Study of Contamination due to EUV Resist Outgassing

Isamu Takagi, Toshiya Takahashi, Norihiko Sugie, Kazuhiro Katayama,
Yukiko Kikuchi, Eishi Shiobara, Hiroyuki Tanaka, and Soichi Inoue
EUVL Infrastructure Development Center, Inc. (EIDEC)

Takeo Watanabe, Tetsuo Harada and Hiroo Kinoshita
Laboratory of Advanced Science and Technology for Industry, University of Hyogo

Outline

- Introduction
- Previous work at EIDEC
- PAG induced contaminants behavior before and after H-Cleaning
- Anion-contamination dependence on anion size
- Summary

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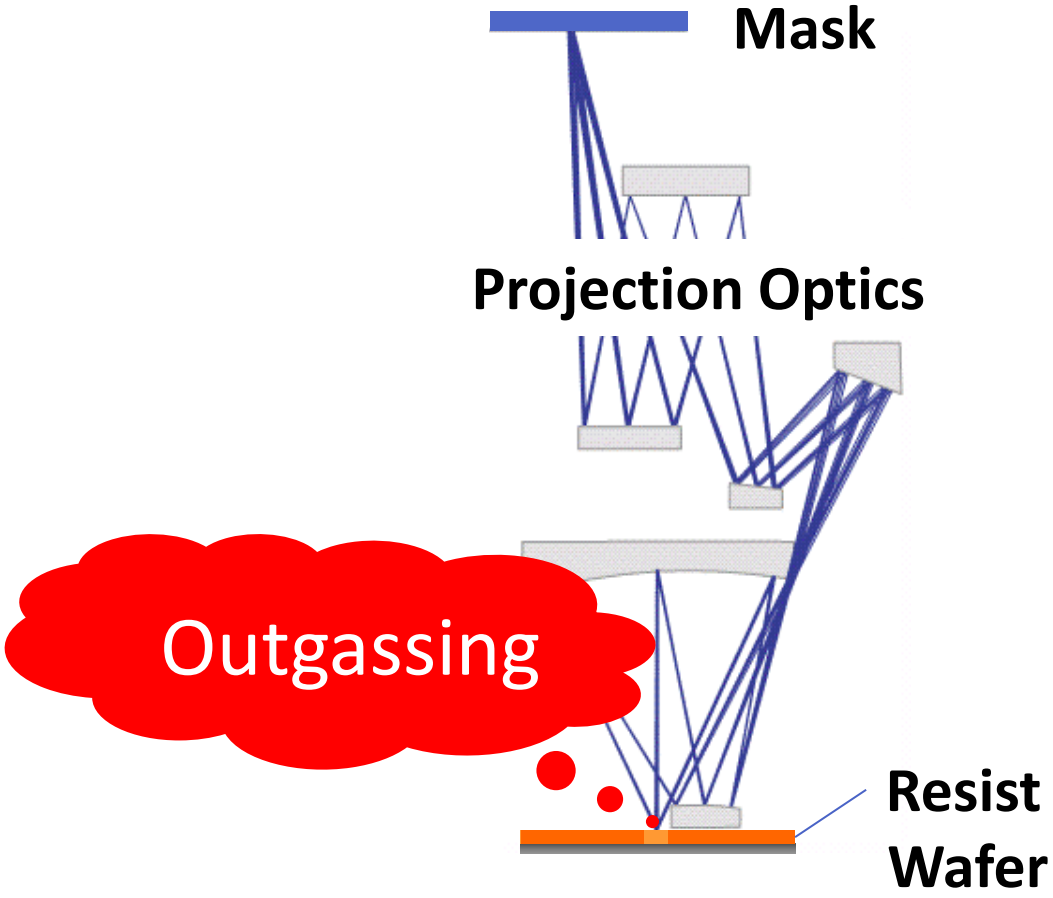
Introduction : Resist-induced Optics Contamination



- Outgassing from EUV resist results in optics contamination.
- **Reduction of resist outgassing** is a key factor for EUVL high volume manufacturing.

Objective of EIDEC Resist Outgas Research program

- To clarify the correlation of light source in generated outgassing
  - ✓ EUV vs. EB
- To provide a guideline for design of resist material
  - ✓ Less or non-outgassing
  - ✓ Easy to clean even if outgassing

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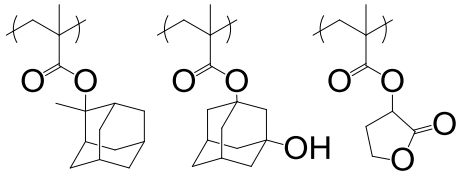
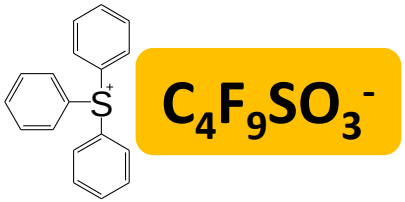
Our previous work

N.Sugie et.al., J. Photopolym. Sci. Technol., 25, 617-624 (2012).

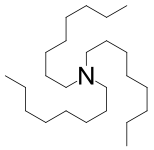
Resist formulation



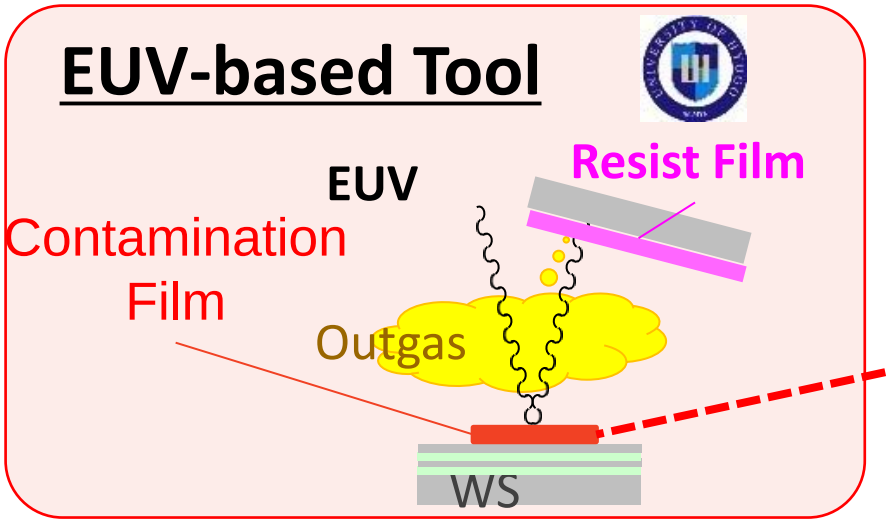
Polymer



PAG



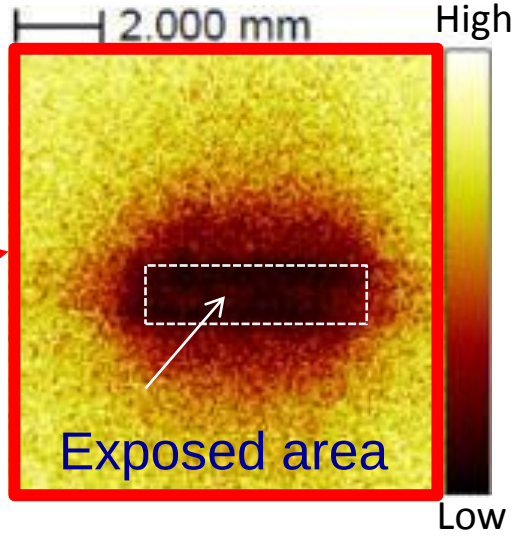
Quencher



TOF-SIMS 2D scan

after H-Cleaning

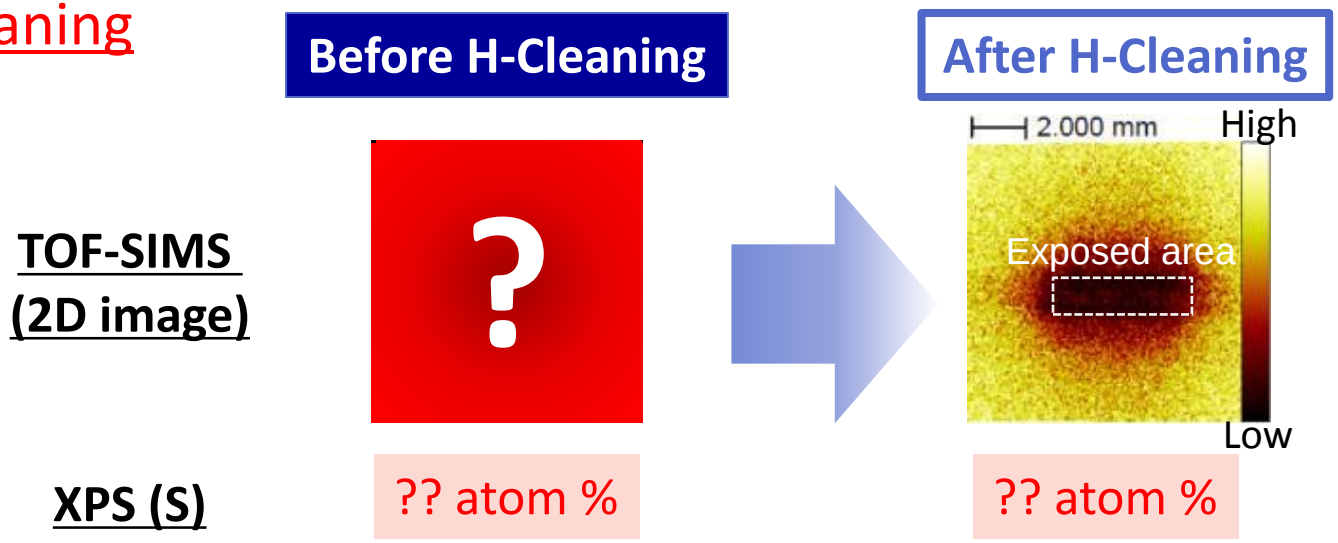
$C_4F_9SO_3^-$



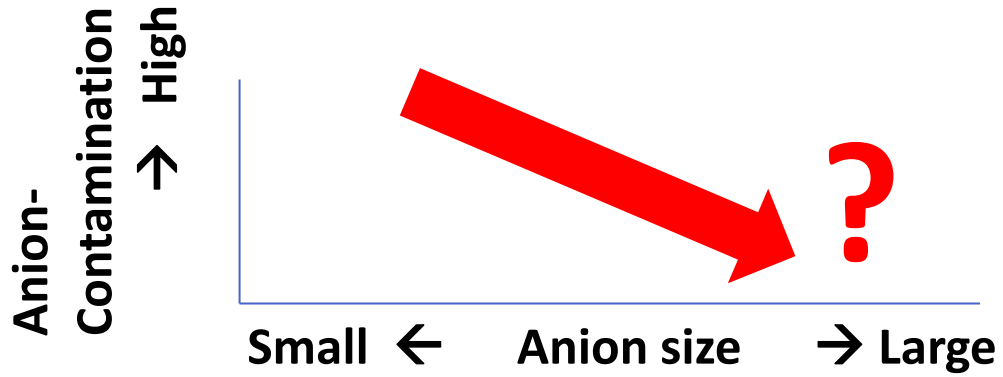
- After H-Cleaning , the residual PAG anion in the **unexposed area** on Witness Sample (WS) plate was observed by TOF-SIMS.

Focus of this study

- This study focuses on following;
  - ✓ PAG induced contaminants behavior before and after H-Cleaning



  - ✓ Anion-contamination dependence on anion size



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- **PAG induced contaminants behavior before and after H-Cleaning**
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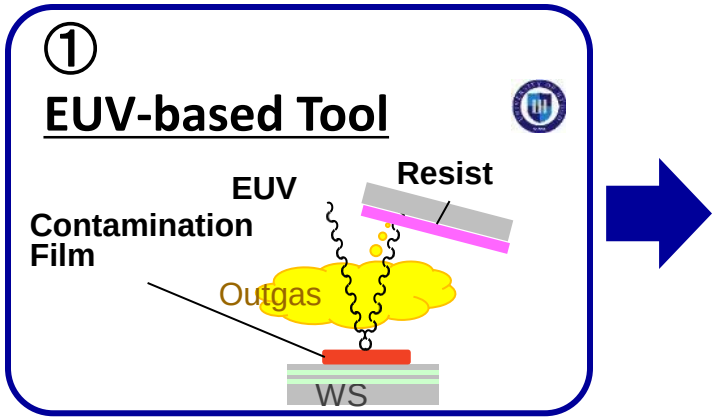
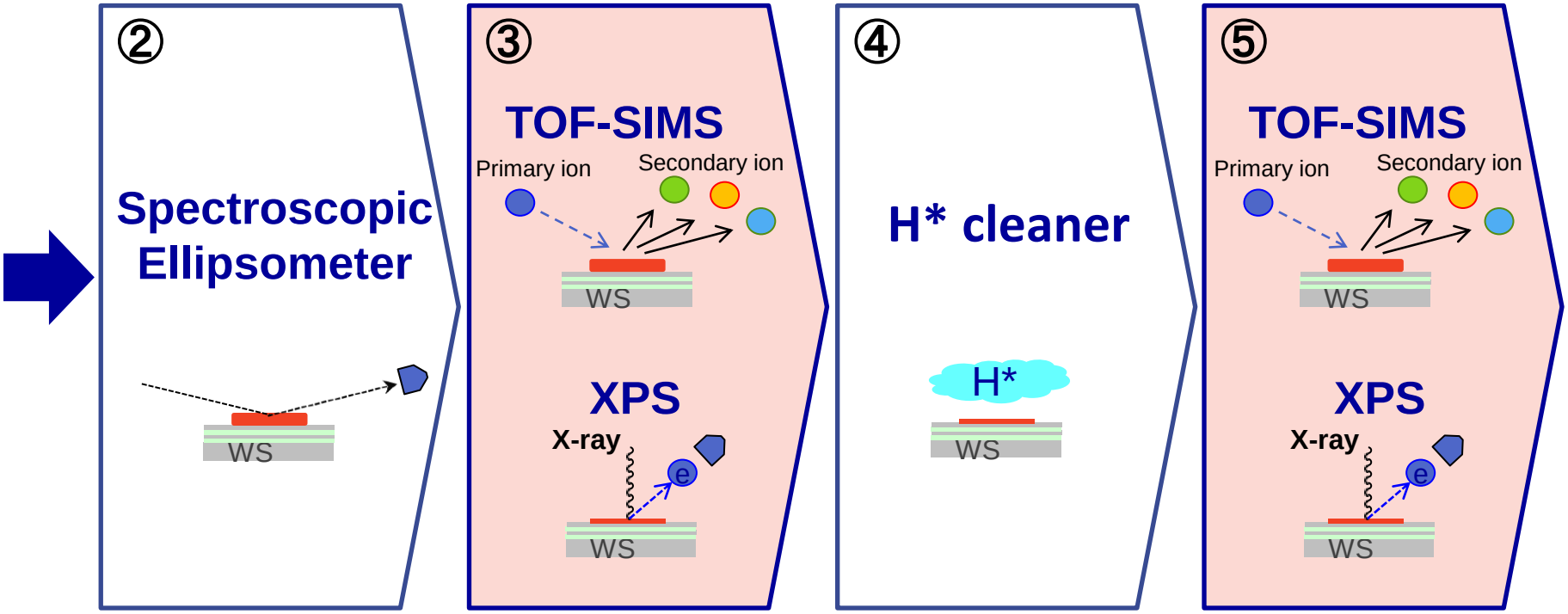
Process flow in this study

① Grow contamination
② Measure contamination film thickness
③ Measure non-cleanable contamination
④ Clean contamination
⑤ Measure non-cleanable contamination

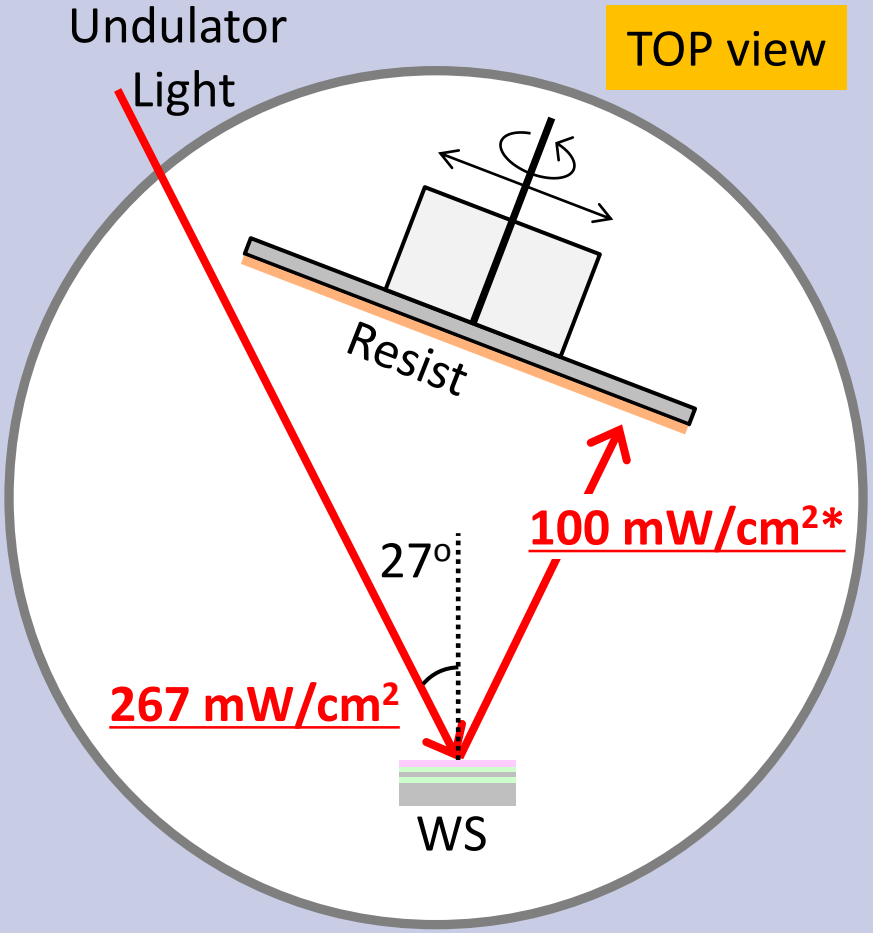




EUV-based outgassing analysis tool

HERC analysis tool
(High power EUV Resist Contamination)

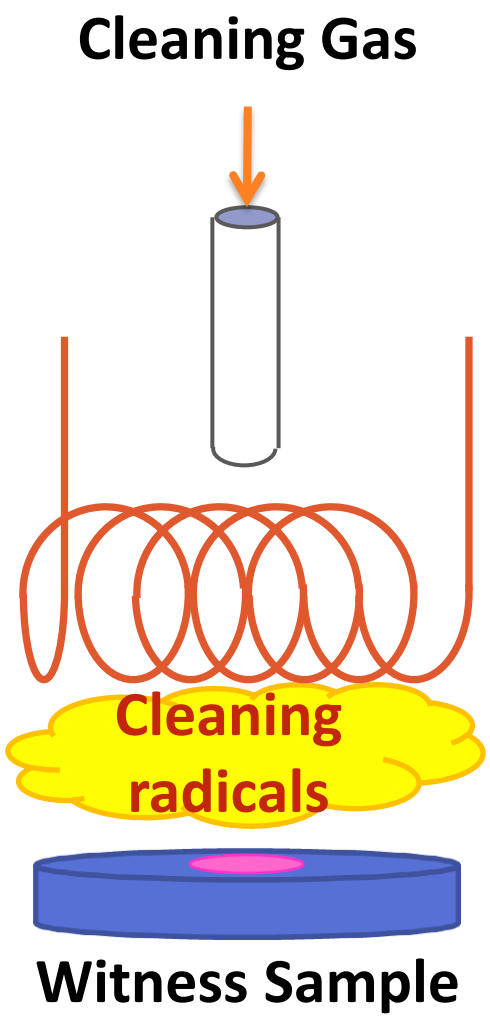
Synchrotron Irradiation (@ New SUBARU BL9c)



Light source	EUV
Base Pressure	2~4 x 10^{-6} Pa
Exposure Pressure	1~2 x 10^{-5} Pa
Resist FT	60 nm
Dose	2.5 x E_0 (E_0 : dose to clear)
Resist wafer	200 mm
Witness Sample (WS)	 Ru 5 nm Mo/Si ML Si-sub.
Reproducibility (3σ/Average)	7.6 %

* Calculation for the WS with average surface roughness

Cleaning process conditions

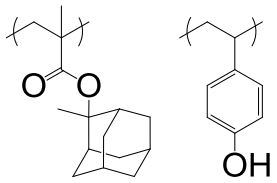


Item	condition
Cleaning Gas	H_2
Filament temperature	1800 ~ 2000 °C
Sample temperature	< 60 °C

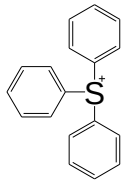
- After H-Cleaning, no remained film thickness is confirmed.

TOF-SIMS result (Anion) before and after H-Cleaning

Resist formulation

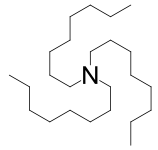


Polymer



$CF_3SO_3^-$

PAG



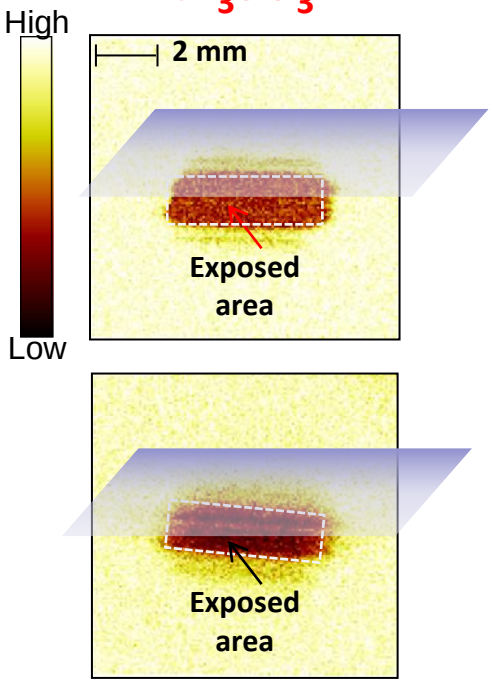
Quencher

Target

$CF_3SO_3^-$

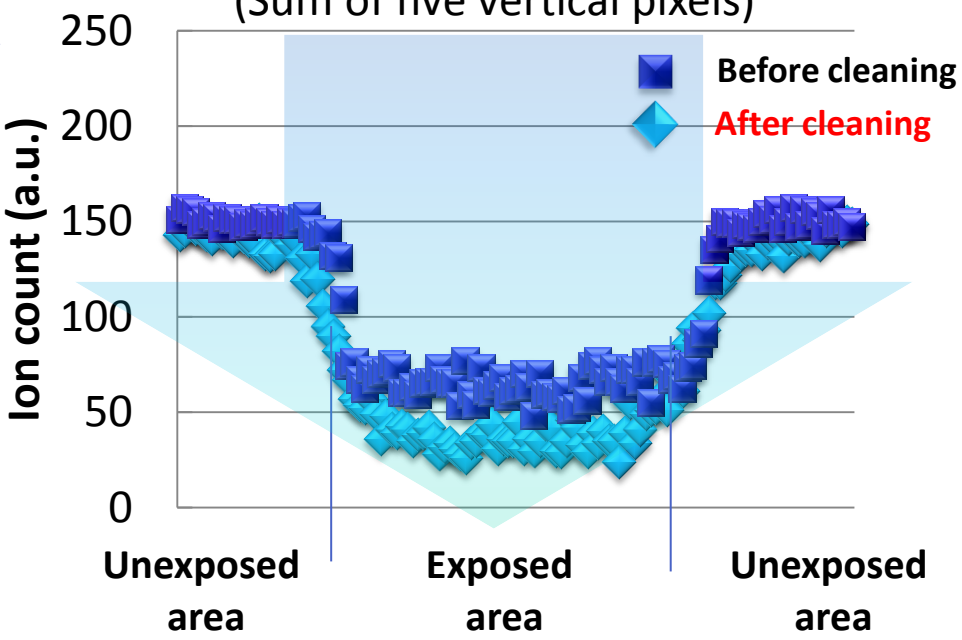
Before Cleaning

After Cleaning



Line profile of **ion count**

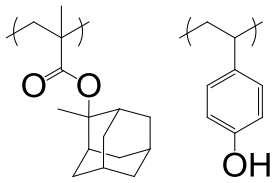
(Sum of five vertical pixels)



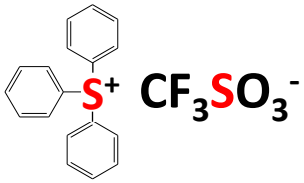
- After H-Cleaning, $CF_3SO_3^-$ was slightly removed.

TOF-SIMS result (Sulfur) before and after H-Cleaning

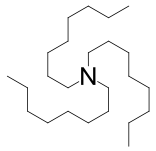
Resist formulation



Polymer



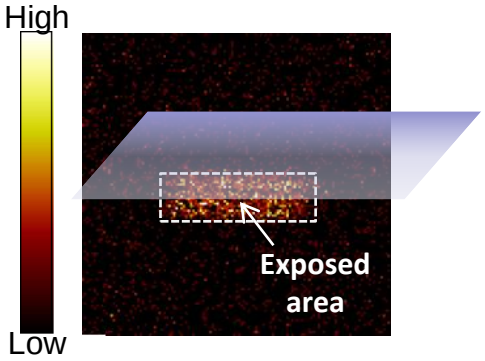
PAG



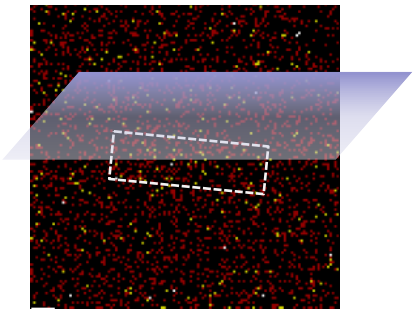
Quencher

Target **S**

Before Cleaning

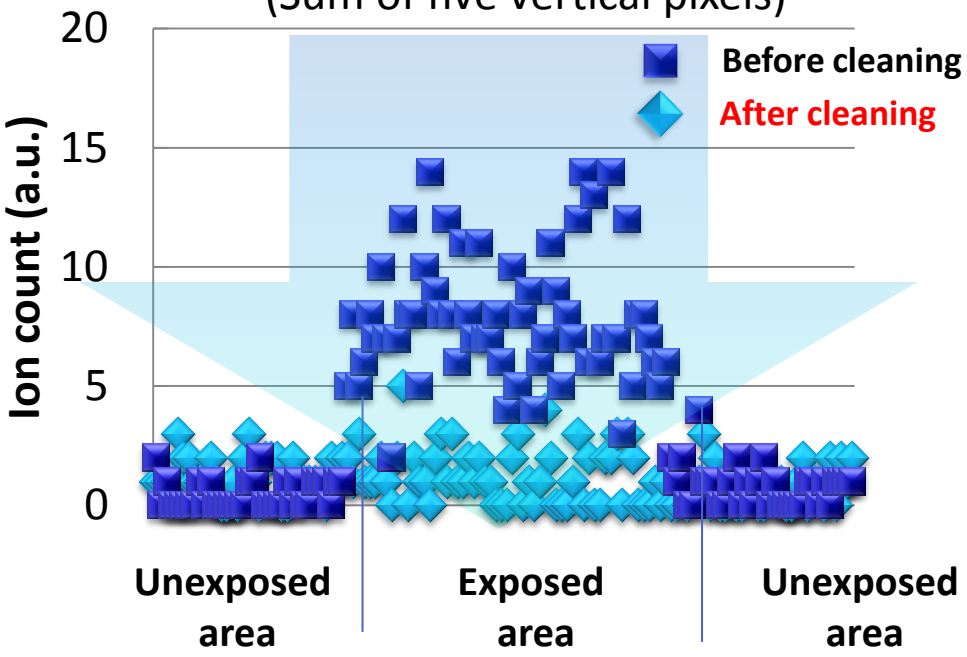


After Cleaning



Line profile of **ion count**

(Sum of five vertical pixels)

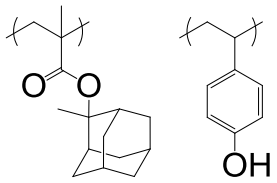


- Sulfur in the exposed area was almost removed by H-Cleaning.

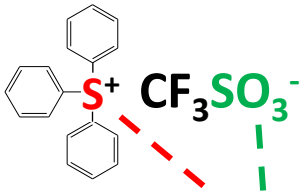
XPS result (Sulfur) before H-Cleaning

Condition : Φ200 μm 50 W 15 kV

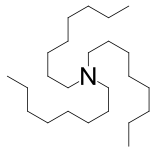
Resist formulation



Polymer



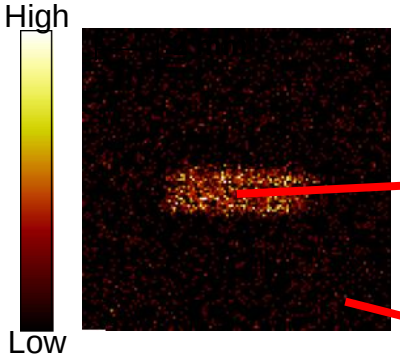
PAG

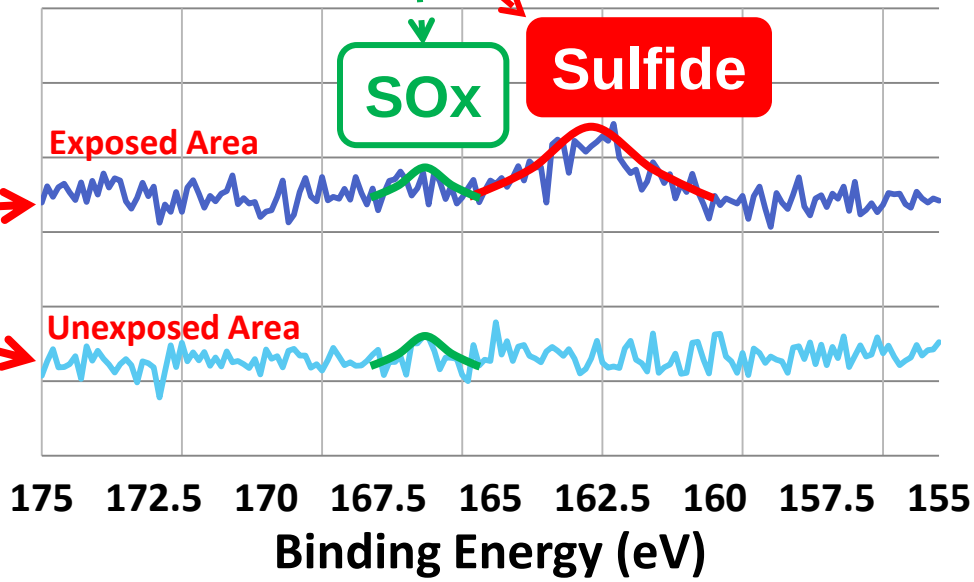


Quencher

Target **S**

Before Cleaning

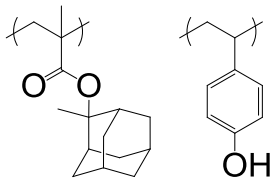




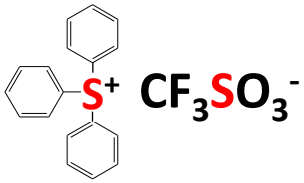
- Sulfur in the exposed area is considered to come from cation mainly.
- It was found that SOx can be deposited without exposure. However, Sulfide deposition needs to be exposed for deposition to occur.

Sulfur comparison between exposed and unexposed area

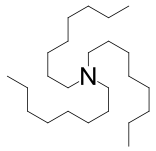
Resist formulation



Polymer

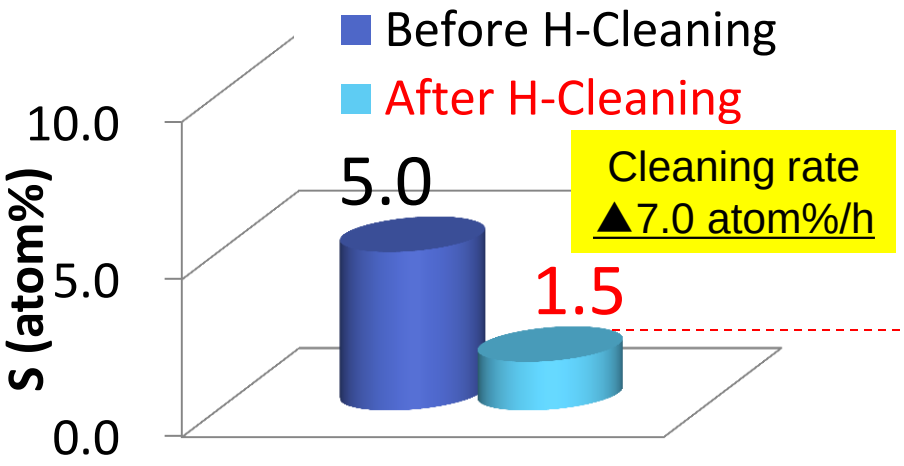


PAG

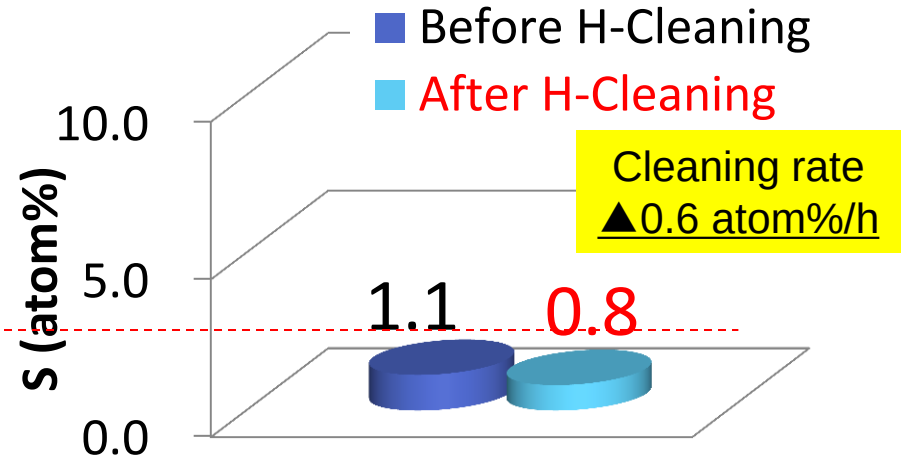


Quencher

Exposed Area



Unexposed Area



- In the exposed area, it is considered that Sulfur attributed from cation can be removed faster together with the cleaning of carbon.
- In contrast, Sulfur attributed from anion in the unexposed area was removed slower compared to the Sulfur attributed from cation in the exposed area.

Note : XPS data is scaled to get to 300 mm full wafer exposure.

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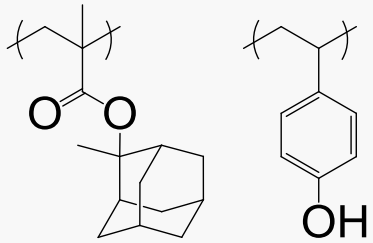
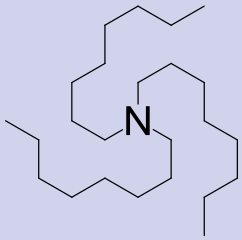
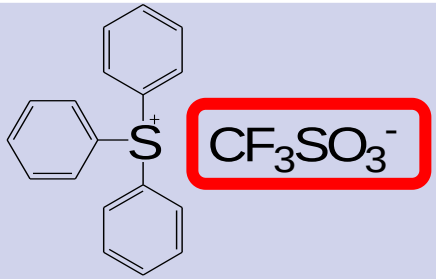
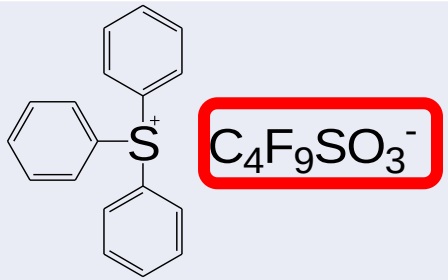
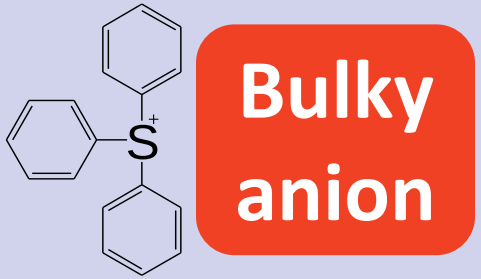
Resist formulations

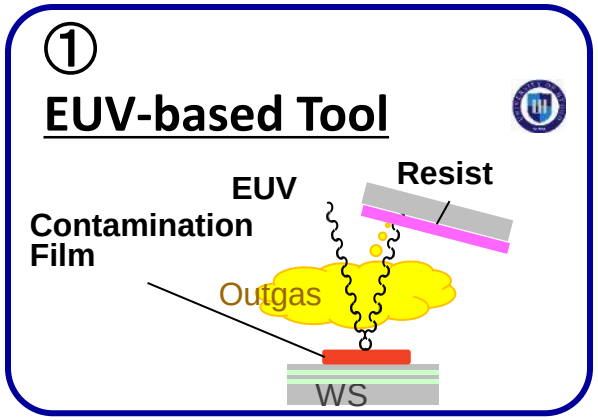
*V.W.V. = Van der Waals Volume
Calculation soft : CAChe ver.6.1

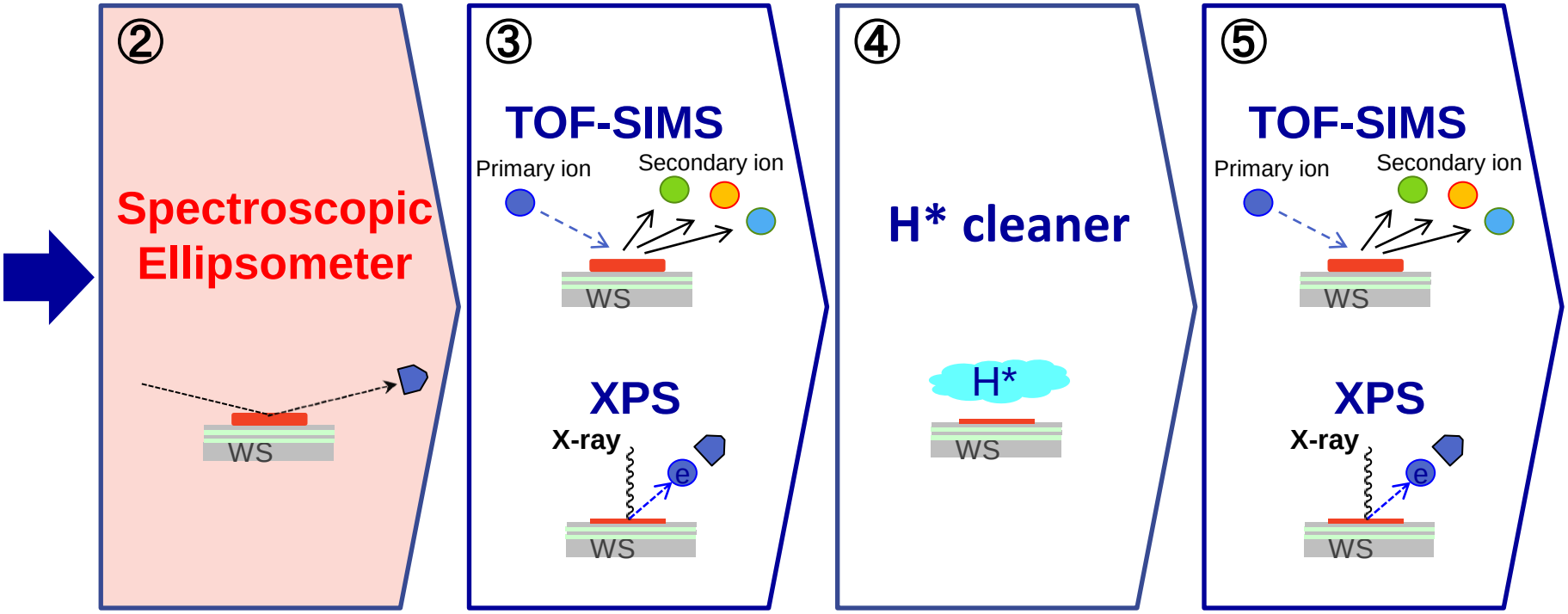
Sample	Polymer	Quencher/ content	PAG / *V.W.V of anion (relative)	
A				1.0
B	PHS-Methacrylate Hybrid	Tri-n-Octyl amine		2.1
C				3.6

- 3 types of PAG of with varied anion size were employed.

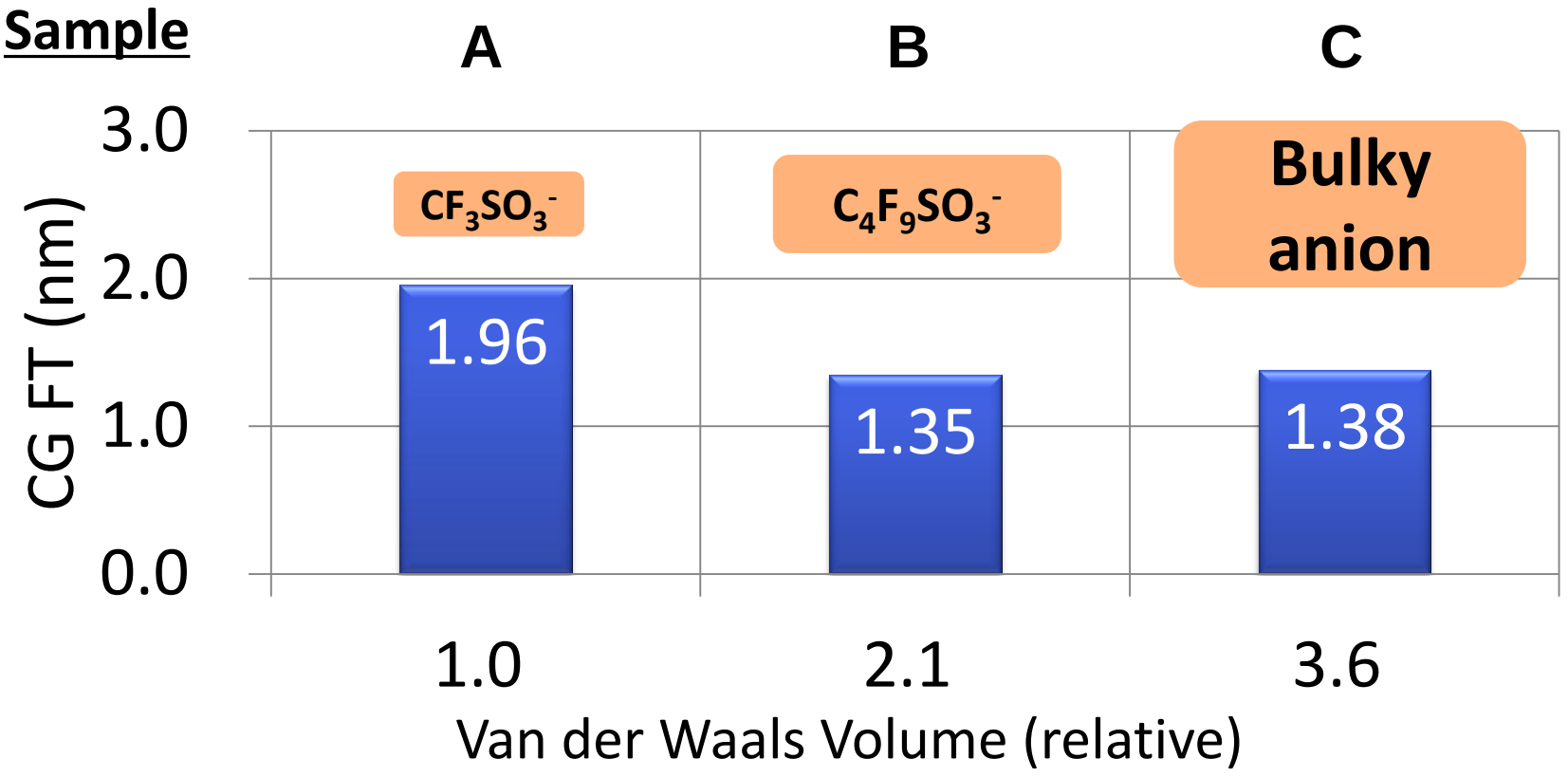
Cleanable contamination evaluation

① Grow contamination
② Measure contamination film thickness
③ Measure non-cleanable contamination
④ Clean contamination
⑤ Measure non-cleanable contamination





Contamination Growth Film Thickness vs. Anion size

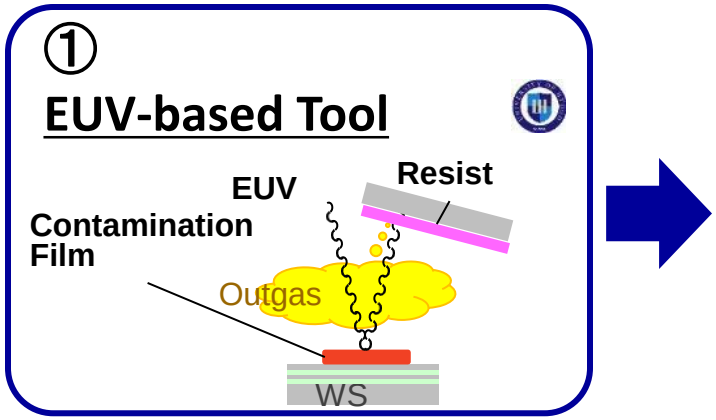


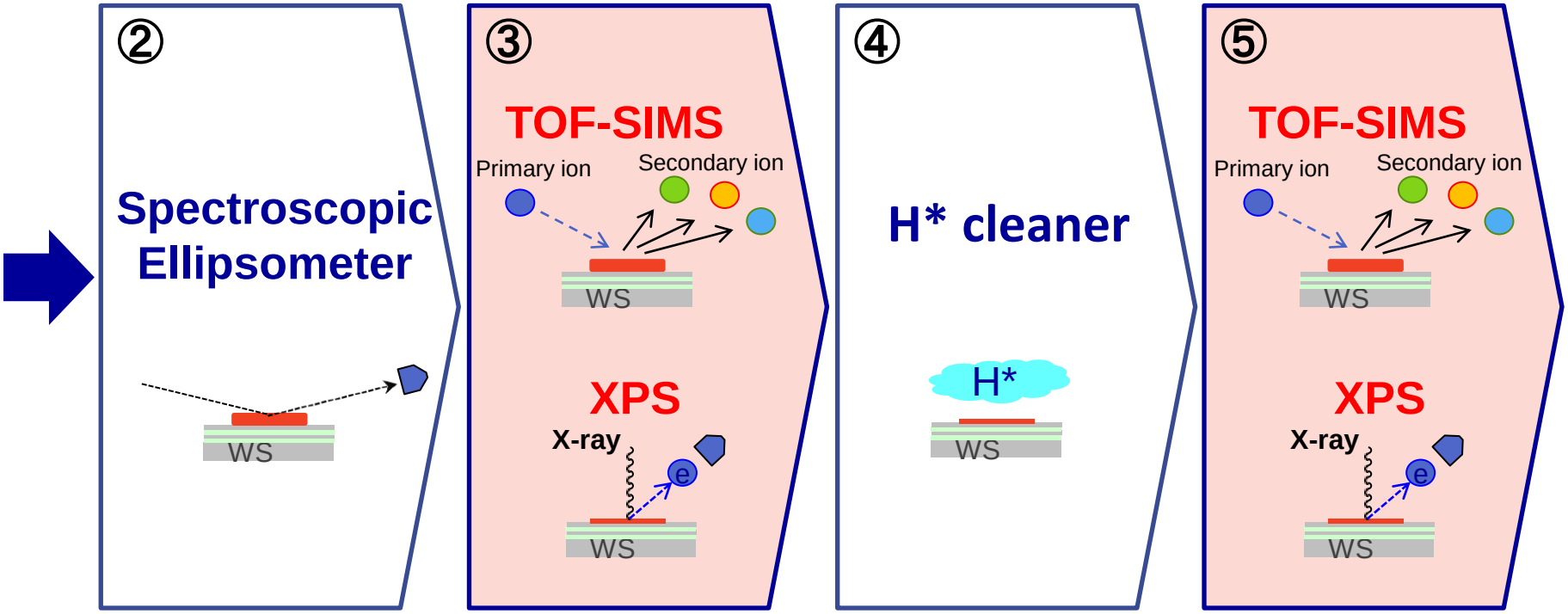
- There is no significant relationship between Contamination Growth Film Thickness (CG FT) and PAG anion size.
- It is considered that $CF_3SO_3^-$ is easily released from the resist film due to long diffusion length in the resist film.

Note : CG FT data is scaled to get to 300 mm full wafer exposure.

Non-cleanable contamination evaluation

① Grow contamination
② Measure contamination film thickness
③ Measure non-cleanable contamination
④ Clean contamination
⑤ Measure non-cleanable contamination



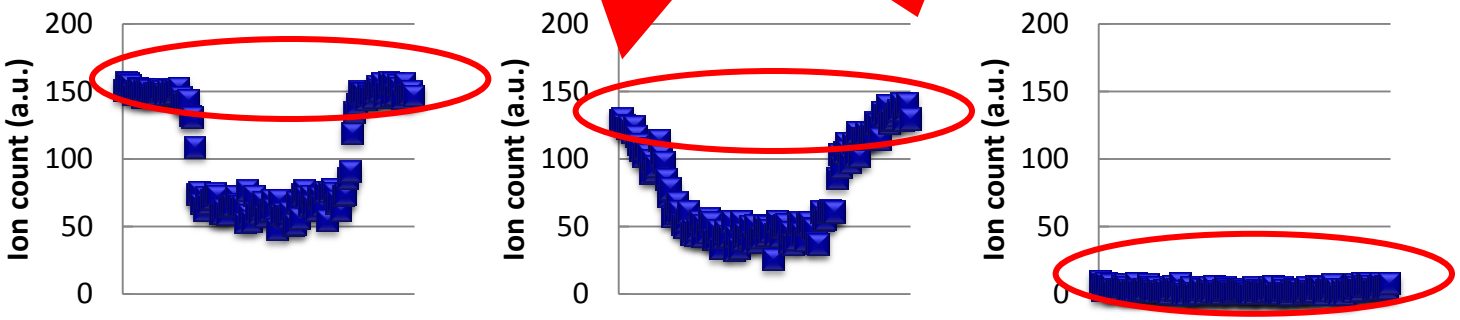


TOF-SIMS result (Anion) before H-Cleaning

Sample	A	B	C
Target	$CF_3SO_3^-$	$C_4F_9SO_3^-$	Bulky anion
Before Cleaning			

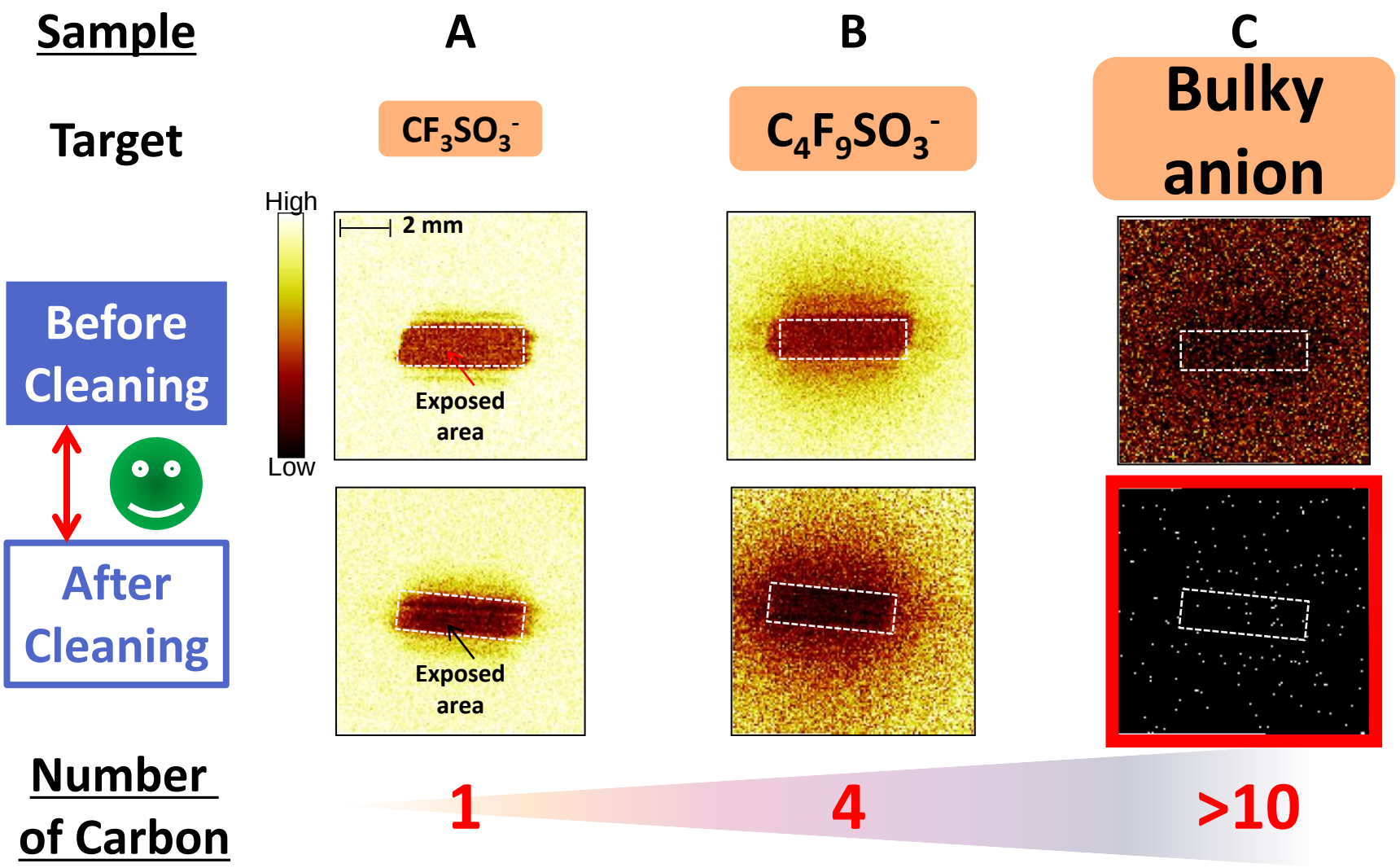
anion-to-anion comparison is NOT good

Line profile of **ion count** (Sum of five vertical pixels)



- Bulky anion seems to be so small amount in the unexposed area.
- But, the anion-to-anion comparison is NOT good, because the ionization rates of each anion are different.

Anion contaminants comparison between before and after cleaning

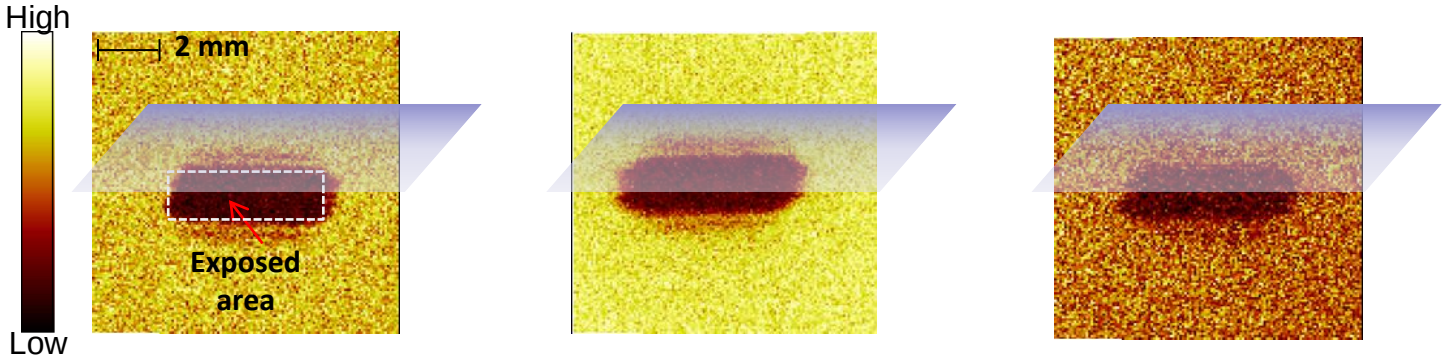


- It is considered that the bulky anion, consisting of large number of carbon, is easily removed together with carbon by H-Cleaning

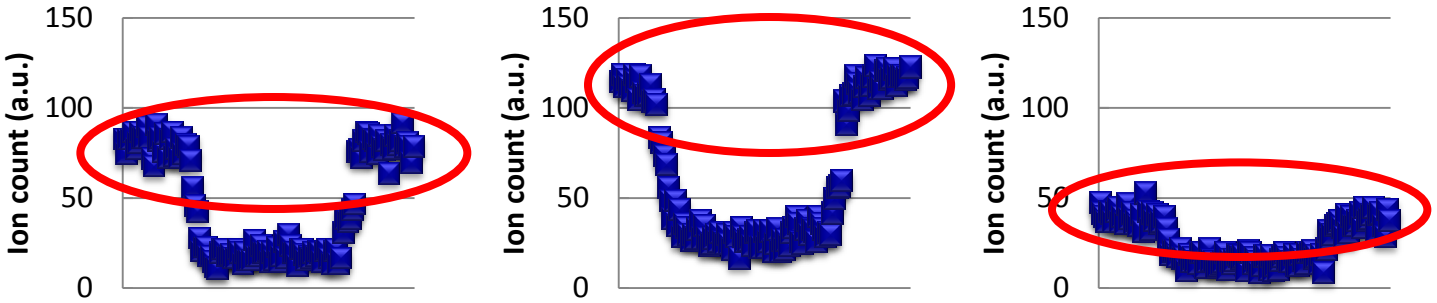
TOF-SIMS (SO_3) and XPS result before cleaning

Sample	A	B	C
Target	SO_3	SO_3	SO_3

Before Cleaning



Line profile of **ion count**
(Sum of five vertical pixels)

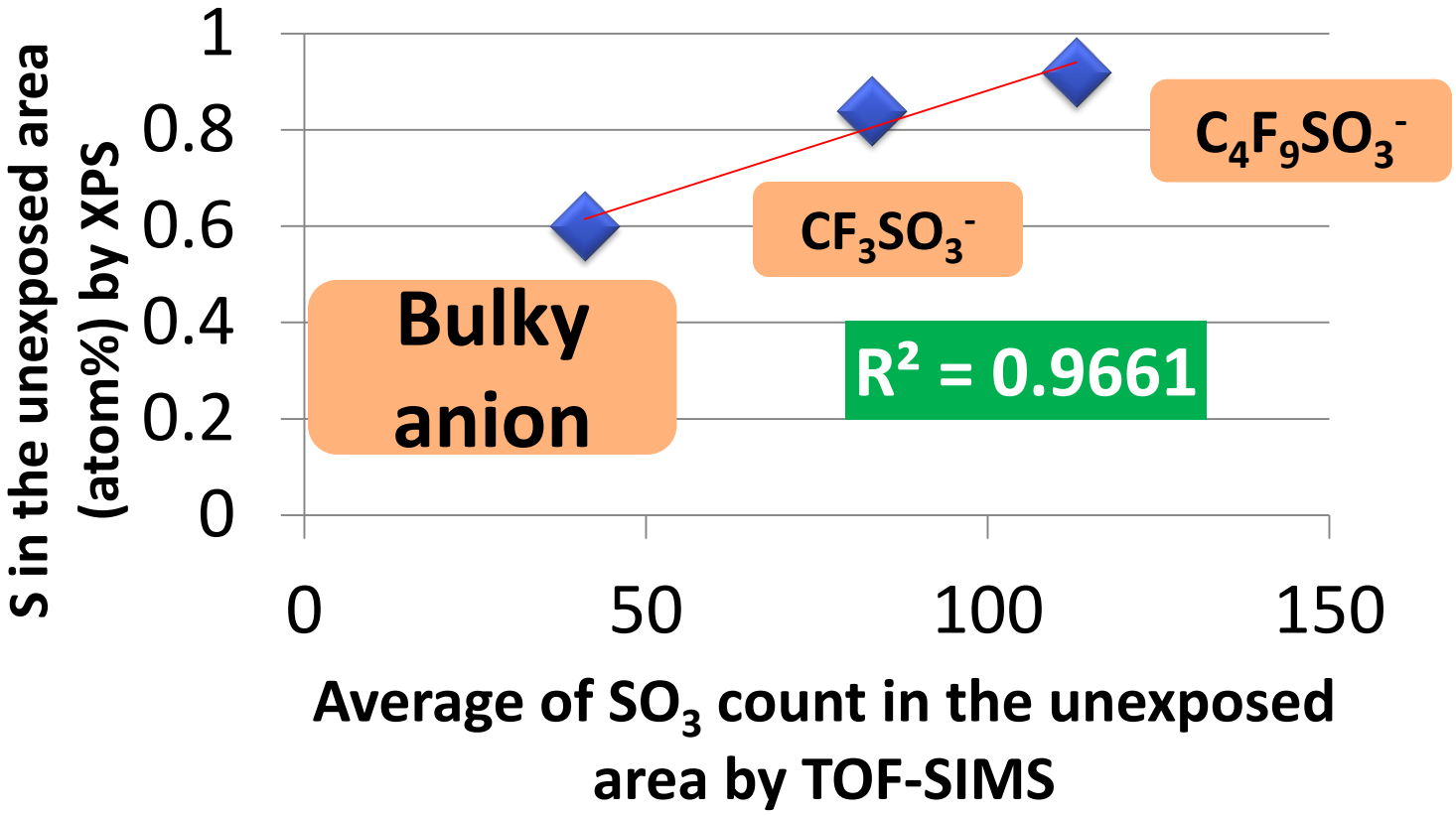


S by XPS
unexposed area, actual
(# of exposed wafer)

A	B	C
0.8 atom%	**0.9 atom%**	**0.6 atom%**
(200mm x 2)	**(200 mm x 2.7)**	**(200 mm x 2)**

- There seems to be a correlation between TOF-SIMS result and XPS result.

Relationship between TOF-SIMS and XPS result

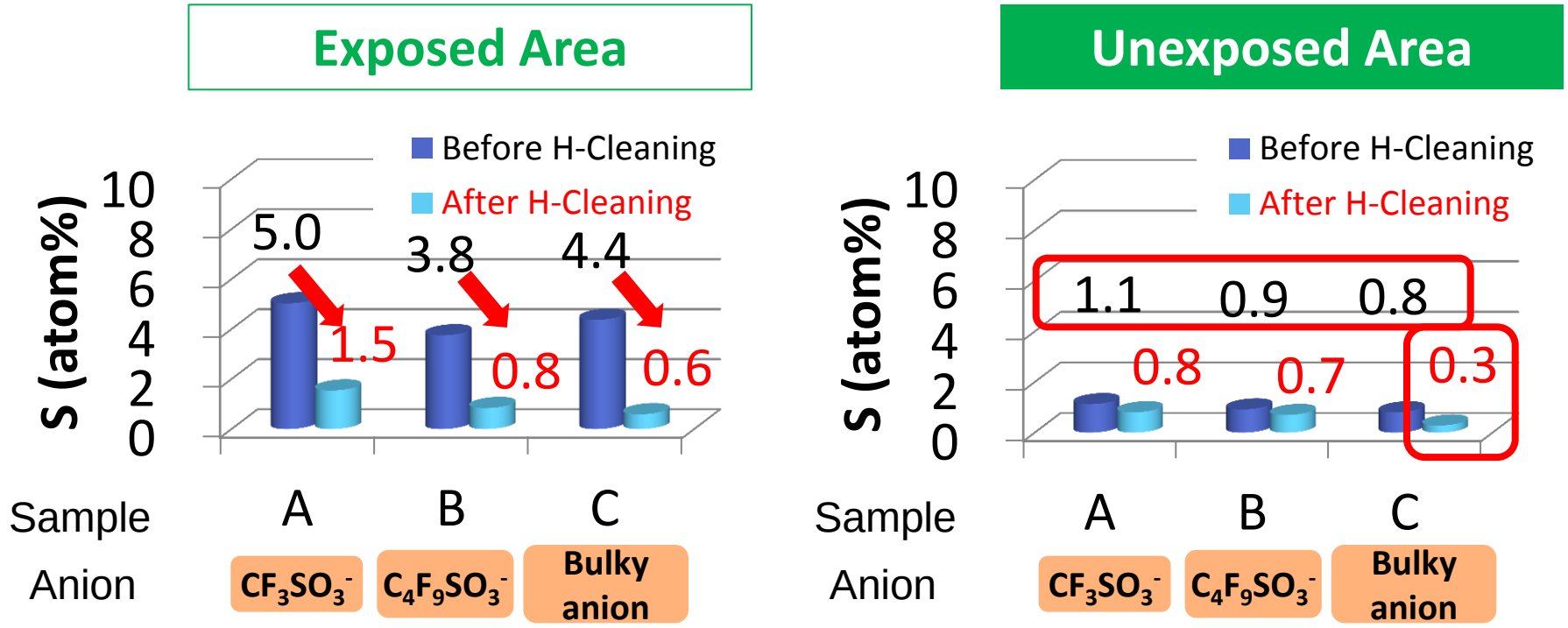


- There is a good correlation between TOF-SIMS results of SO_3 and XPS result of S.
- It is considered that targeting SO_3 ion is reasonable, in comparing with anion in the unexposed area by TOF-SIMS.

XPS result (Sulfur)

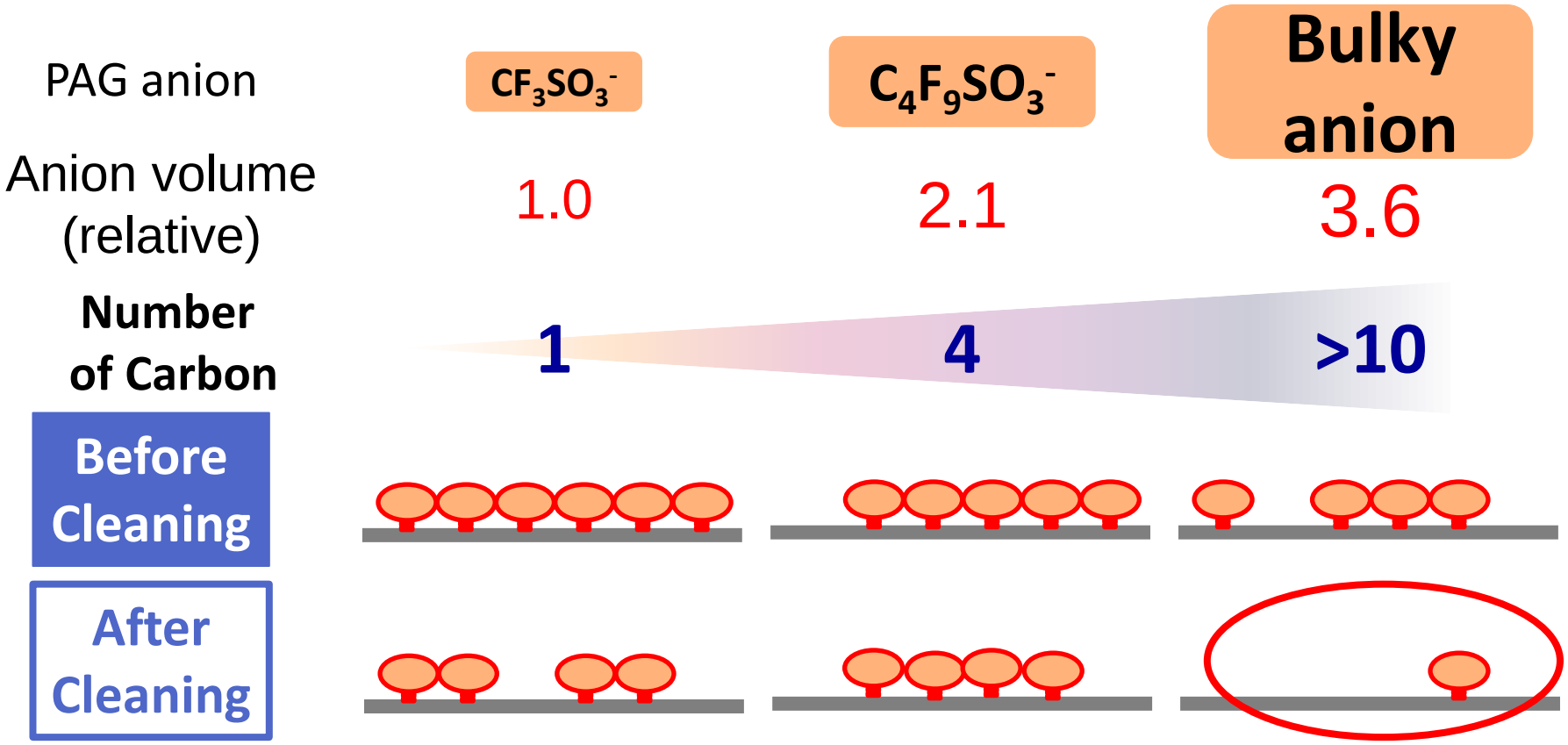
Condition : Φ200 μm 50 W 15 kV

Note : XPS data is scaled to get to 300 mm full wafer exposure.



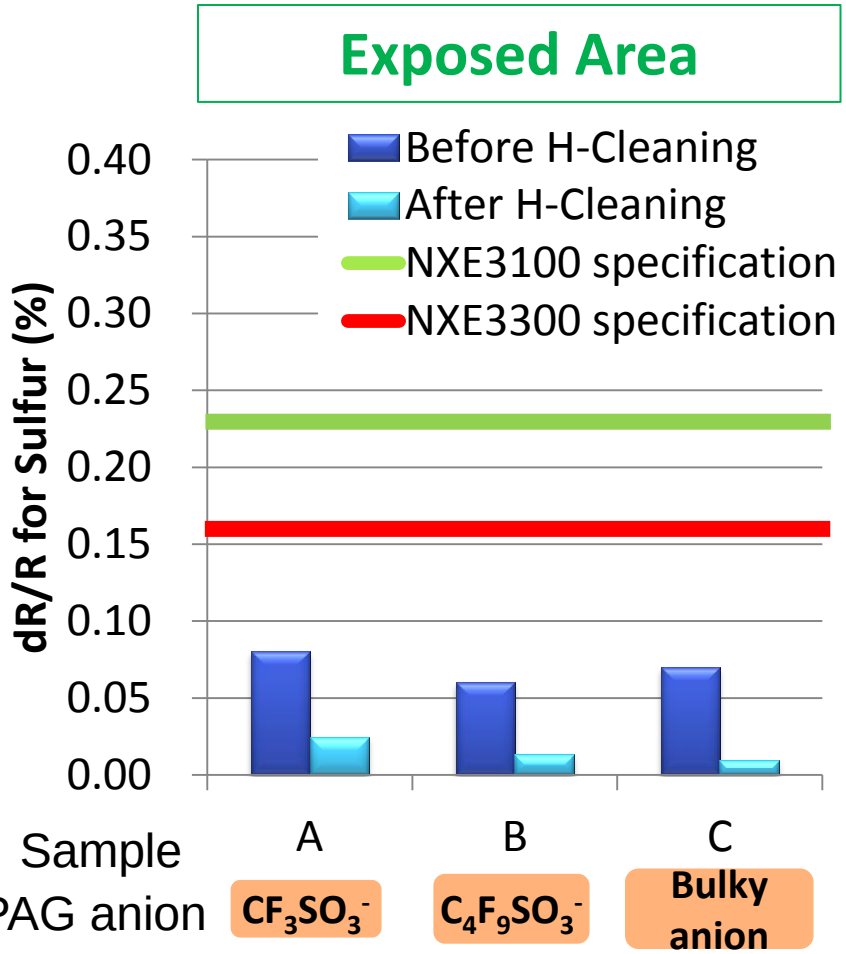
- At the exposed area, S was removed to about 1 % by H-Cleaning.
- At the unexposed area, anion-based contamination is inversely proportional to anion size.
- Bulky anion consisting of many carbons was removed easily by H-Cleaning as shown in TOF-SIMS results.

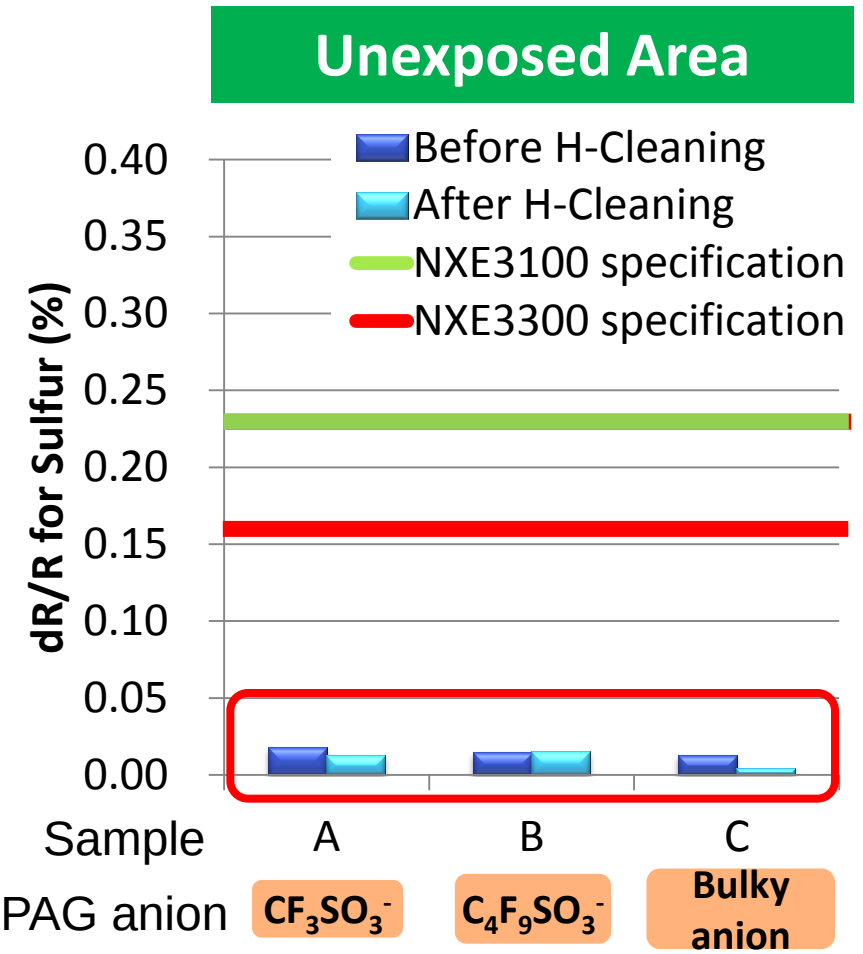
Anion at the unexposed area before and after H-Cleaning



- Based on the TOF-SIMS and XPS result, there is a little anion contamination dependency on the anion size before cleaning.
- It is considered that bulky anion consisting of a large number of carbon can be easily removed together with carbon by H-Cleaning.

Estimation of reflection loss for Sulfur (dR/R*)





- The reflection loss for sulfur estimated in unexposed area for the 3 type of PAGs are small enough compared to the set spec.

*dR/R were calculated with the method prepared by the ASML

Outline

- Introduction
- Previous work at EIDEC
- PAG induced contaminants behavior before and after H-Cleaning
- Anion-contamination dependence on anion size
- **Summary**

Summary

- PAG induced contaminants behavior before and after H-Cleaning
  - ✓ Anion-based contamination amount in the unexposed area is very small, but that is hard to be removed by H-Cleaning.
- Anion-based contamination dependence on anion size
  - ✓ For the cleanable component, there is no significant relationship between CG and PAG anion size.
  - ✓ Based on the XPS result of Sulfur, there is a little anion-based contamination dependence on the anion size (from analysis before H-cleaning).
  - ✓ Bulky anion consisting of large number of carbon can be easily removed by H-Cleaning.
  - ✓ For the resist design, employing the bulky anion would be preferable.

Acknowledgement

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Thank you for your kind attention!