

✓Motivation

✓Experimental procedure / facility

✓Experimental results (Polymer A,I)

✓Irradiation durability as pellicle

✓Summary and future plan

Motivation

1. Results of 157nm pellicle

   ▪Oxygen-contained gas environment is effective for improvement in durability.

2. Technical issue

   ▪Degradation of the polymer's mechanical strength is pronounced with increasing oxygen content in the environmental gas.

3. Improvement of fracture strength

   ▪Development of polymer which is excellent in mechanical strength for irradiation in oxygen-contained gas environment.

157nm soft pellicle requirements

Optical Property	Unit	Requirement
Transmittance	[%]	>98
Transmittance uniformity	[%]	±0.2
Irradiation durability	[J/cm^2]	>6,000 (Transmittance variation : Δ% 1.0)
Membrane Reflectance	[%]	≦1.0

157nm Durability of modified Cytop※

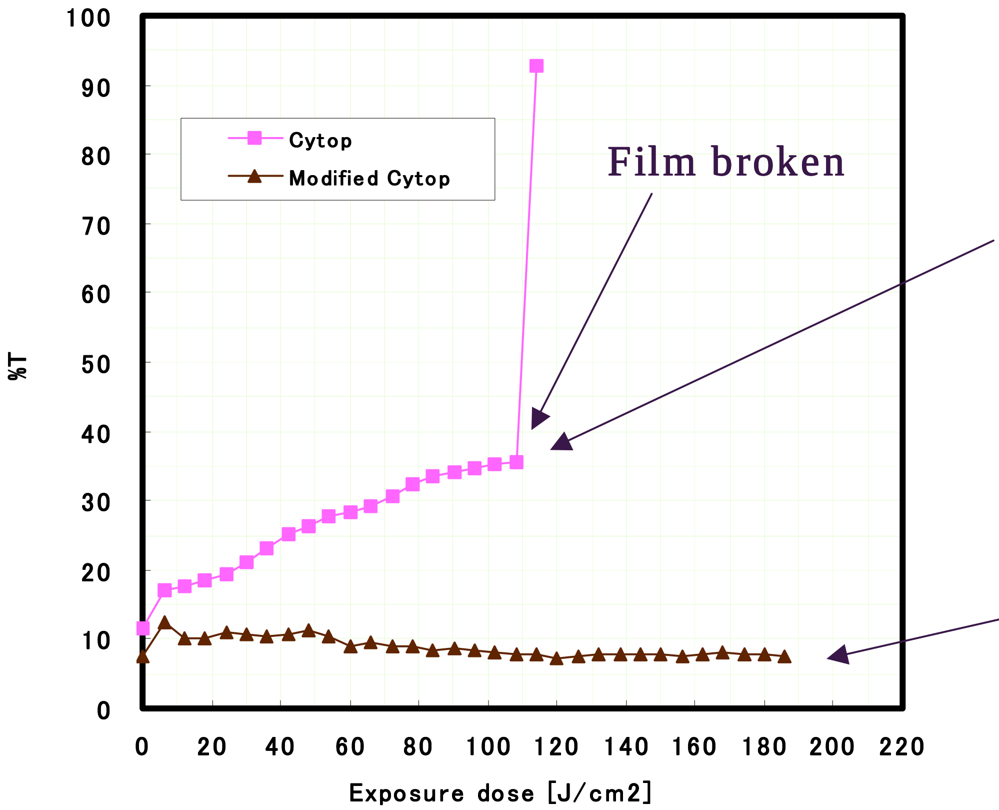


Fig.1. Dependence of transmittance on exposure dose at original/modified Cytop.

Cytop

Modified Cytop

※: Cytop is polymer for 193nm pellicle by Asahi-Glass Co.Ltd.

Environmental gas : N_2

Light source : F_2 laser

(λ =157.6nm)

The modified Cytop isn't broken after irradiation but its transmission doesn't meet industry requirements : >98%

Results of 157nm pellicle (polymer A)

- Improvement of initial transmittance -

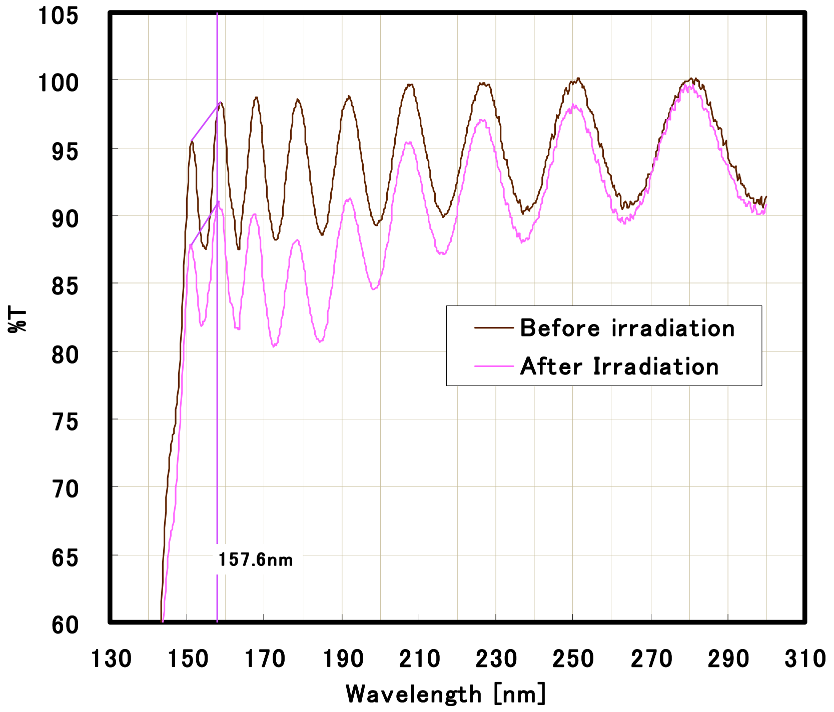


Fig.2. Transmittance loss of polymer A before and after irradiation.

Initial transmittance @ 157.6nm : 97.9%
Transmittance after irradiation : 90.7%
Exposure dose : 4.4J/cm2
Environmental gas : N_2
Sample : Self-standing film (t=1um)

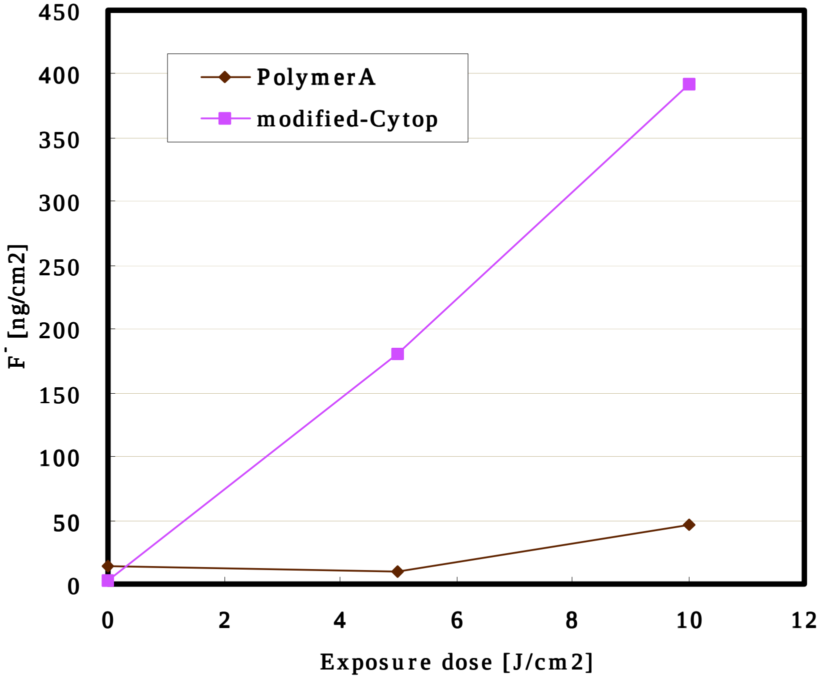


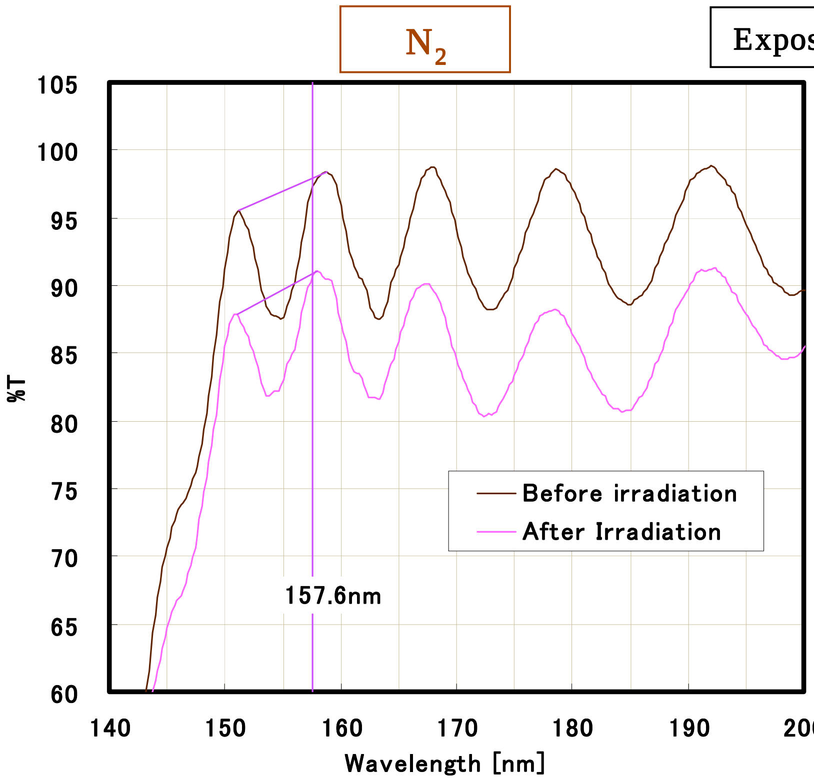
Fig.3. A comparison of modified-Cytop with Polymer A for the amount of fluoride ion in outgas by 157nm Laser irradiation.

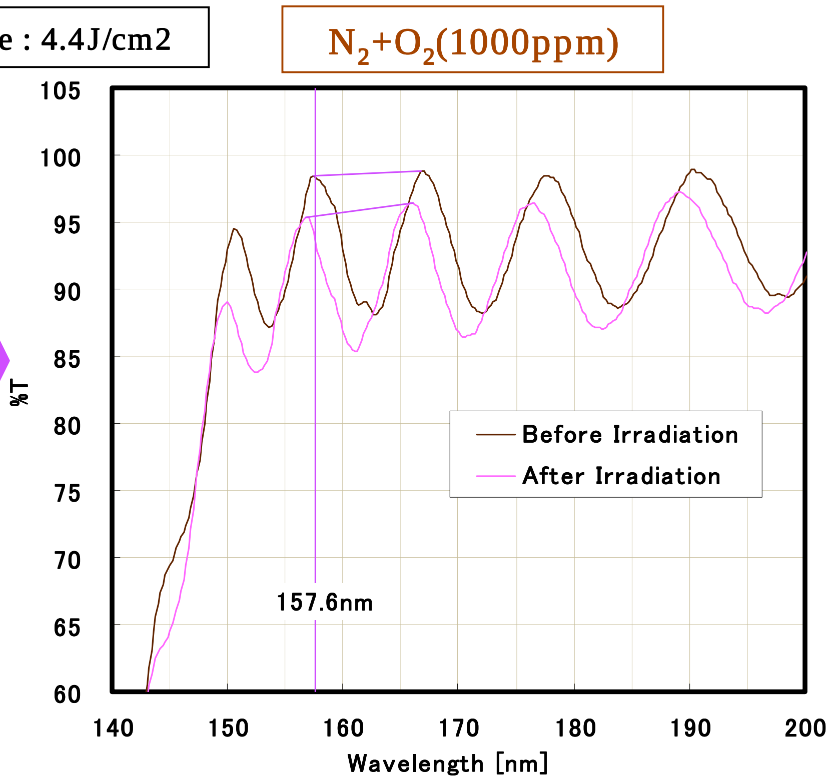
It seems that the degradation of polymer A by 157nm laser irradiation is less slightly than modified Cytop.

Effect of oxygen content on durability

(Polymer A)

Exposure dose : 4.4J/cm2





Δ%T = 7.0% → Δ%T = 2.9%

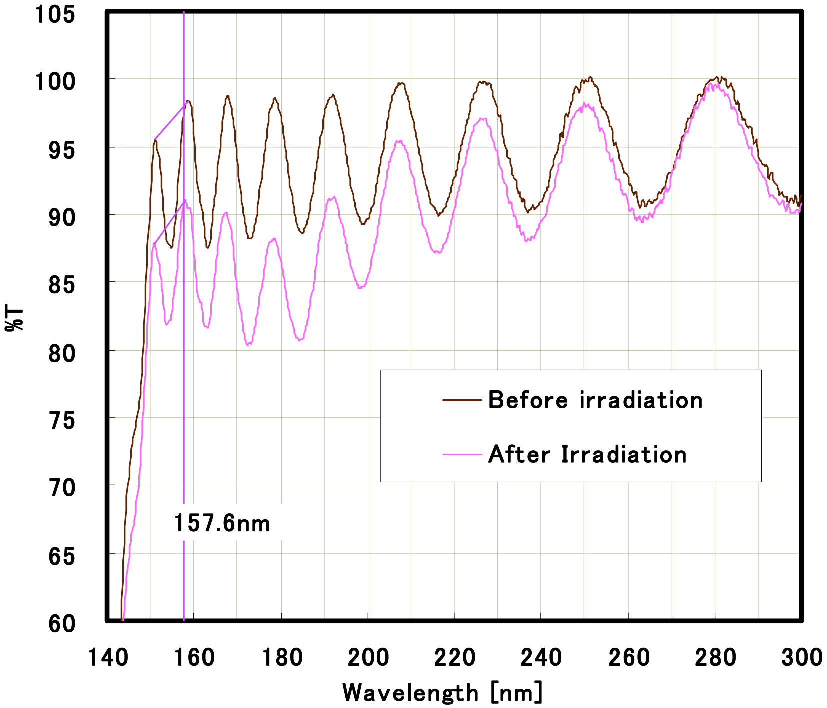
Fig.4. Effect of oxygen content in the environmental gas on transmittance loss by 157nm laser irradiation.

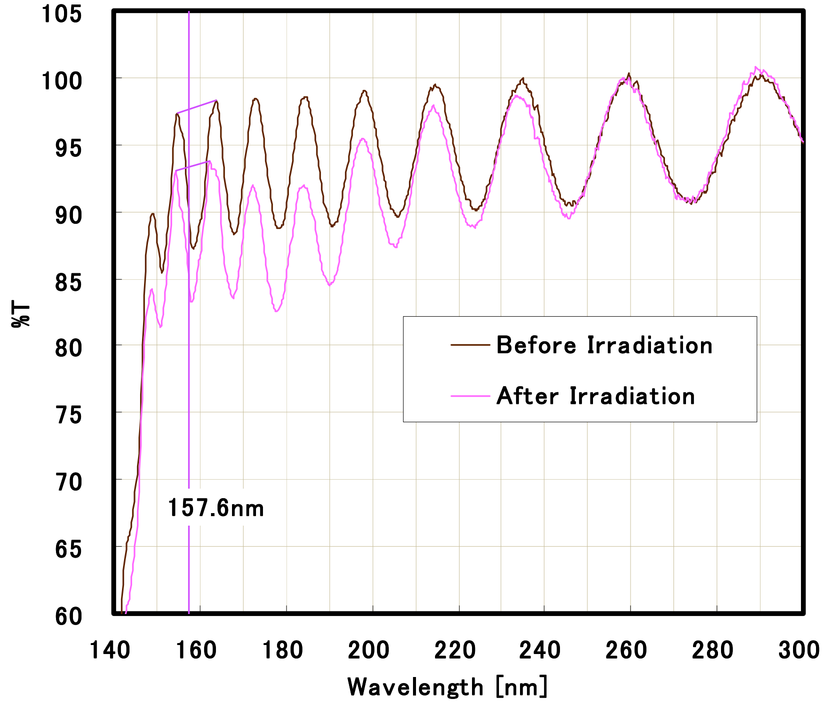
Δ%T =
Transmission (before irradiation)
- Transmission (after irradiation)

Effect of environmental gas on durability

(Polymer A)

N_2 | Exposure dose : 4.4J/cm2 | He





Δ%T = 7.0% → Δ%T = 4.4%

Fig.5. A comparison of nitrogen gas environment with helium gas environment for transmittance loss by 157nm laser irradiation.

Technical issue

The transmittance loss of the polymer film by irradiation decreases with increasing oxygen contents in the environmental gas.

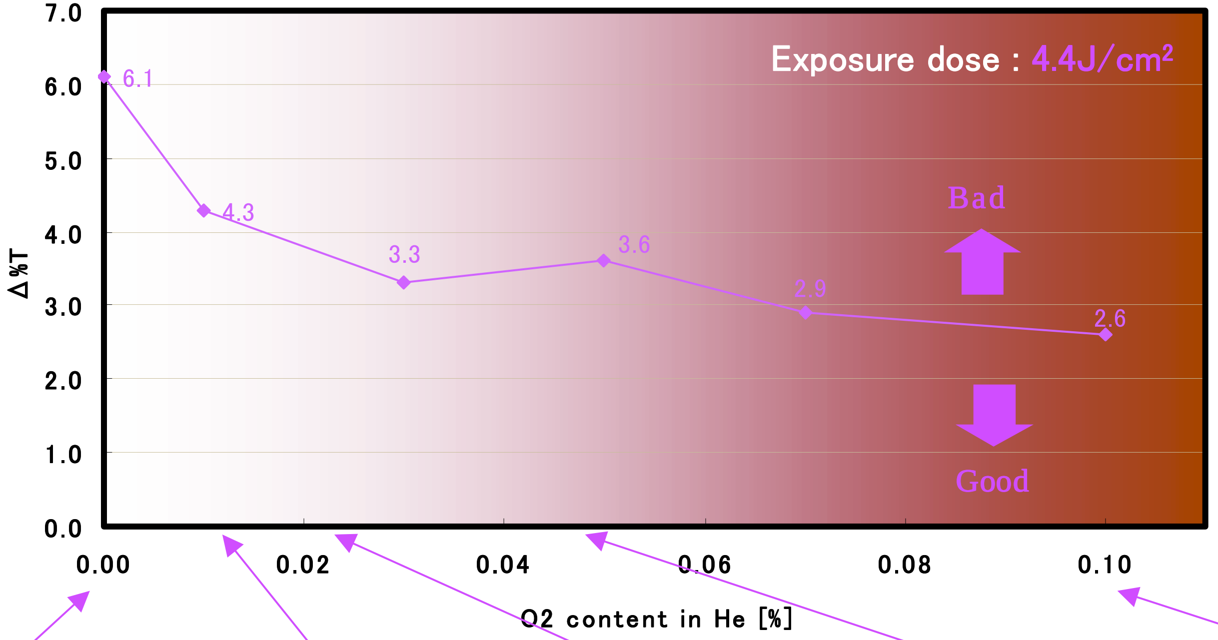
↓

However, film damage is pronounced with increasing oxygen content in the environmental gas as the following page shows.

↓

For further improvement in irradiation durability, it is necessary to decrease degradation of mechanical strength by the irradiation in the oxygen-contained gas environment.

Film damage (Polymer A)



Δ%T =
Transmission (before irradiation)
- Transmission (after irradiation)

Exposure dose : 10.8J/cm²

O_2 content 0.00% | 0.01% | 0.02% | 0.05% | 0.10%

Film damage by the irradiation is pronounced with increasing the O_2 content in the environmental gas.

Improvement of fracture strength

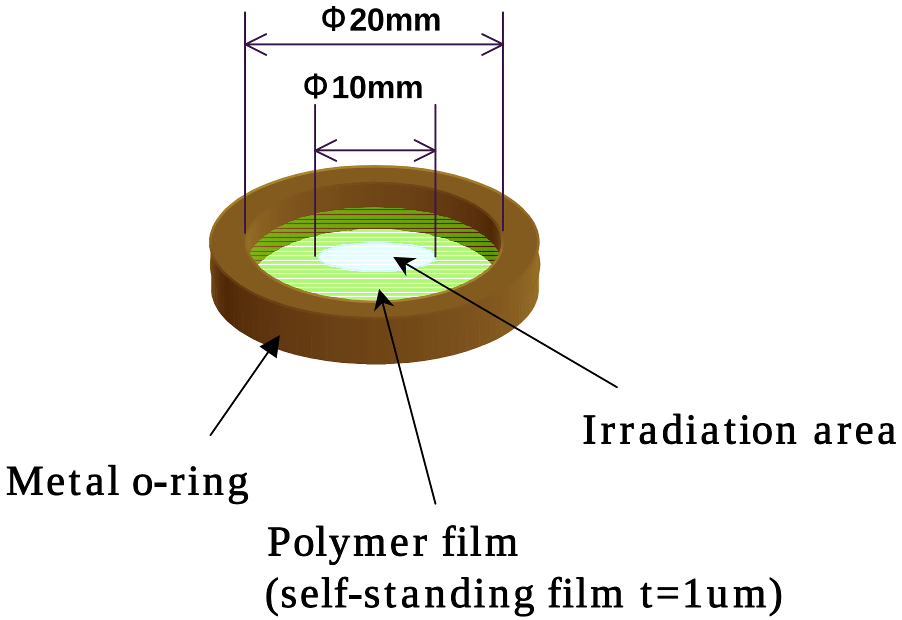
Table 1. Mechanical properties of trial polymer film.

	Tensile Test (before irradiation)	
	Fracture Strain (εf)	Fracture Stress (σf)
Polymer A	4.4%	24MPa
Polymer I	183%	52MPa

In order to improve durability in oxygen-contained environment, the trial polymer which is excellent in initial mechanical strength is made by AGC.

Experimental procedure

Sample



Experimental procedure

Step 1.

Polymer selection

- Mechanical strength evaluation (by tensile tests)
- Initial transmittance

Step 2.

Sample preparation

- Self standing film

↓

Irradiation

- In-situ transmittance
- Irradiation environment
  - pure-He
  - $He+O_2$(1000ppm)

→ GPC※ analysis

→ Mechanical strength evaluation

Air blowing test

※GPC: Gel Permeation Chromatography

Experimental facility

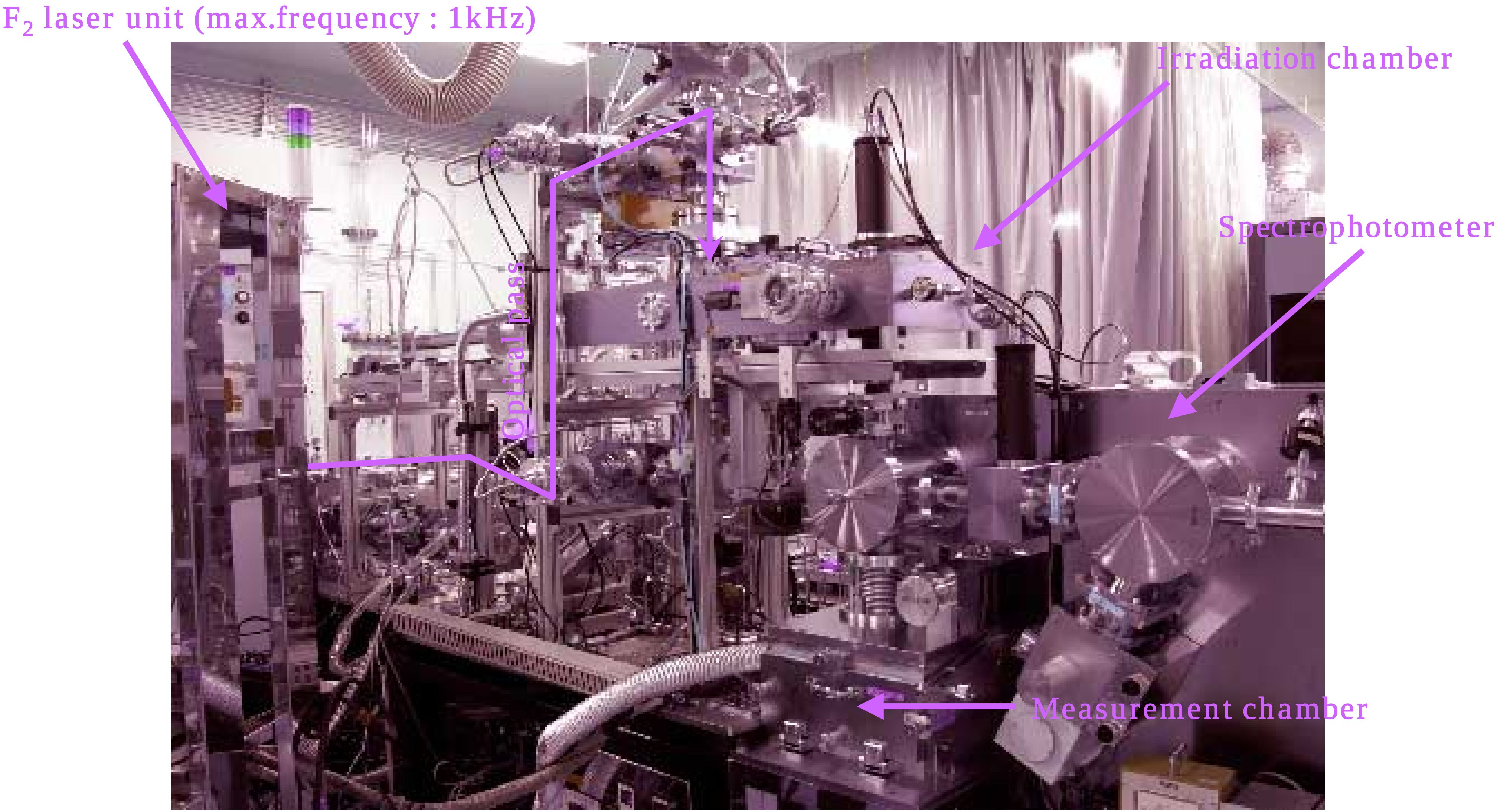


Photo 1. Irradiation and measurement system for 6025 size photo mask and test peace at Komatsu.

Experimental results (Polymer A,I)

Film breaking is started

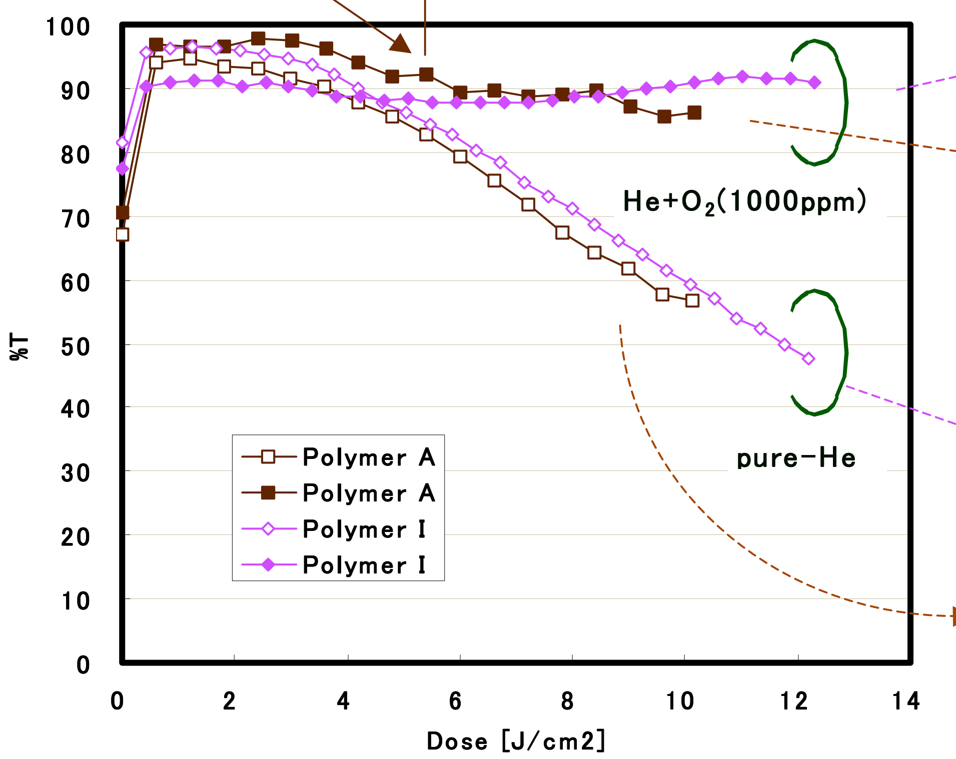
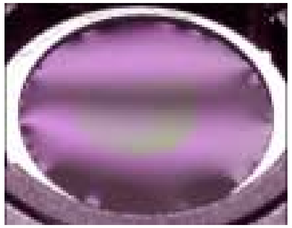
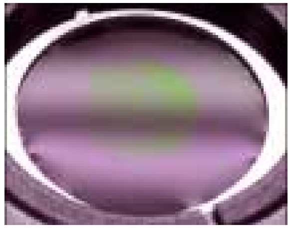


Fig.6. Dependence of transmittance on exposure dose at different polymer film and gas environment.



Weak irradiation mark is revealed but film isn't broken

Film broken

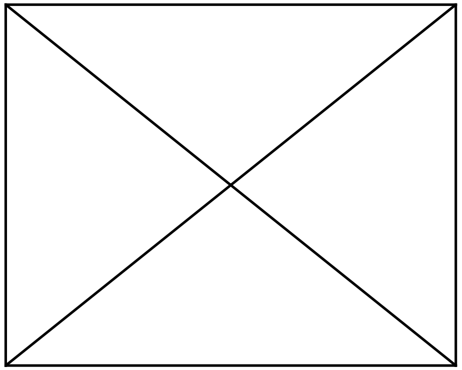


Strong irradiation mark is revealed but film isn't broken

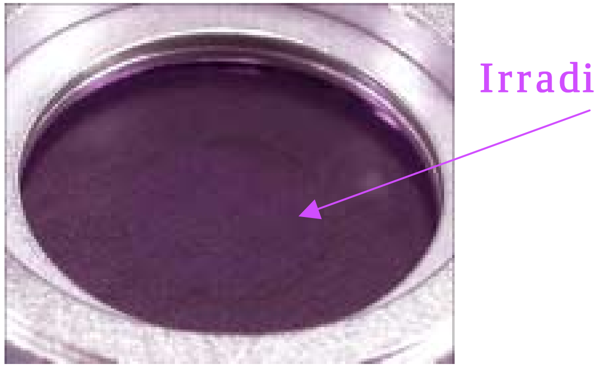
Film is deformed at irradiation area

Mechanical strength evaluation result

Irradiation environment : He+O_2(1000ppm)



Polymer A is broken during irradiation.



Polymer I isn't broken

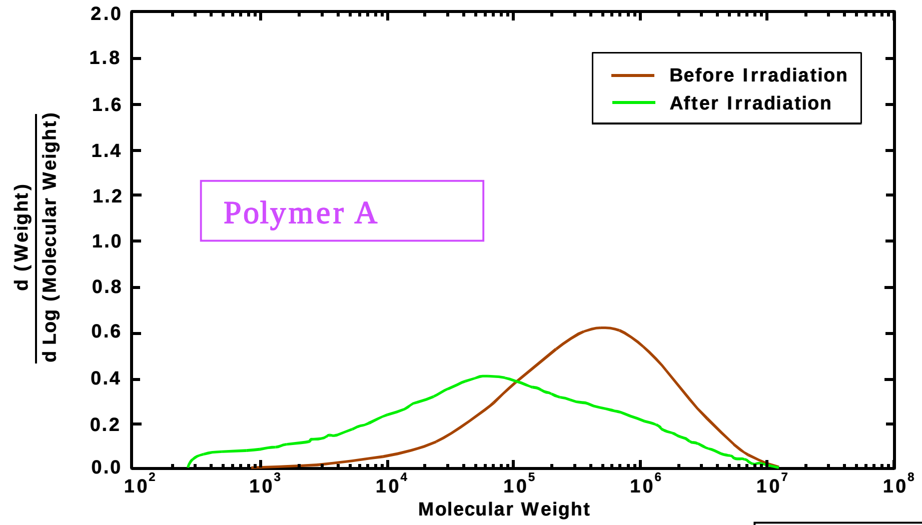
◆Evaluation conditions (Temporary)

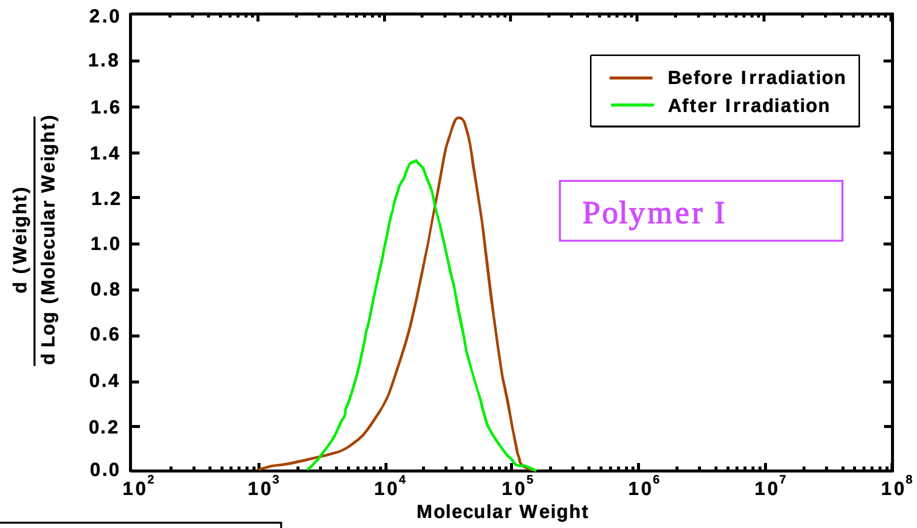
- Air blowing after irradiation (50J/cm^2)
  - Air gun : MODEL306 (Hugle Electronics Inc.)
    nozzle diameter : Φ2.5mm with 0.1um filter
  - Air pressure 1kgf/cm^2 (Air supply side)
  - Distance between nozzle and film : 50mm
  - Air blowing time : 5sec

GPC analysis of polymerA/I

Table 2. A comparison of polymer I with polymer A for the molecular weight change and distribution by F2 laser irradiation

Irradiation environment : He+O2(1000ppm)						
		Mn/10^4	Mw/10^4	Mz/10^4	Mw/Mn	Mz/Mw
Polymer A	before irradiation	5.92	85.20	274.00	14.39	3.22
	after irradiation	0.65	39.90	270.00	61.38	6.77
Polymer I	before irradiation	2.01	3.53	4.76	1.76	1.35
	after irradiation	1.57	2.30	3.05	1.47	1.33

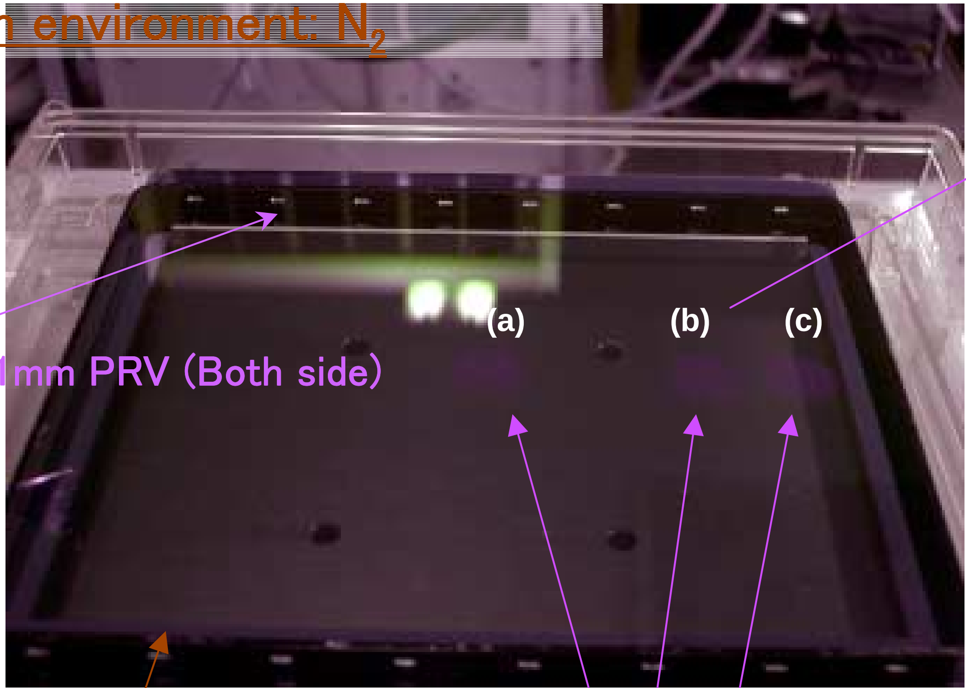




Exposure dose : 5.4 J/cm^2

As compared with polymer A, it seems that molecular weight change of polymer I is decreasing.

Irradiation durability as pellicle (1)



8 x 3mm x 1mm PRV (Both side)

Irradiation marks

Pellicle & pellicle frame using the new polymer by Mitsui Chemicals

After irradiation(50J/cm2)

Polymer I

Polymer A (reference)

Photo.2. Comparison of polymer I with polymer A for the appearance of pellicle that is attached to 6025 size photo mask.

Irradiation durability as pellicle (2)

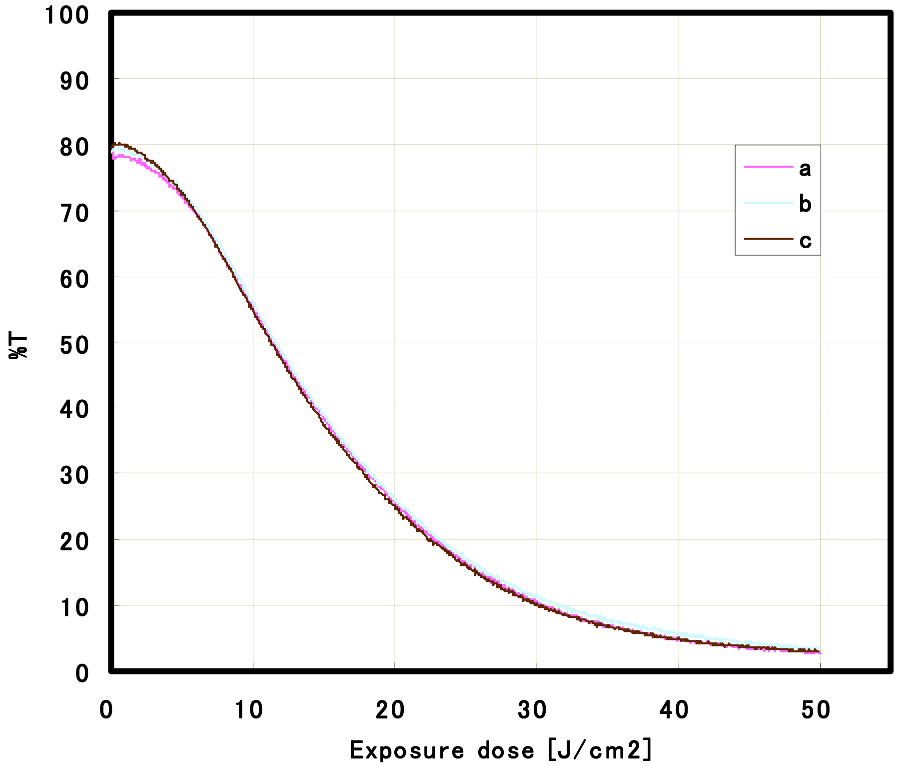


Fig.7. Dependence of transmittance on exposure dose at different position of photo mask.

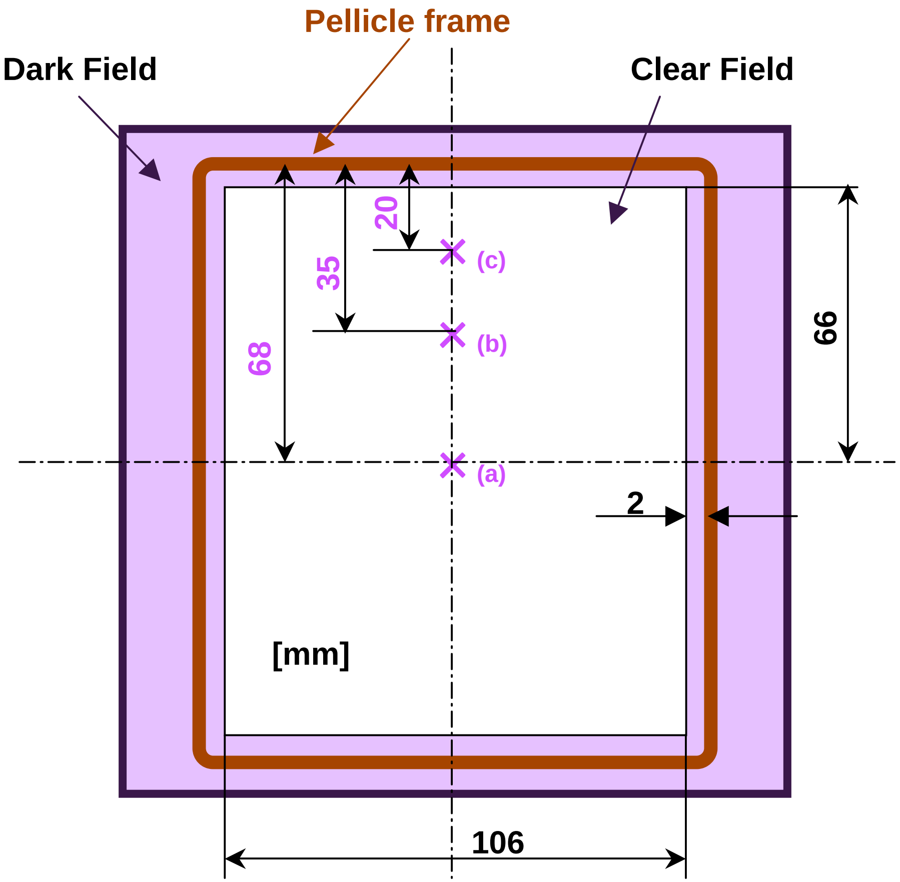


Fig.8. Schematic diagram of trial 6025 size photomask and irradiation points.

The variation of durability isn't observed in this condition.

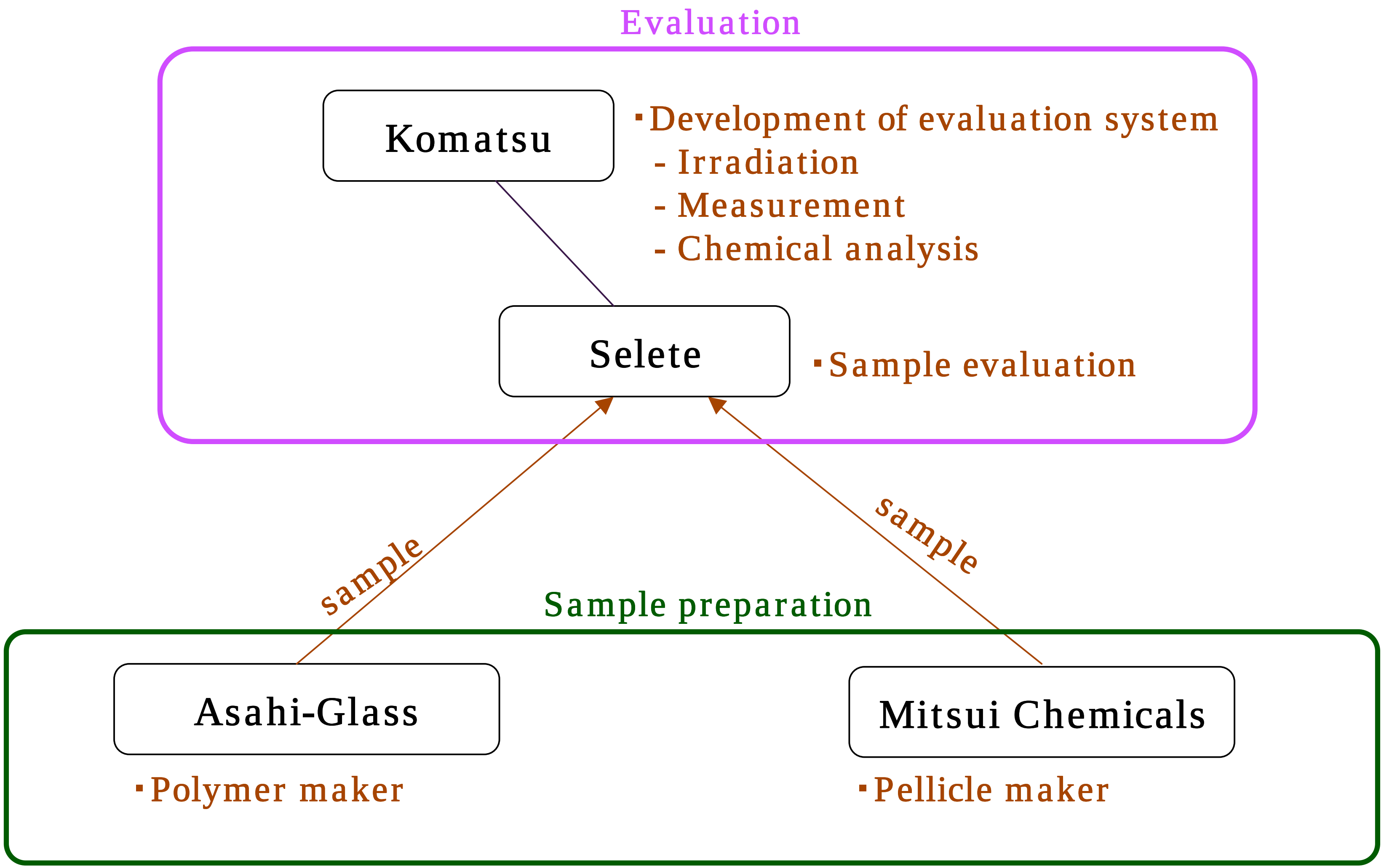
Summary and future plan

i. The durability including transmittance change and mechanical strength degradation of polymer I has improved more than twice compared with polymer A.

ii. The average molecular weight changing by irradiation of polymer I is less than polymer A. It seems that polymer I is more preferably for irradiation in oxygen-contained environmental gas than polymer A.

iii. Although the durability of soft pellicle is slightly improved in our investigation, it is far from industrial requirements. It seems that it is necessary to find a more effective technique to improve durability of polymer from now on.

Soft pellicle development organization



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