Carbon Deposition on Si-Capped Multi-layer Mirrors by Extreme Ultraviolet Ray Irradiation

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*EUVA: Extreme Ultraviolet Lithography System Development Association

Background

- **Background**

  Organic gases in EUV litho tool

  Carbon deposition on the mirror by EUV irradiation

  Reflectance degradation of the mirror

- **Study**

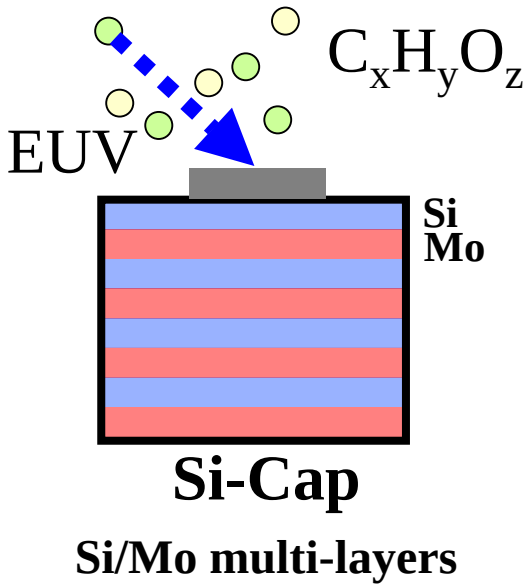
  Dependence on

  organic gas species,

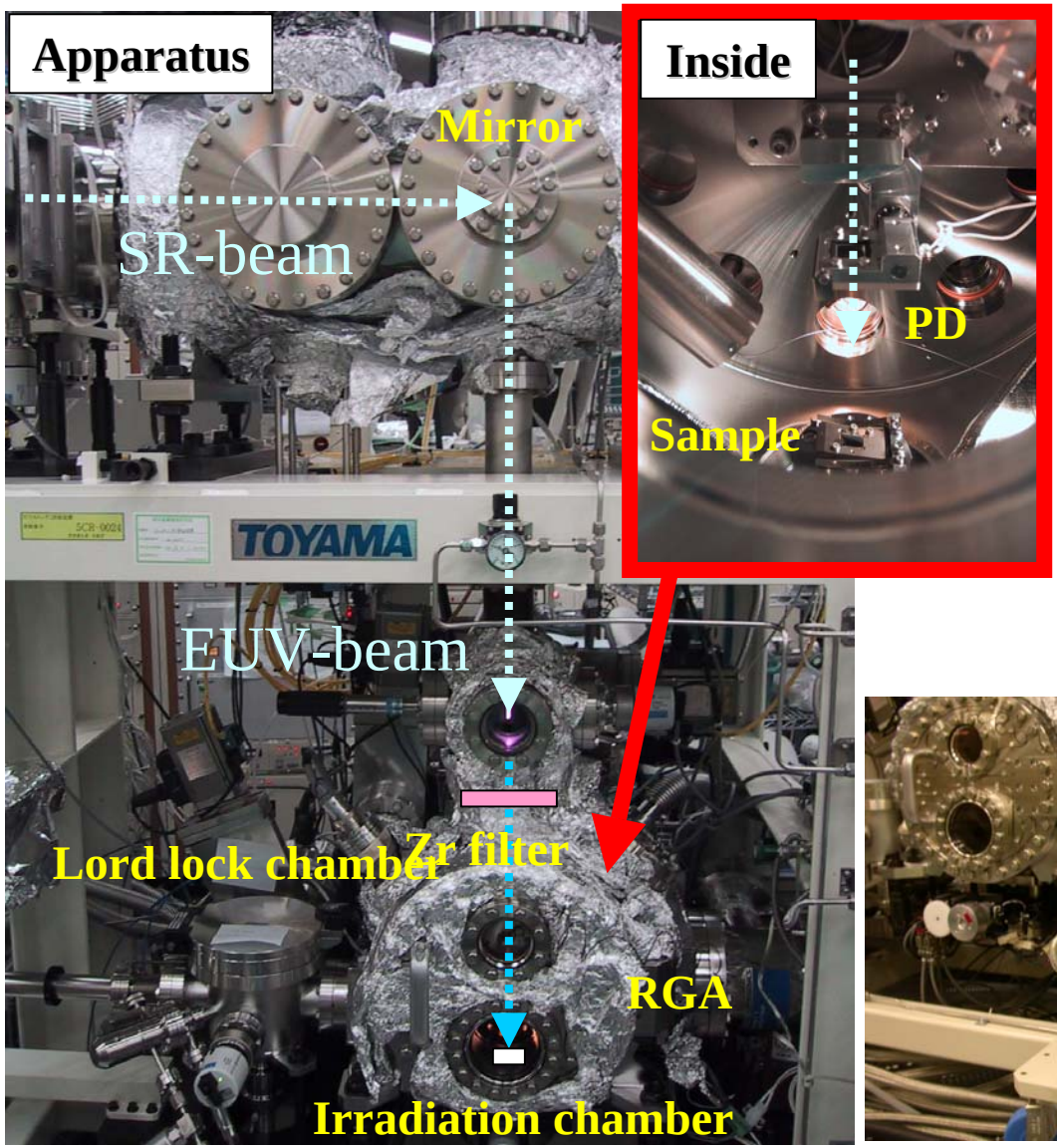
  organic gas pressure and

  EUV light intensity

  in the carbon deposition

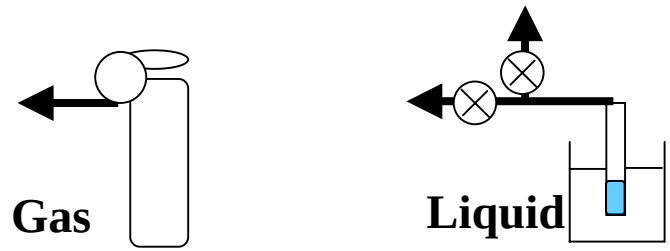


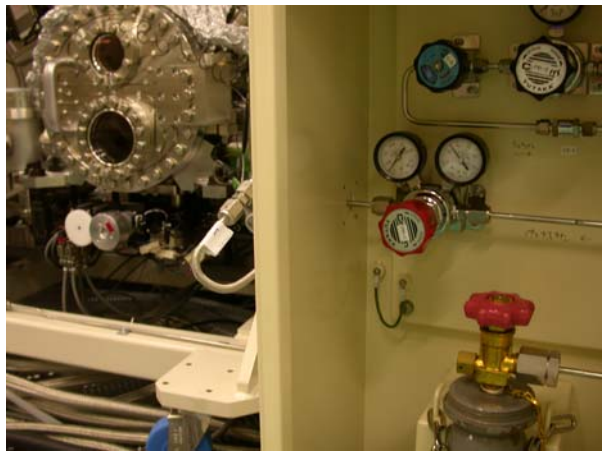
Apparatus

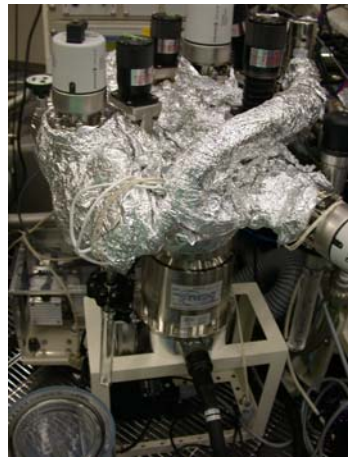


SR-beam:Super-ALIS SBL2
Light intensity:32~mW/mm^2
Beam size:1 × 1.5mm
Background Pressure:5e-7Pa

1. Organic gas injection
2. In-site reflectance measurement







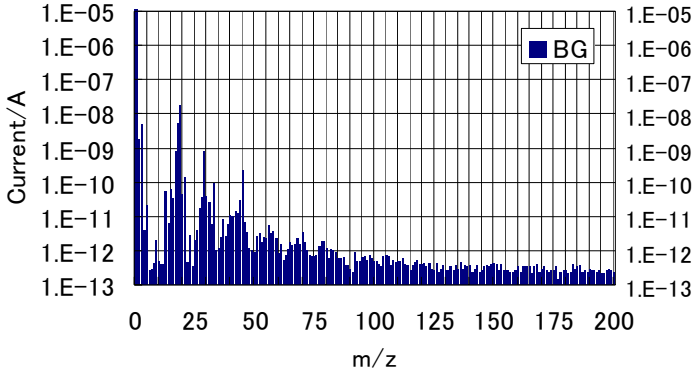
Experiments

Si-Cap samples ware irradiated by EUV light with organic gas injections.

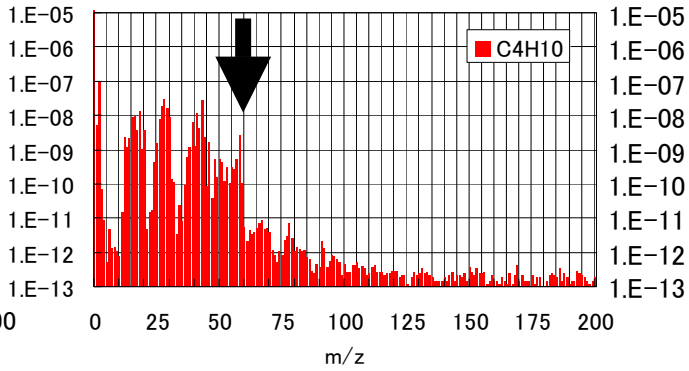
1.	**Buthane**	C_4H_{10}	aliphatic hydrocarbon
2.	**Buthanol**	$C_4H_{10}O$	aliphatic alcohol
3.	**Methyl propionate**	$C_4H_8O_2$	aliphatic ester
4.	**Hexane**	C_6H_{14}	aliphatic hydrocarbon
5.	**Perfluoro octane**	C_8F_{18}	aliphatic fluorocarbon
6.	**Decane**	$C_{10}H_{22}$	aliphatic hydrocarbon
7.	**Decanol**	$C_{10}H_{22}O$	aliphatic alcohol
8.	**Methyl nonanoate**	$C_{10}H_{20}O_2$	aliphatic ester
9.	**Diethyl benzene**	$C_{10}H_{14}$	aromatic hydrocarbon
10.	**Dimethyl phthalate**	$C_{10}H_{10}O_4$	aromatic ester
11.	**Hexadecane**	$C_{16}H_{34}$	aliphatic hydrocarbon

RGA Spectrums of Organic Gases

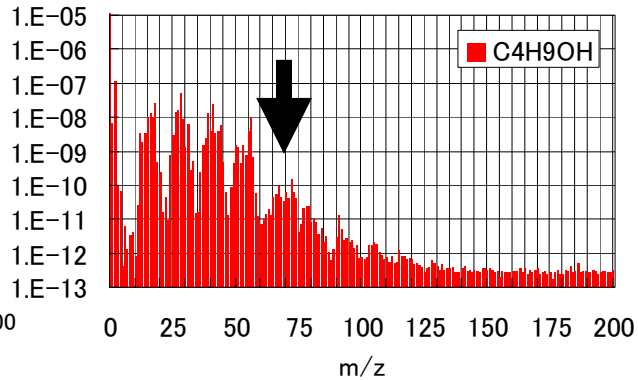
Background



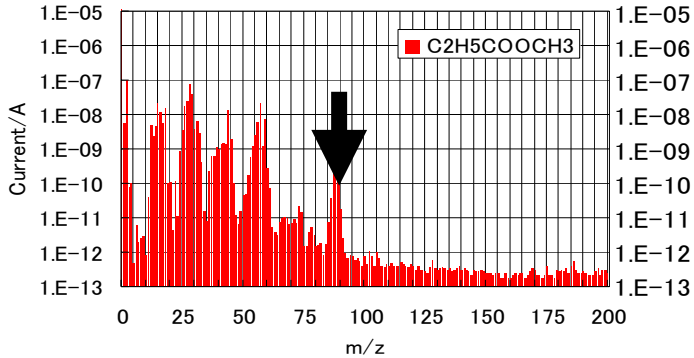
Buthane
C_4H_{10} M.W.=58



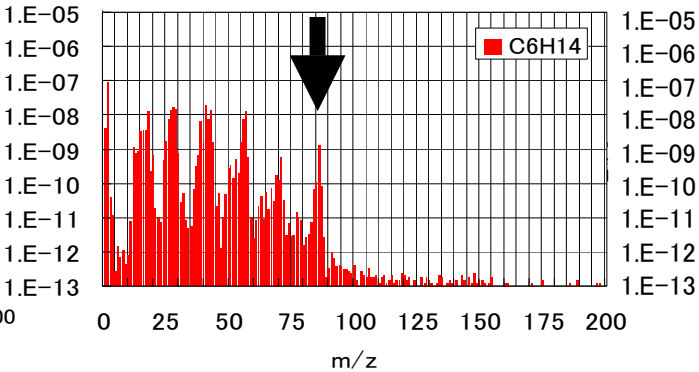
Buthanol
$C_4H_{10}O$ M.W.=74



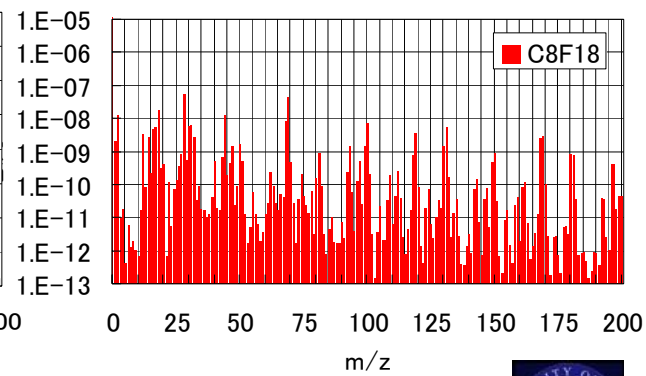
Methyl propionate
$C_4H_8O_2$ M.W.=88



Hexane
C_6H_{14} M.W.=86

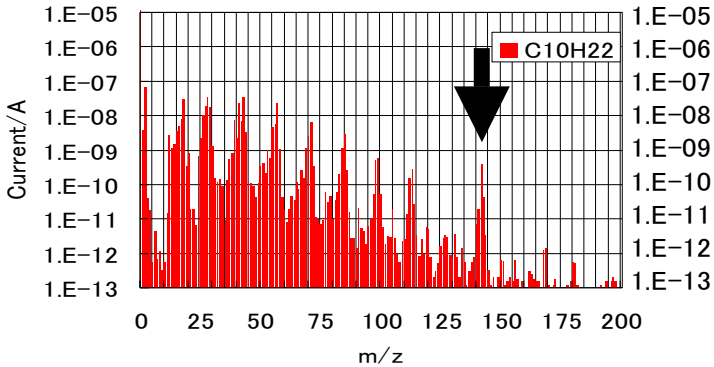


Perfluoro octane
C_8F_{18} M.W.=438

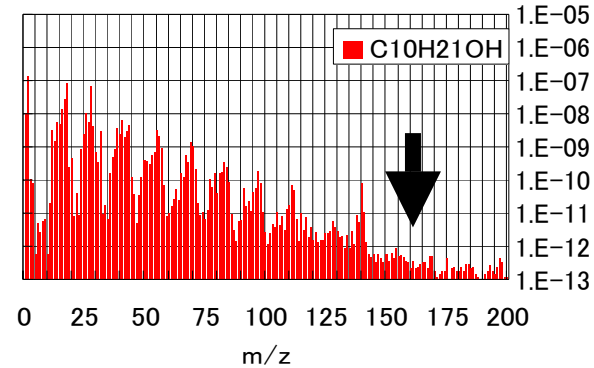


RGA Spectrums of Organic Gases

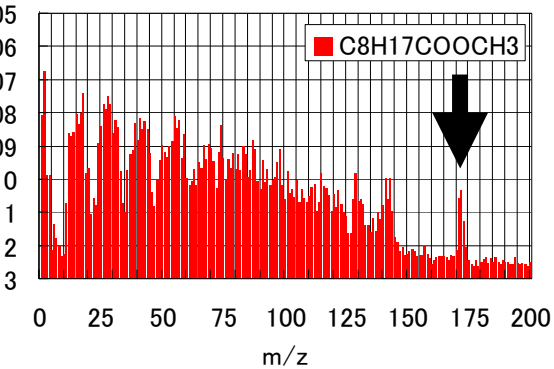
Decane
$C_{10}H_{22}$ M.W.=142



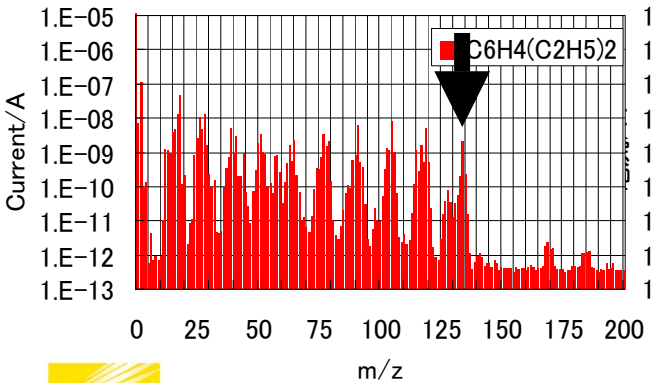
Decanol
$C_{10}H_{22}O$ M.W.=158



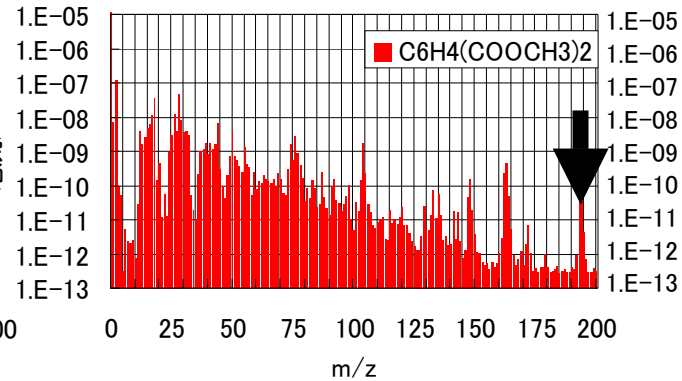
Methyl nonanoate
$C_{10}H_{20}O_2$ M.W.=172



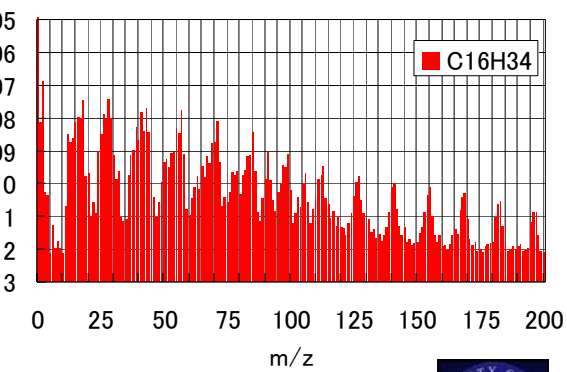
Diethyl benzene
$C_{10}H_{14}$ M.W.=134



Dimethyl phthalate
$C_{10}H_{10}O_4$ M.W.=194

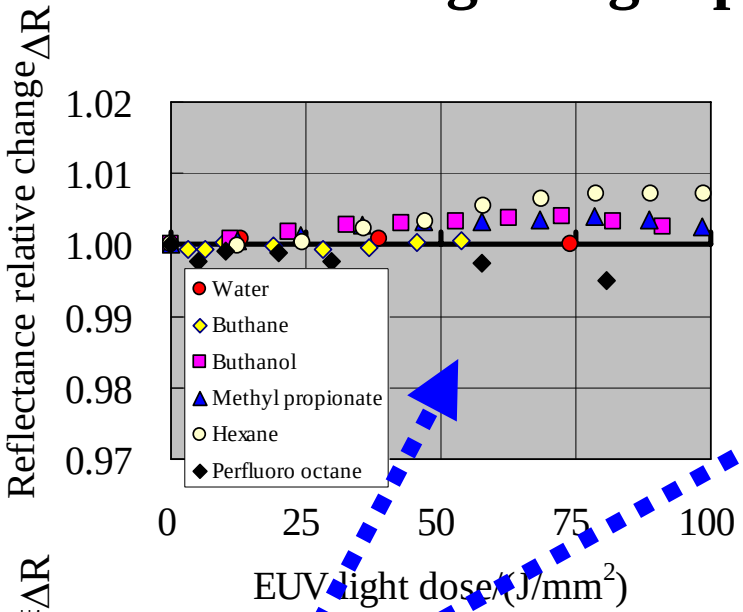


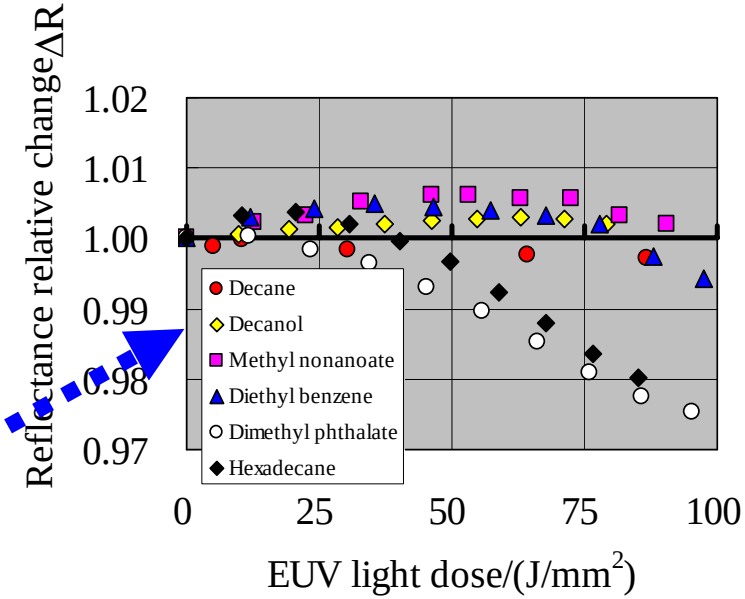
Hexadecane
$C_{16}H_{34}$ M.W.=226

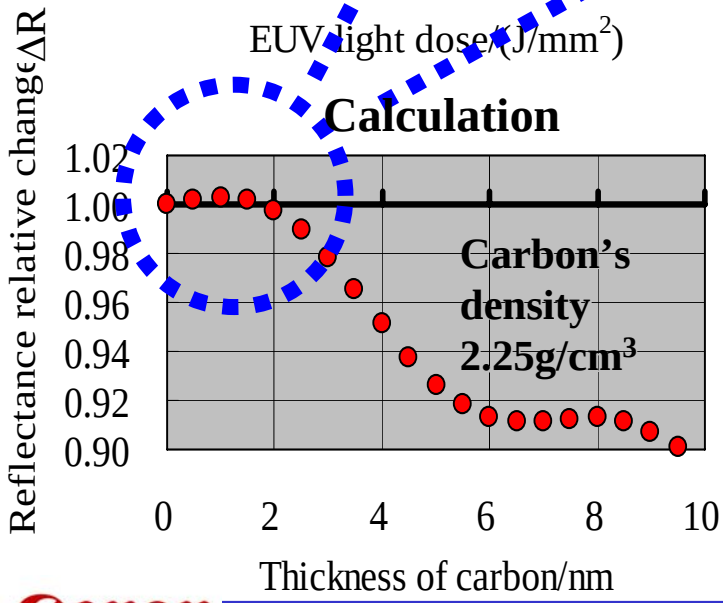


Reflectance Changes

Condition: 1E-5Pa organic gas pressure, 16mW/mm^2 EUV intensity





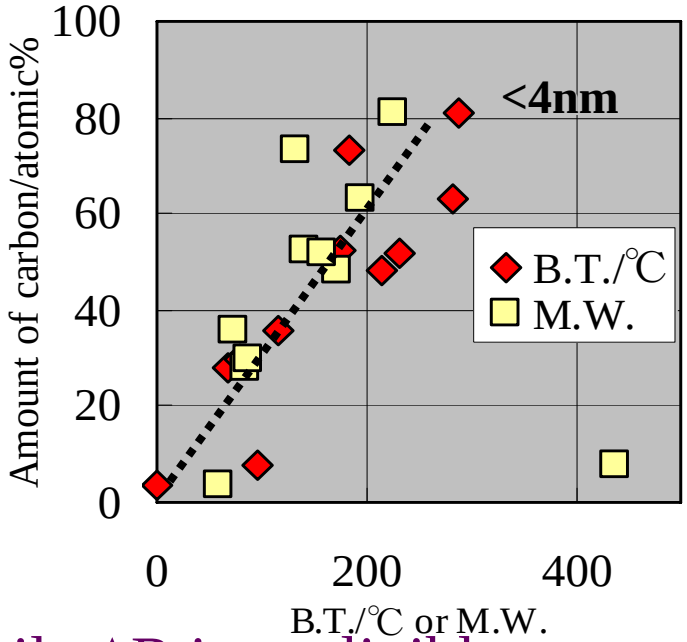


- **Thin carbon films**
- **Small difference in ΔR**

Dependence on Organic Gas Species

Amount of deposited carbon was measured by XPS
Condition: 1E-5Pa organic gas pressure, 180J/mm^2 EUV dose

Organic gas	B.T./℃	M.W.
Buthane	-1	58
Buthanol	117	74
Methyl propionate	79	88
Hexane	69	86
Perfluoro octane	97	438
Decane	174	142
Decanol	231	158
Methyl nonanoate	214	172
Diethyl benzene	183	134
Dimethyl phtalate	283.7	194
Hexadecane	287	226

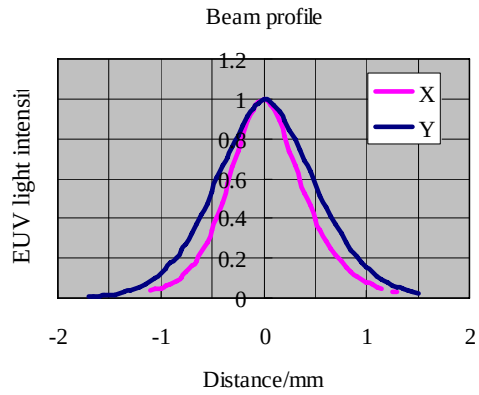


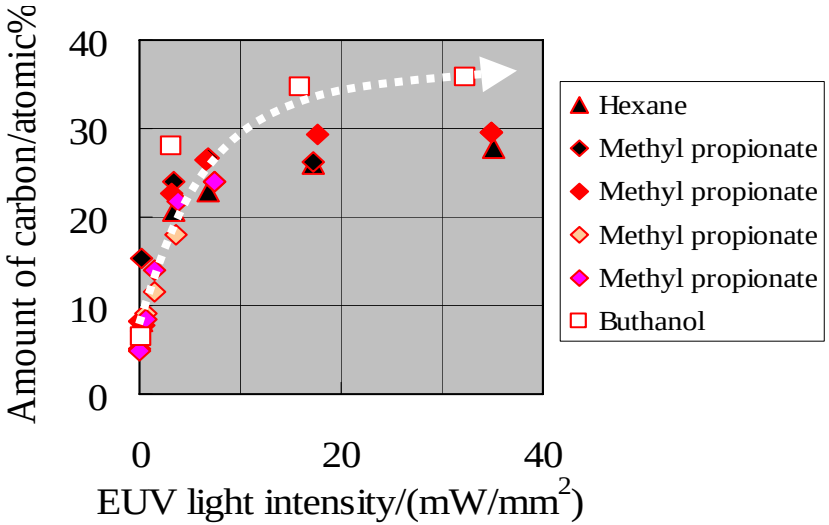
- ✓ XPS can revealed the difference while ΔR is negligible.
- ✓ Organic gases with higher boiling temperature or heavier molecular weight show larger carbon deposition rates.

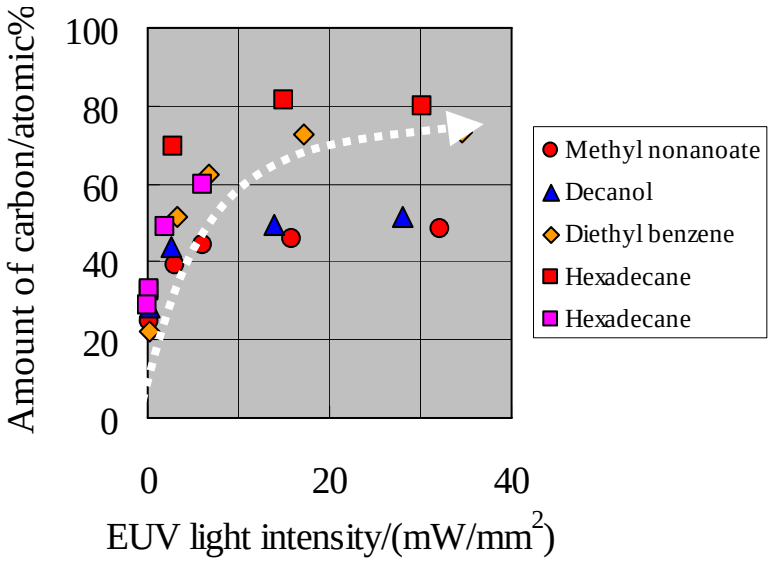
Dependence on EUV Light Intensity

From carbon distributions on irradiated samples.

(90 min. irradiation)



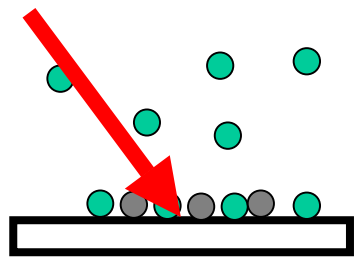




Carbon deposition rates increase rapidly, while it becomes saturated.

Carbon Deposition Model

Absorbed organic gases meet EUV light efficiently.



1. Absorption and desorption

$$[\text{Organic gas}]+[\text{Surface}] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [\text{Organic gas-Surface}]$$

2. Carbon deposition by EUV irradiation

$$[\text{Organic gas-Surface}]+[\text{EUV}] \xrightarrow{k_2} [\text{Deposited carbon}]$$

This model leads to the carbon deposition rate

$$\frac{d[\text{Carbon}]}{dt} = \frac{k_1 k_2 [\text{Organic gas}][\text{EUV}]}{k_{-1}+k_2[\text{EUV}]}\{1-e^{-(k_{-1}+k_2[\text{EUV}])t}\}$$

[Organic gas]:organic gas pressure, [(Deposited) carbon]:surface concentration of carbon, [EUV]:EUV light intensity, t:time, k_1:reaction rate constant of absorption, k_{-1}:reaction rate constant of desorption, k_2:reaction rate constant of organic gas

Carbon Deposition Model

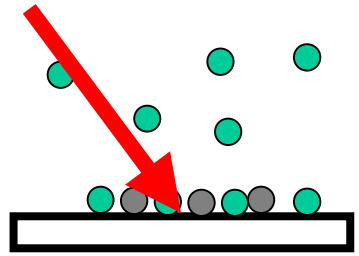
$$\frac{d[\text{Carbon}]}{dt} = \frac{k_1 k_2 [\text{Organic gas}][\text{EUV}]}{k_{-1} + k_2[\text{EUV}]} \{1 - e^{-(k_{-1} + k_2[\text{EUV}])t}\}$$

$$k_{-1} \sim 0 \text{ or } k_{-1} << k_2[\text{EUV}]$$

$$\frac{d[\text{Carbon}]}{dt} = k_1[\text{Organic gas}](1 - e^{-k_2[\text{EUV}]t})$$

$$[\text{EUV}] \rightarrow \infty$$

$$\frac{d[\text{Carbon}]}{dt} = k_1[\text{Organic gas}]$$

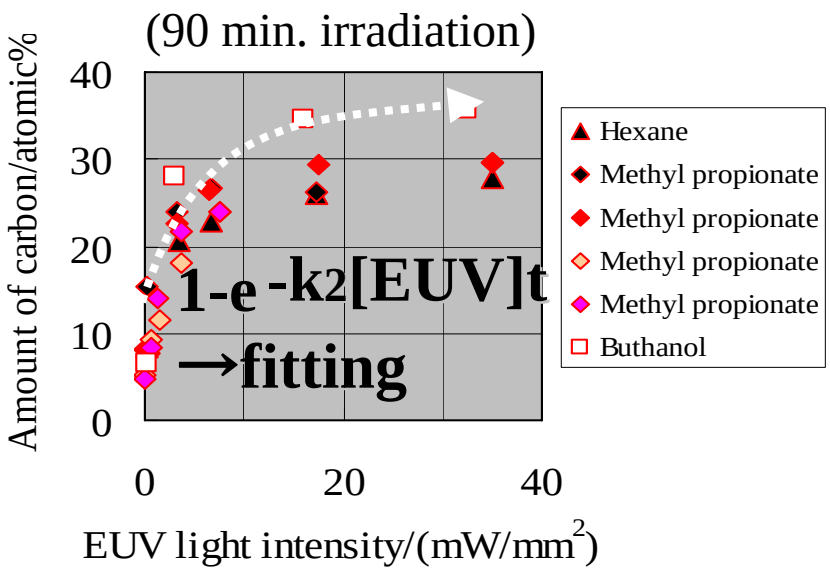


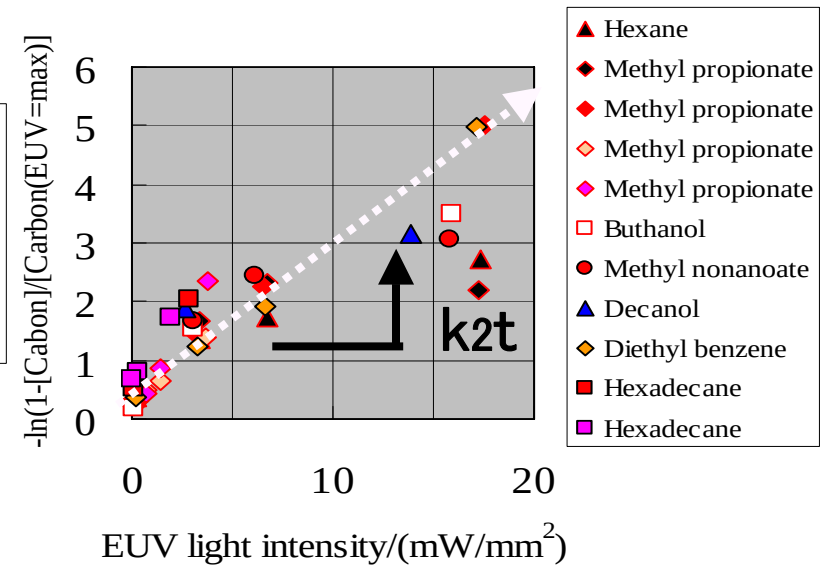
Dependence on organic gas species: gas pressure, k_1

Dependence on EUV light intensity: $1 - e^{-k_2[\text{EUV}]t}$

Dominant factor

$$\frac{d[\text{Carbon}]}{dt} = k_1[\text{Organic gas}](1-e^{-k_2[\text{EUV}]t})$$





- **k2 factors are almost constant.**
- **k1 factors are dominant.**

Summary

Dependence was researched to understand the carbon deposition.

✓Si-Cap samples were irradiated with organic gas injections. Reflectance changes and surface carbon were measured.

✓ Organic gases with higher B.T. or heavier M.W. show faster carbon deposition rates.

✓ Carbon deposition rates increase rapidly, but become saturated.

Carbon deposition model

Absorbed organic gases result in the carbon deposition by EUV.

The reaction rate constant of absorption (k_1) is dominant.

Acknowledgments

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