Contamination Removal of EUV Multilayer Optics Utilizing Atomic Hydrogen Generated by Heated Catalyzer

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Contamination Mitigation or Control :
One of Critical Issues in EUV lithography

Surface oxidation → Control of atmosphere in EUV exposure system
Oxidation resistant capping layer materials (Ru)

Carbon-contamination → Control of atmosphere in EUV exposure system
Cleaning methods

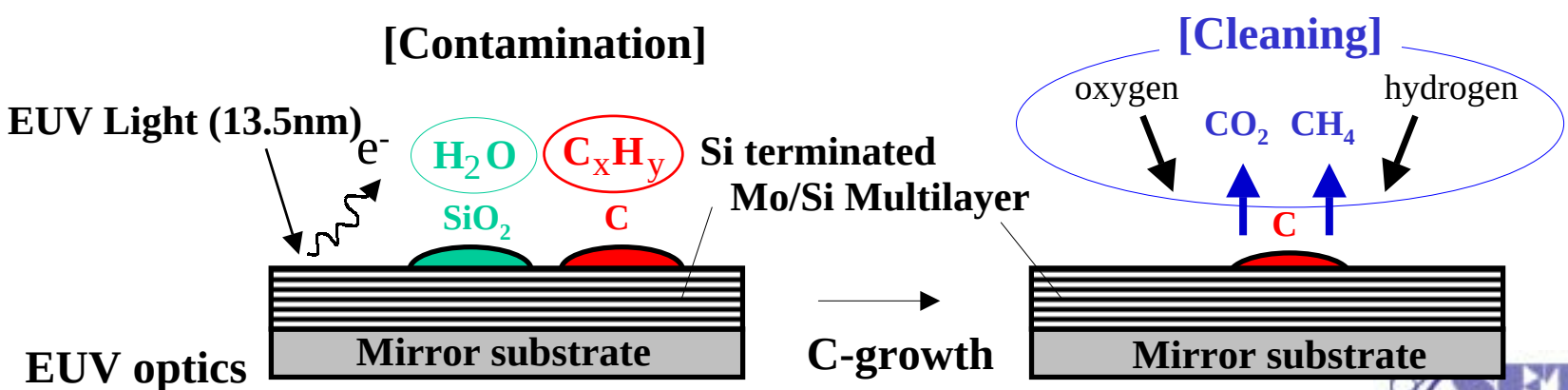
1. Oxidation (active oxygen excited by plasma, EUV, or synchrotron radiation (SR))

   Risk of Surface Oxidation

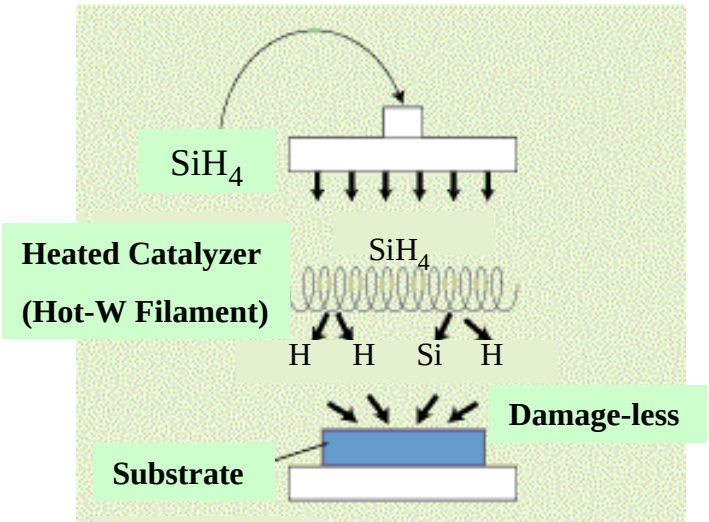
2. Reduction (atomic hydrogen produced by a filament of analysis-use source)

   Carbon Etching Rate:< 0.1 nm/min

Highly speedy and damage-less cleaning method is required.



Cleaning of Carbon Contamination with Catalytic or Hot-Wire CVD Apparatus



Catalytic (Hot-Wire)-CVD

Radical Formation by Heated Catlyzer (Hot-Wire Filament)

- no plasma damage
- large-area homogeneous film formation
- high radical density (~10^{14}/cm^3)
- Resist can be removed.

This Work

Apply to atomic hydrogen cleaning of carbon contamination on Mo/Si multilayer to aim highly speedy and damage-less cleaning

Sample preparation:

- Mo/Si Multilayer sputtered on Si wafer
- Carbon deposited on Multilayer

Measurement:

- Surface carbon amount by XPS
- Carbon film thickness by optical system
- EUV reflectivity by reflectometer

Experimental Procedure

- Bare Si-capped Mo/Si Multilayer (40-pair, a period of 7 nm) on 200mmΦSi wafer was sputtered by helicon DC sputtering system (ULVAC).

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- Initial EUV reflectivity measurement by reflectometer located on the beamline SBL-1 at the Super-ALIS SR ring in NTT
  (Measurement error: ΔR：< 1% (3σ), Δλ：< 0.01 nm (3σ))

- Carbon contamination on Mo/Si multilayer was deposited by SR-irradiation.
  - Surface carbon amount by *ex situ* XPS
    (S-PROBE :SURFACE SPECTROMETER)
  - Carbon film thickness by optical thickness measuring system
  - EUV reflectivity measurement

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- Atomic hydrogen cleaning of carbon contamination
  - Surface carbon amount by *ex situ* XPS
  - Carbon film thickness by optical thickness measuring system
  - EUV reflectivity measurement

Carbon contamination deposition and Carbon film thickness

- Carbon contamination on Mo/Si multilayer was deposited by SR-irradiation.

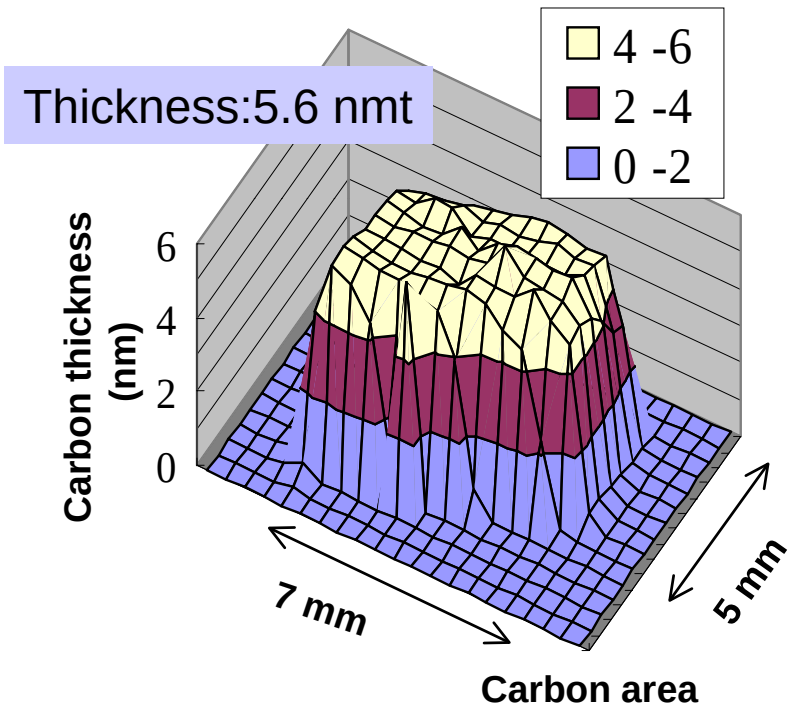
SR-irradiation conditions

SR Wavelength：1 nm～20 nm (grazing mirror, Zr 0.2 umt filter)

Back-Pressure：$2*10^{-4}$～$7*10^{-6}$ Pa

Dose：10000 A・sec

- Carbon film thickness measurement by optical thickness measuring systems

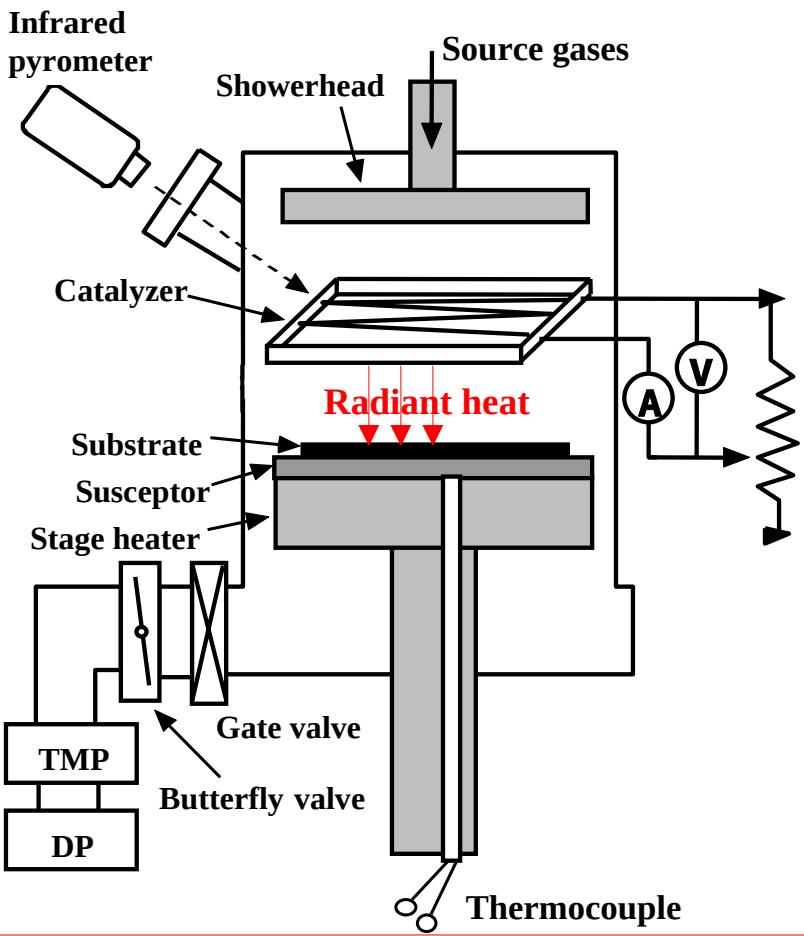


Measurement conditions

Refractive index of carbon film:
Spectro-ellipsometer NPDM-100M (Nikon)

Thickness Distribution of carbon film:
M5100A (NAMOMETARICS)

Preliminary cleaning test: Catalytic (Hot-wire)-CVD apparatus as Atomic Hydrogen Cleaning System



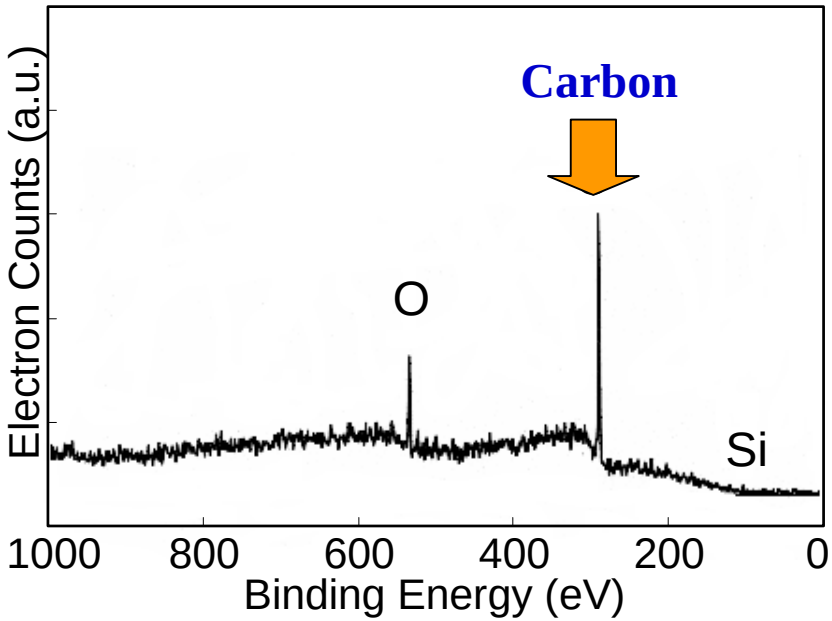
Catalytic (Hot-wire)-CVD apparatus

Table 1. Cleaning Conditions

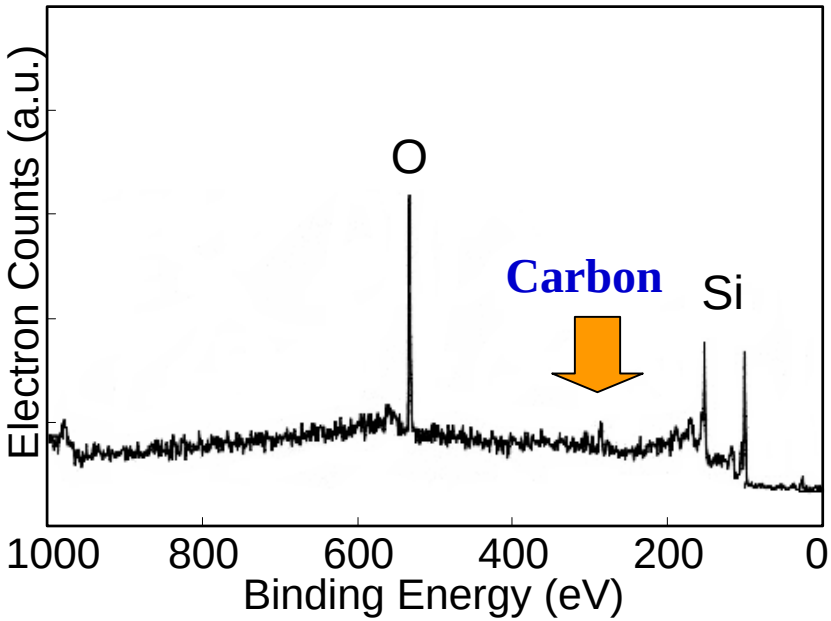
Catalyzer Material	Tungsten
Catalyzer Temperature	1800 ℃
Substrate Temperature	> 100 ℃
Chamber back-Pressure (Pump system: TMP+DP)	< $7*10^{-5}$ Pa
Hydrogen(H2) Pressure	10 Pa
Hydrogen(H2) flow rate	200 sccm
Cleaning time	1- 10 min.
Distance between Catalyzer and sample	100 mm

Ex situ XPS measurement of ML surface before and after cleaning treatment

As carbon-deposited (5.6 nm-thick C deposition)



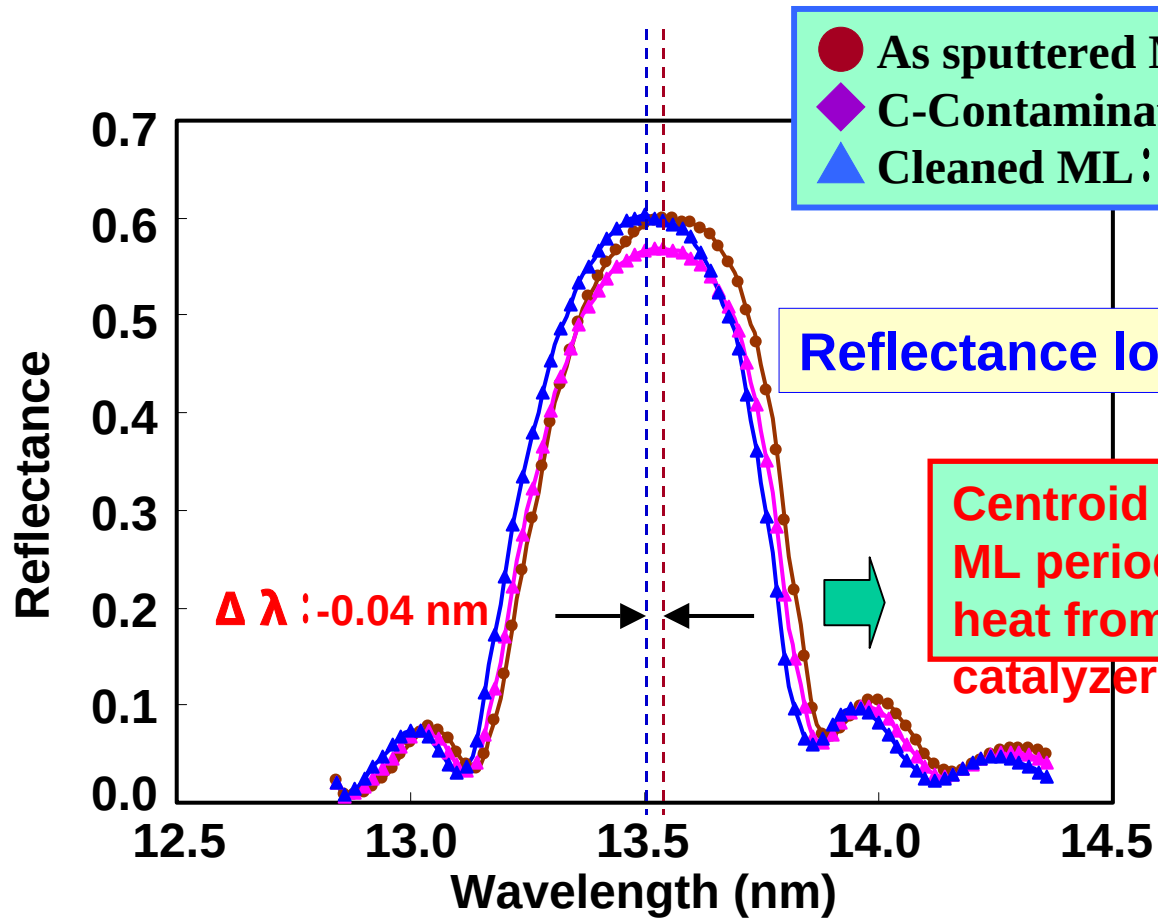
After cleaning treatment



Catalyzer temperature：1800 ℃
Treatment time ： 1 min.

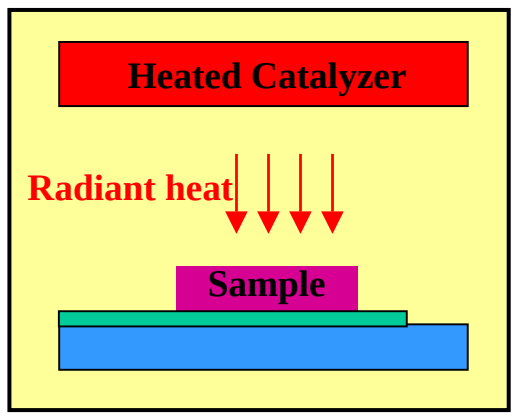
Carbon contamination has been removed.

Reflectance Loss by Carbon Deposition and Its Recovery, but Damage (Centroid shift) by Atomic H Cleaning



Reflectance loss has been recovered.

Centroid shift (shrink of ML period) due to radiant heat from heated catalyzer.



To intercept radiant heat from heated catalyzer is required.

Improved Cleaning apparatus utilizing Atomic Hydrogen Generated by Heated Catalyzer

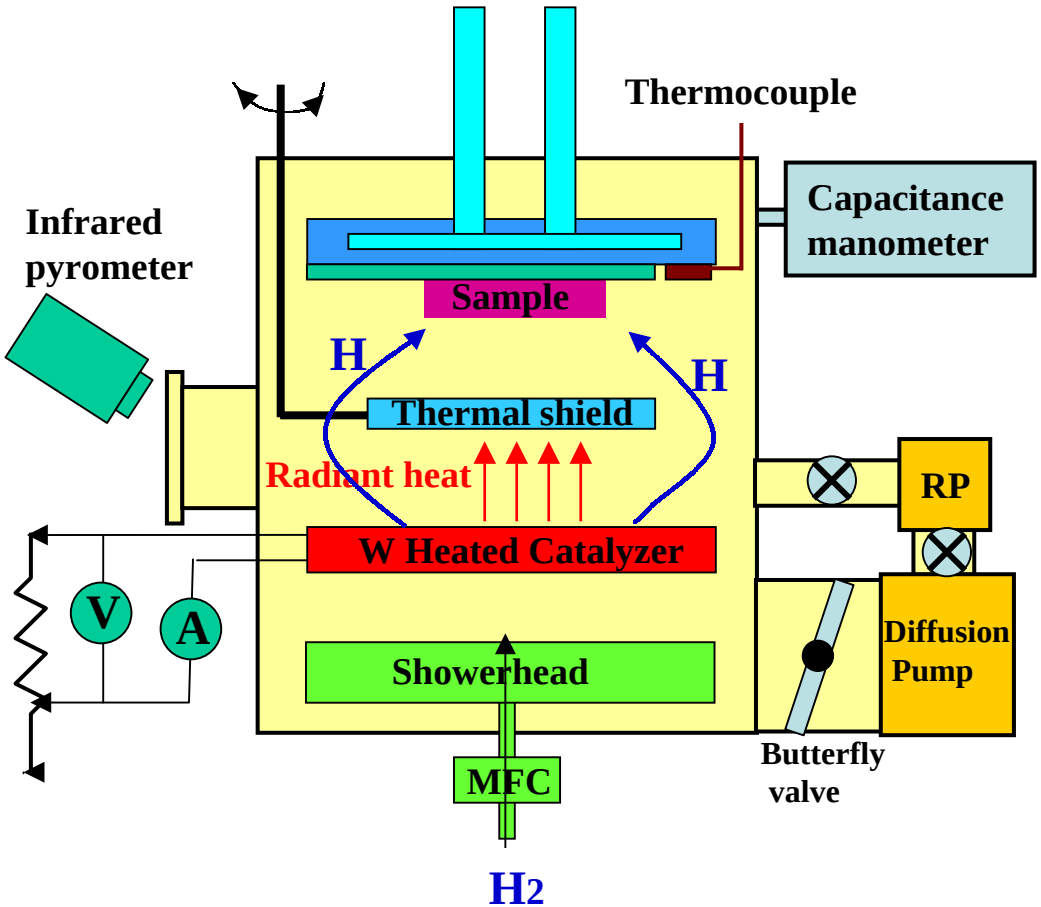
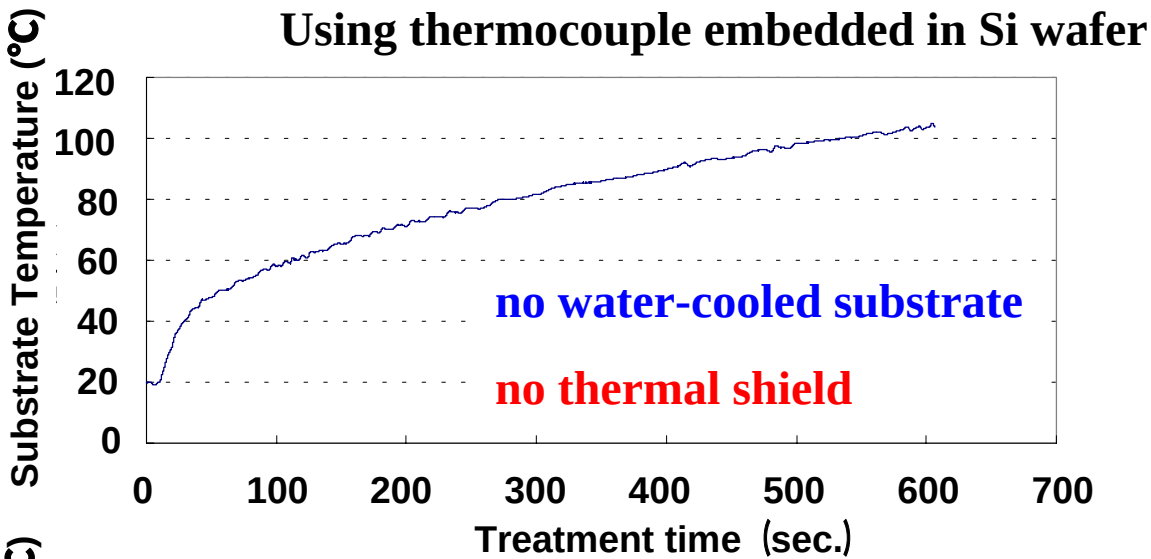
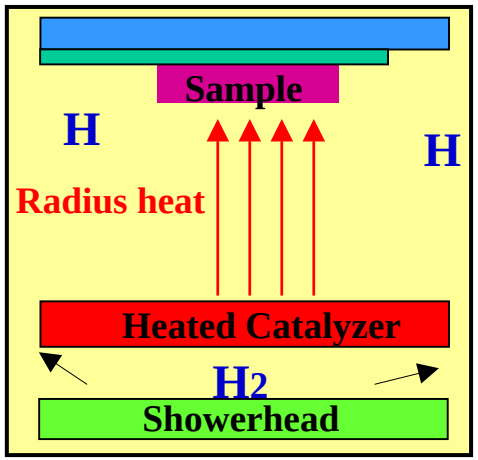


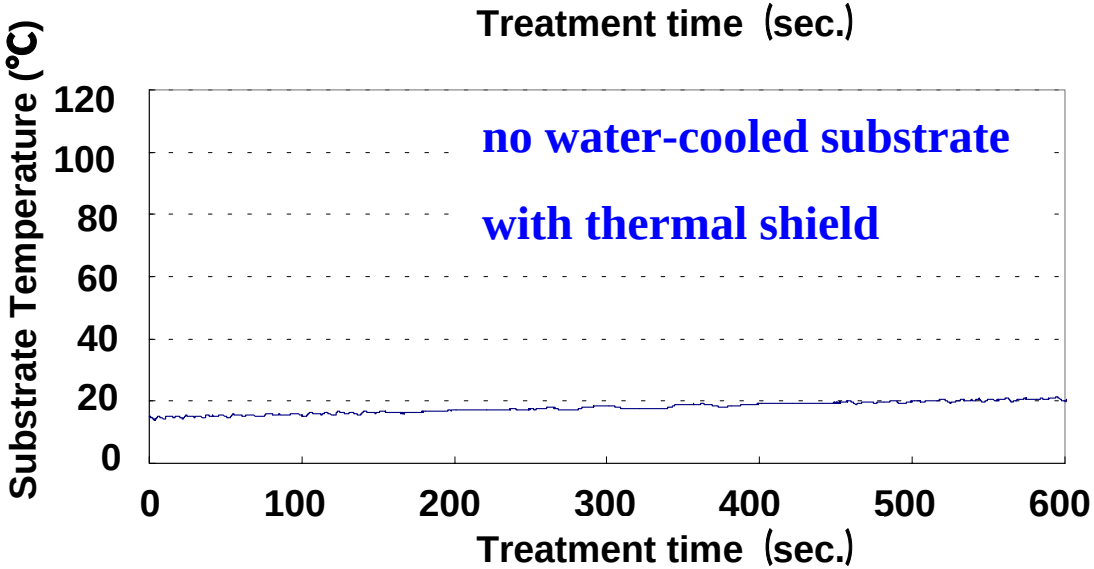
Table 2. Cleaning Conditions

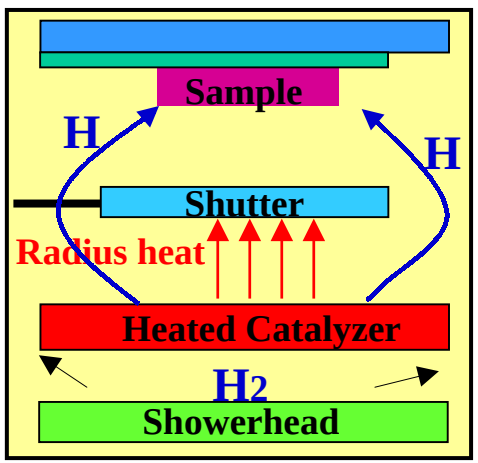
Catalyzer Material	Tungsten
Catalyzer Temperature	1800 ℃
Water-cooled Substrate	No
Thermal Shield	Yes
Chamber back-Pressure	$7*10^{-4}$ Pa
(Pump system: Diffusion-P+RP)	
Hydrogen(H_2) Pressure	66.5 Pa
Hydrogen(H_2) flow rate	100 sccm
Cleaning time	10 min.
Distance between Catalyzer and sample	50 mm

Preliminary Experiment 2：Substrate Temperature









Thermal shield is available to intercept radiant heat from heated catalyzer.

Preliminary Experiment 3：Resist Etching

Table 3. Resist etching Conditions

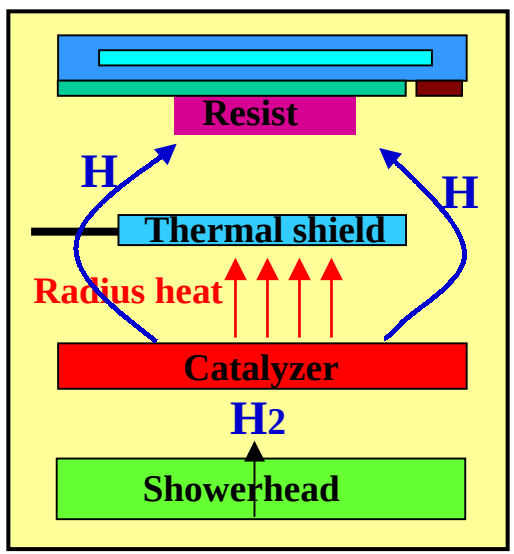
Negative tone resist (ZPN103-39)	1.2 um^t
Catalyzer Material	Tungsten
Catalyzer Temperature	1800 ℃
Water-cooled Substrate	No
Thermal shield	Yes
Substrate Temperature	about 20 ℃
Chamber back-Pressure (Pump system: Diffusion-P+RP)	$7*10^{-4}$ Pa
Hydrogen(H_2) Pressure	66.5 Pa
Hydrogen(H_2) flow rate	100 sccm
Resist etching time	30 min.
Distance between Catalyzer and sample	50 mm

After treatment

Resist thickness :0.7 um^t (Δt：-0.5 um^t)

Resist etching rate:16.7 nm/min

Treatment with thermal shield is able to clean or etch carbon by atomic hydrogen turning the thermal shield.

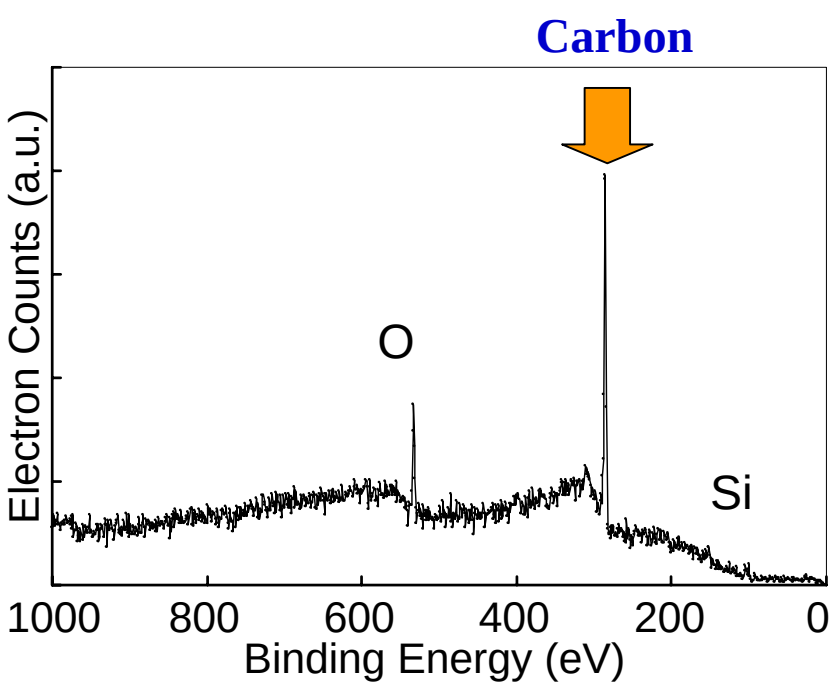


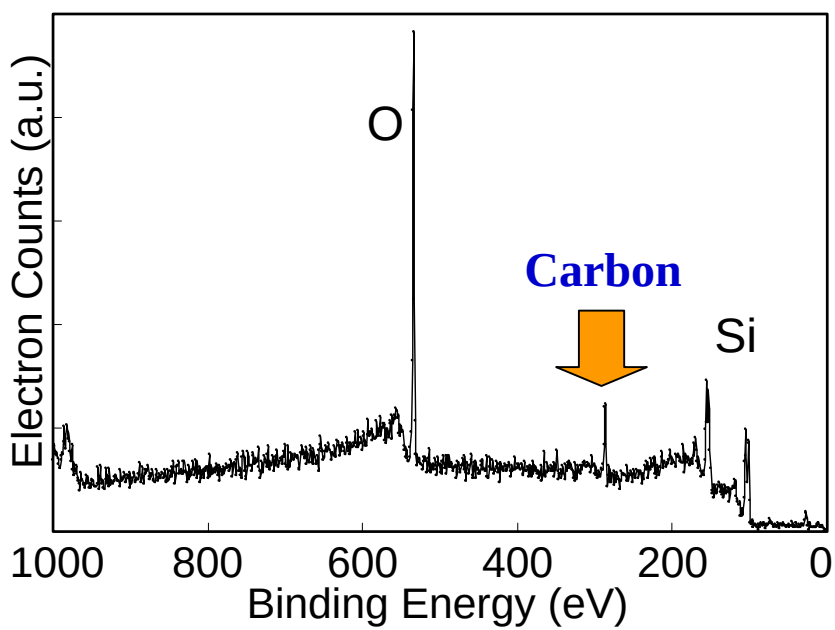
Ex situ XPS measurement of ML surface before and after cleaning treatment with thermal shield

As carbon-deposited (5.6 nm-thick C deposition)

After cleaning treatment with thermal shield

Catalyzer temperature：1800 ℃
Treatment time ： 10 min.



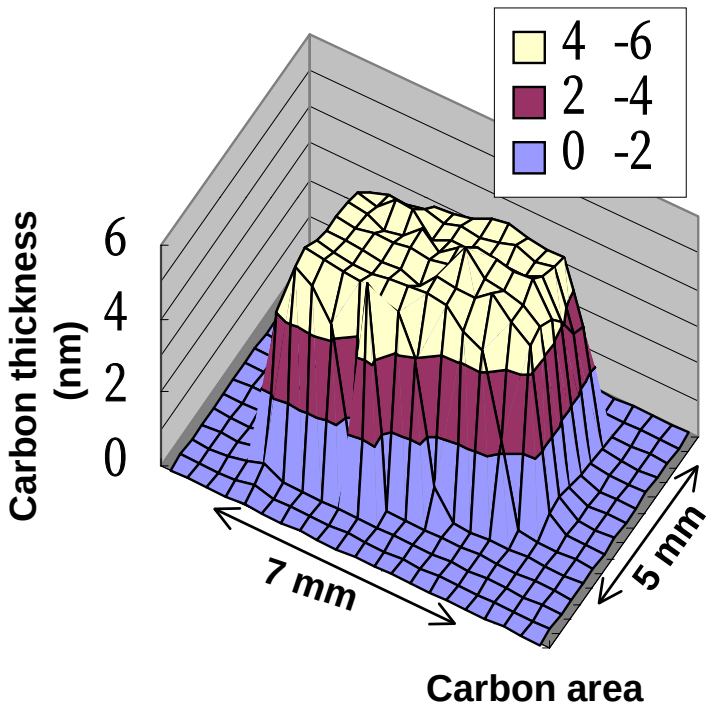


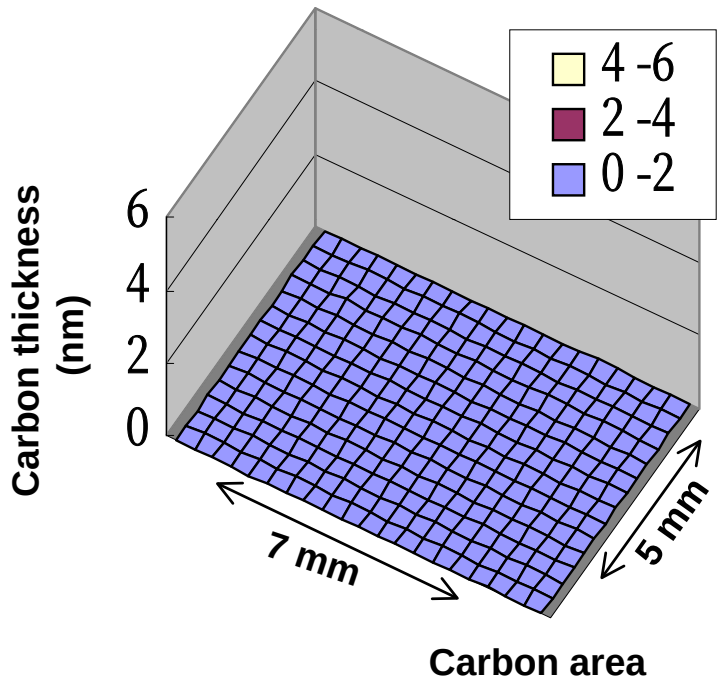
Remaining carbon may result from the back diffusion of diffusion pump.

Thickness measurements of Carbon on ML before and after cleaning treatment

As carbon deposited
(5.6 nm-thick C deposition)

After cleaning treatment
Thickness: negligible





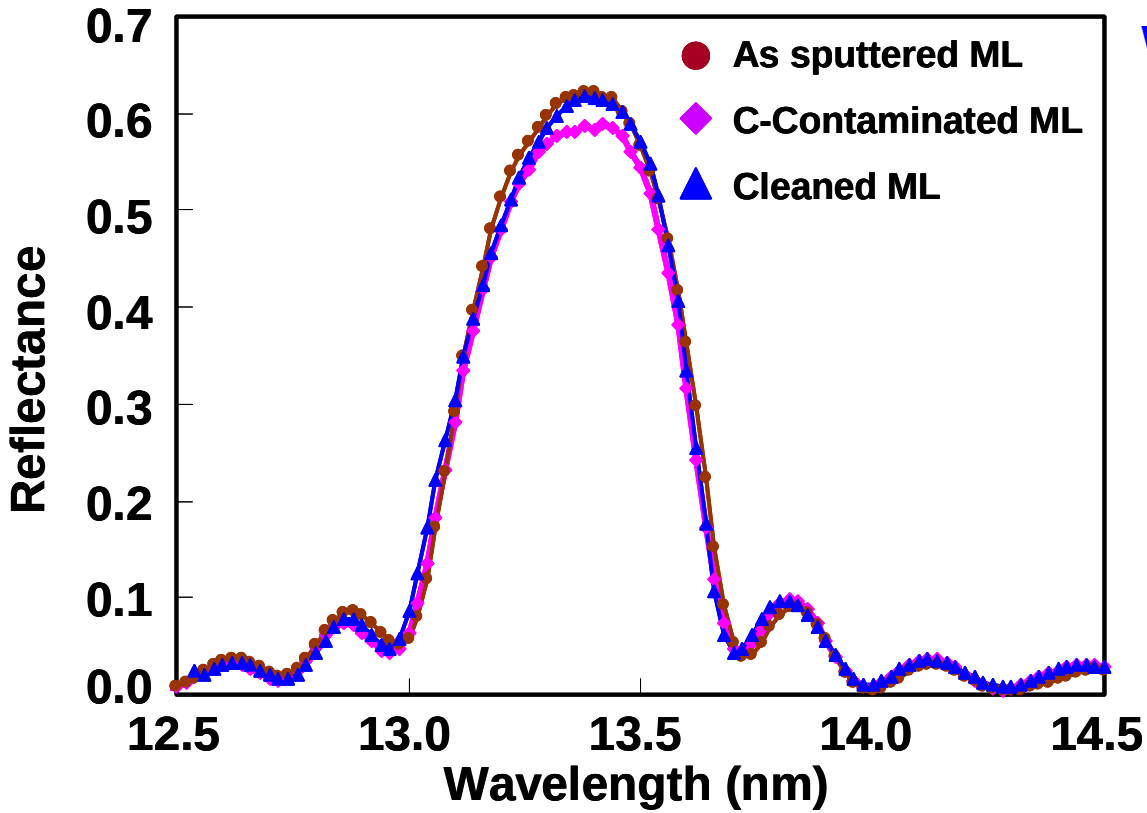
Carbon contamination has been removed.

Carbon-etching rate: > 0.6 nm/min.

Measurements of EUV Reflectivity as sputtered, Carbon deposited and after cleaning treatment with thermal shield

	As sputtered ML	→	C deposition 5.6 nm-thick C	→	After cleaning treatment (10 minutes)	
R_{peak}	: 62.2%	→	58.9%	→	61.7%	ΔR : -0.5 %
λ Centroid	: 13.361 nm	→	13.356 nm	→	13.353 nm	Δλ : -0.008 nm

Within measurement error



Summary

We proposed carbon contamination removal of EUV multilayer optics utilizing atomic hydrogen generated by the heated catalyzer as highly speedy and damage-less cleaning method.

1. **Thermal shield located between catalyzer and sample realized cleaning treatment to intercept radiant heat from heated catalyzer.**
2. **XPS and carbon thickness measurements showed that carbon contamination on multilayers after cleaning was completely removed.**
3. **EUV reflectivity and its centroid of multilayers were marginally changed within measurement accuracy before and after cleaning treatment.**

EUV reflectivity loss $\Delta R < -0.5\ \%$ Centroid shift $\Delta \lambda < -0.01$ nm

This cleaning method restores EUV reflectivity of a multilayer without any damage.

Next concern : Transport of atomic hydrogen