Outgassing study of resist for extreme ultraviolet lithography at PAL

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Abstract

As extreme ultraviolet (EUV) wavelength has a high generic absorbance properties to almost all elements, EUVL requires a vacuum environment for resist exposure. At these low pressures, contamination through the system due to the free molecular flow of particles is possible. Contamination of optics and mask decreases the reflectivity of the EUVL imaging systems. Hence, we discuss the resist outgassing characteristics under EUV exposure.

The system for the evaluation of EUV resist was established at the 11B1 beamline of Pohang Accelerate Laboratory (PAL) in Korea. It is essentially used to derive optimized chemical components of photo-acid-generator (PAG) as well as resin, suitable resist thickness and PEB conditions. The outgassing species collected from the resist during the EUV exposure were analyzed with quardruple mass spectrometer connected to the resist evaluation chamber. In this research, we investigated outgassing characteristics of EUV resist with various PAG combinations. Also we studied outgassing characteristics of resin itself. Finally we investigated outgassing characteristics with the change of resist thickness and PEB conditions. Detailed chemical properties and outgassing characteristics will be discussed at the presentation.

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- Summary

EUVL : Critical issues

- Light Source : Power. Efficiency. Source materials.
- Optics : Reflectance accuracy. Efficiency
- Perfect Mask : Defect. Mask inspection. Cleaning
- Environment Control from contamination

Optics contamination from resist outgassing

Specification	2006 ITRS
Resolution 1:1 (nm)	32
Resolution isolated lines (nm)	21
Low frequency LWR (nm, 3 σ)	1.7
Photospeed, EUV (mJ/cm^2)	5–15
Ougassing rate for 2 minutes under the lens ($molecules/cm^2$-sec)	< 5E+13

Selected 2006 ITRS goals for EUV resist.
- Proc. Of SPIE Vol. 6519 65191p-1

EUVL : Resist outgassing

- ITRS goals for EUV resist

  resolution. low frequency LWR. Photo speed, outgassing rate

Optics contamination

- WHY resist outgassing test

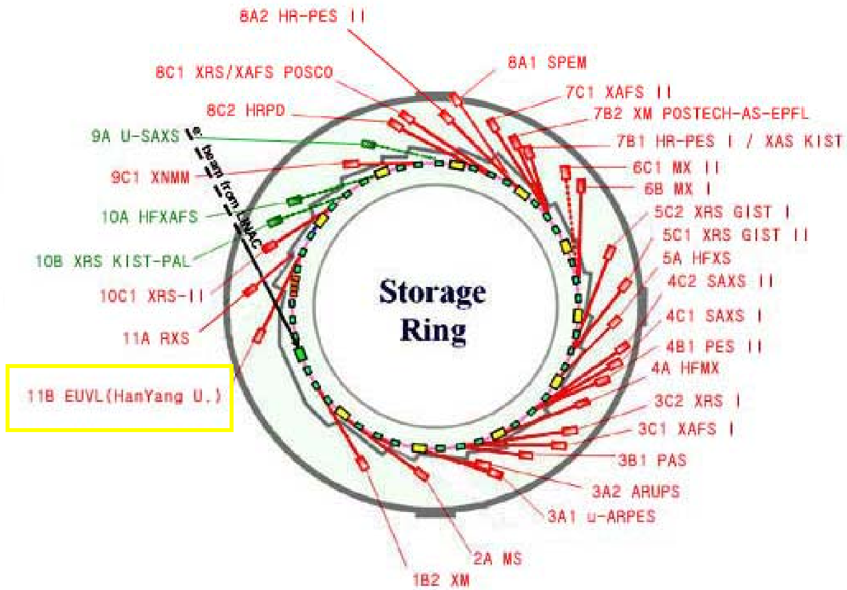
  Extreme ultraviolet (EUV) lithography requires a vacuum environment for exposure

  : Critical issue to understand the outgassing hydrocarbon ion species of the photoresist

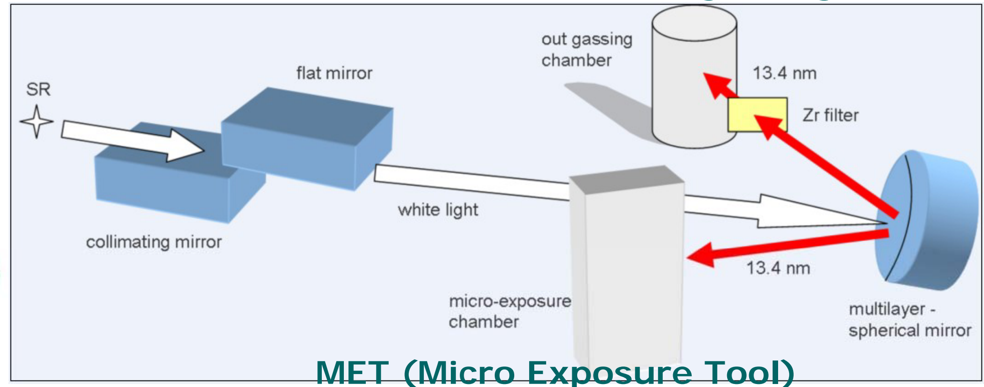
- Disadvantage of resist outgassing

  ⇨ Reduce the reflectivity of the mask and the imaging mirror (Optics Lifetime Issue : Reflectivity loss < 1.6%)

Experimental set-up at PAL



EUV resist outgassing



MET (Micro Exposure Tool)

Pohang Accelerator Laboratory in Korea

11B EUVL beam line

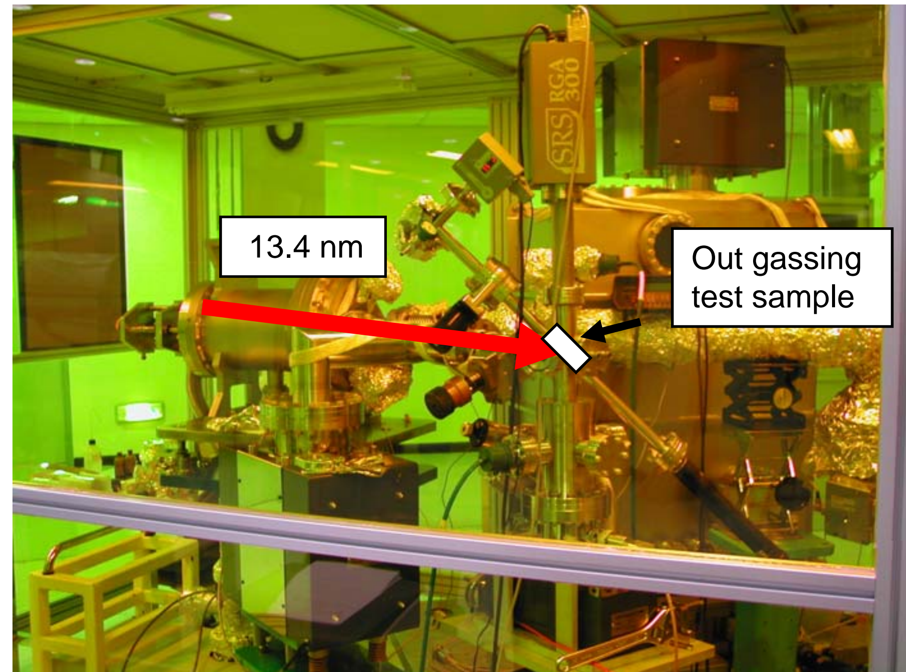
Experimental set-up at PAL

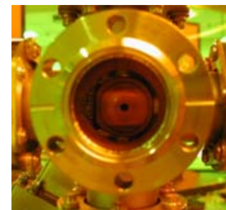
Purpose of PR evaluation chamber
- Photo-chemical reaction properties
- Out-gassing characteristic of photo-resist

Light Source
- Type : bending magnet

Photon at Sample
- Photon energy : 13.4nm(92.5 eV @2.5GeV)
- Beam Size : 2mm @ out-gassing sample position

Equipment (QMS)
- Mass Spectroscopy : 1~300 AMU
- Clean booth : < class 1000

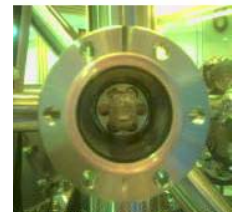




Pin Hole (φ 5mm)
2mm beam size control

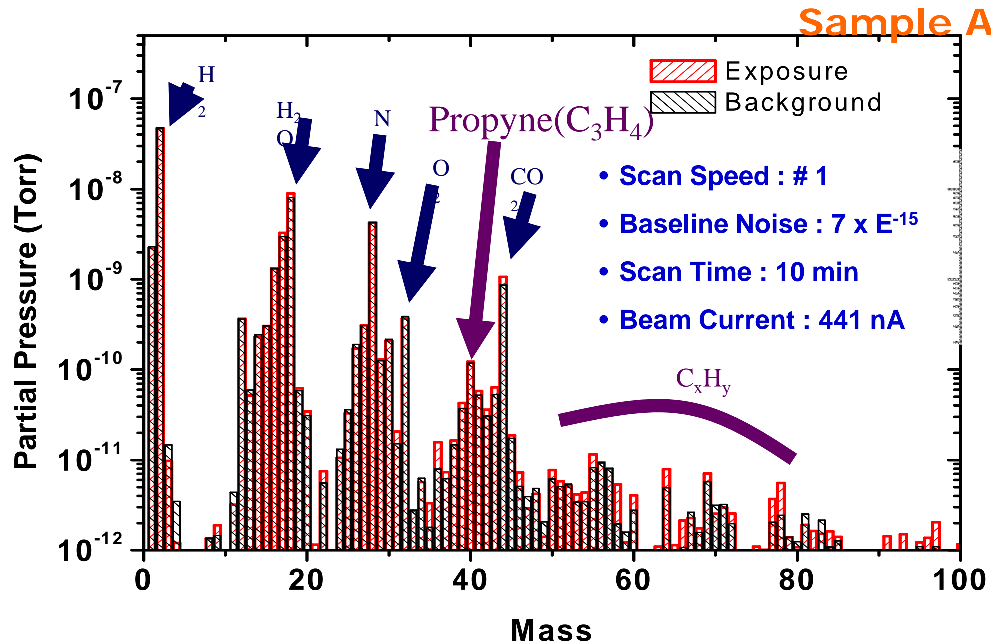
Zr filter

monochromatic wavelength 13.4nm



Resist out-gassing analysis

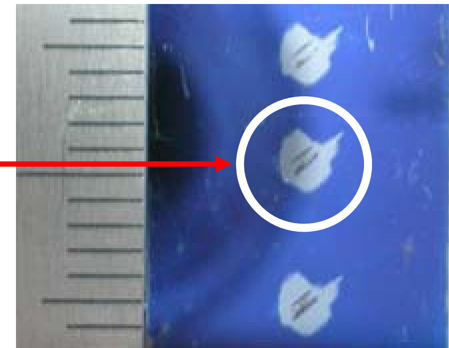
- Analysis of outgassing components and quantity



Outgassing result (molecules/cm2) correction between HYU / Wisconsin

HYU : 6.2E+13
Wisconsin : 2.0E+13

Developed area



P : Partial pressure at exposure

P_0 : Partial pressure before exposure

A : beam size(cm^2) = developing area

$$760\,Torr \Rightarrow 22.4L, 6.02\times 10^{23}$$

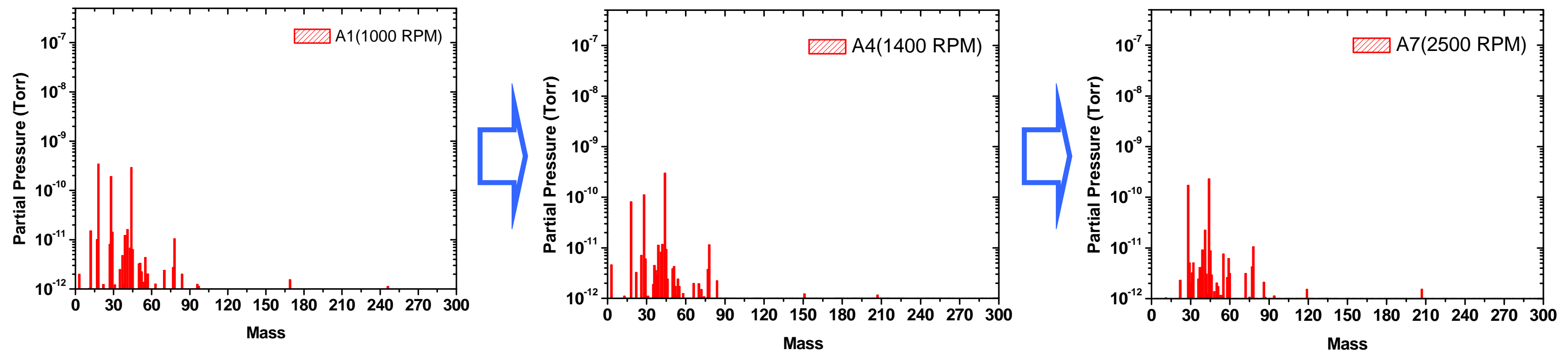
$$760\,Torr : 6.02\times 10^{23} = (P-P_0) : n$$

$$\frac{(P-P_0)\times 6.02\times 10^{23}}{760} \approx n$$

∴ Quantity of out-gassed molecules $= \frac{n}{A}(molecules/cm^2)$

Change of resist thickness

- Outgassing result with resist thickness change



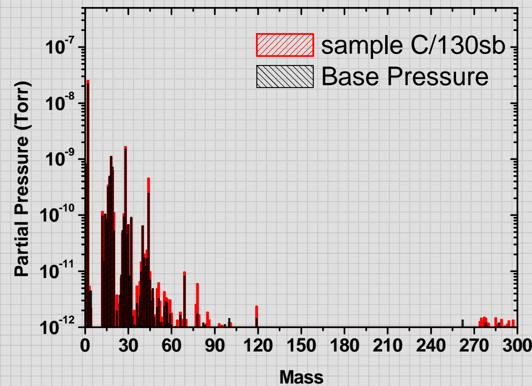
	A1 (coating speed 1000 RPM)	A4 (coating speed 1400 RPM)	A7 (coating speed 2500 RPM)
Out-gassing (molecules/cm^2)	$3.43E^{13}$	$2.15E^{13}$	$1.66E^{13}$

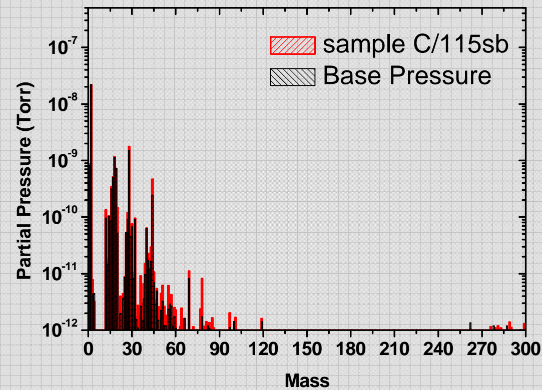
Resist coat RPM increase ➔ Thickness decrease

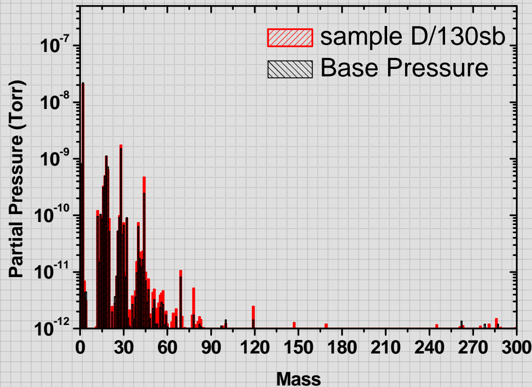
Thickness decrease ➔ Outgassing molecules decrease

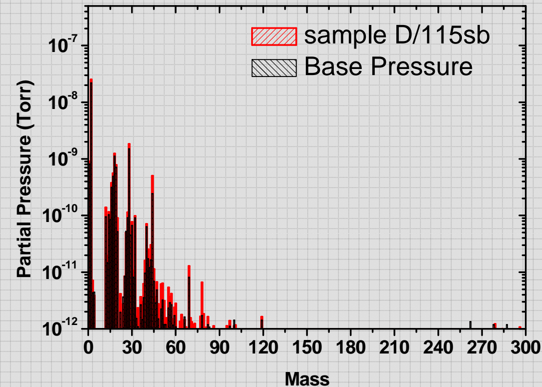
Change of PAG & soft bake

Decrease quantity of PAG









Increase SB temperature

Change of PAG & soft bake

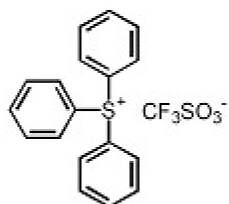
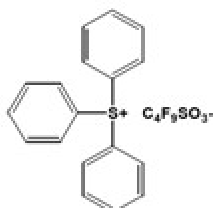
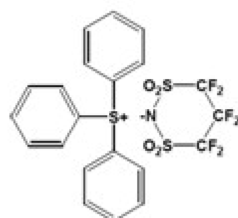
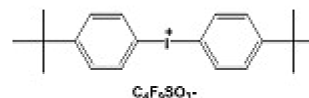
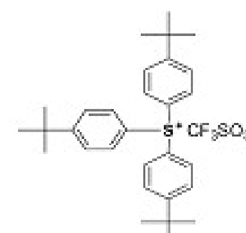
- Outgassing result

sample No.	SB(℃)	Coating speed (RPM)	Base Pressure (Torr)	Exposure Area (Cm^2)	Total Out-gassing (molecules)	Out-gassing (molecules/Cm^2)
Sample C	**130**	1400	7.8x10^-9	2.00E-02	4.37185E+11	**2.19E+13**
Sample C	**115**	1400	7.8x10^-9	2.00E-02	6.94359E+11	**3.47E+13**
Sample D (low PAG)	**130**	1400	7.8x10^-9	2.00E-02	4.88456E+11	**2.44E+13**
Sample D (low PAG)	**115**	1400	7.8x10^-9	2.00E-02	9.27224E+11	**4.64E+13**

- Soft bask temperature decrease
  : remaining solvent increase
    ➡ outgassing quantity increase

Changing type of PAG

- Different type of PAG

Resist 1	Resist 2	Resist 3	Resist 4	Resist 5
				

Resist 1 : triphenylsulfonium trifluoromethanesulfonate (TPS-TFS)

Resist 2 : triphenylsulfonium perfluorobutanesulfonate (TPS-PFBS)

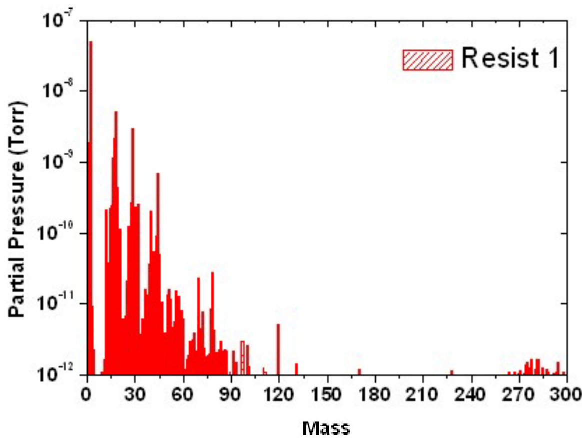
Resist 3 : triphenylsulfonium cyclo(1,3-perfluoropropanedisulfone) imidate (TPS-IMIDATE)

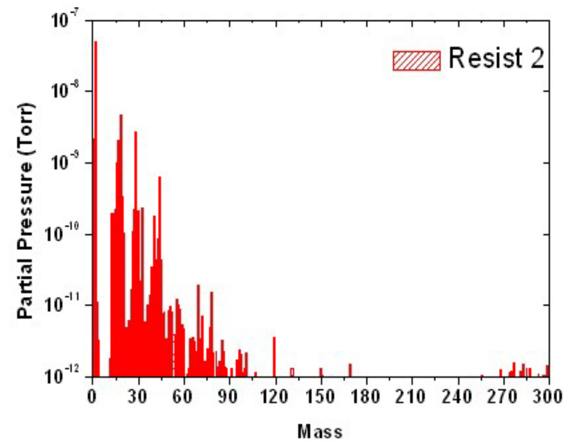
Resist 4 : bis-4-(tert-butyl)phenyliodonium perfluorobutanesulfonate (BPI-PFBS)

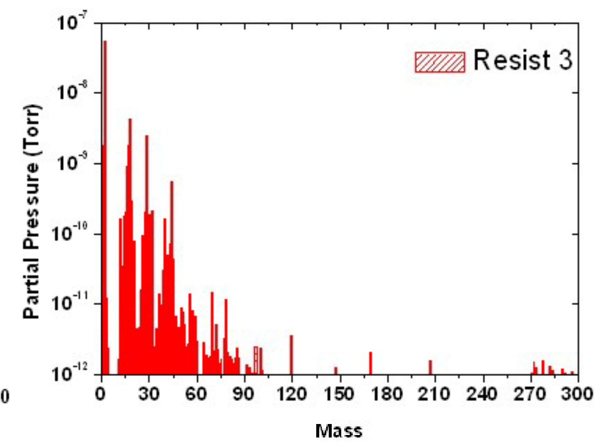
Resist 5 : tri(4-tert-butyl)phenylsulfonium trifluoromethanesulfonate (TPS-TFS)

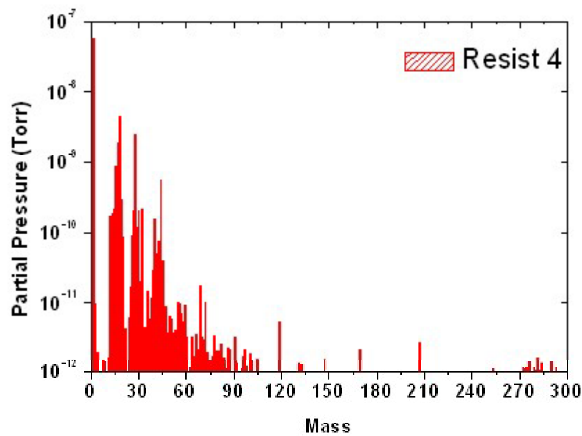
Changing type of PAG

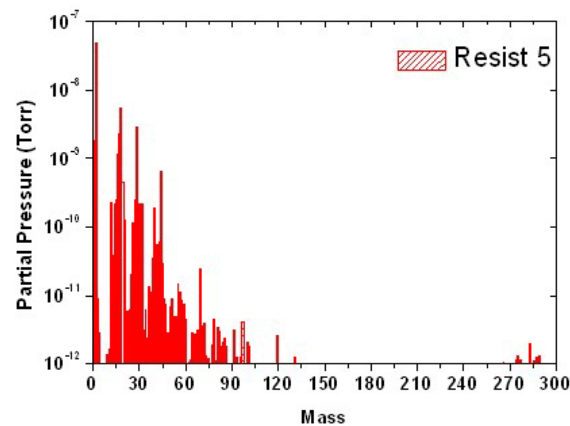
- Total outgassing result : Different type of PAG

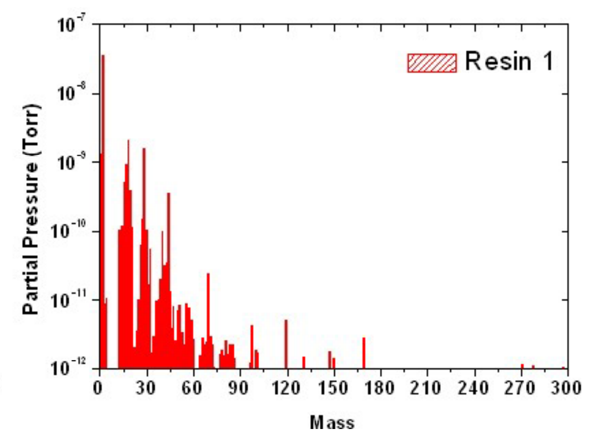












Changing type of PAG

- Different type of PAG

sample No.	SB(℃)/Sec	Coating speed (RPM)	Base Pressure (Torr)	Exposure Area (Cm2)	Total Out-gassing (molecules)	Out-assing (moecules/Cm2)
Resist 1	110/60	1400	2.0x10^-8	2.30E-02	2.58E+11	1.12E+13
Resist 2	110/60	1400	2.0x10^-8	2.10E-02	2.78E+11	1.33E+13
Resist 3	110/60	1400	2.1x10^-8	1.73E-02	3.22E+11	1.86E+13
Resist 4	110/60	1400	2.2x10^-8	1.77E-02	6.30E+11	3.56E+13
Resist 5	110/60	1400	2.0x10^-8	4.14E-02	1.71E+11	4.14E+12
Resin 1	110/60	1400	2.0x10^-8	2.00E-02	7.80E+10	3.90E+12

Anion difference

Cation difference

Sulfonium vs Iodonium

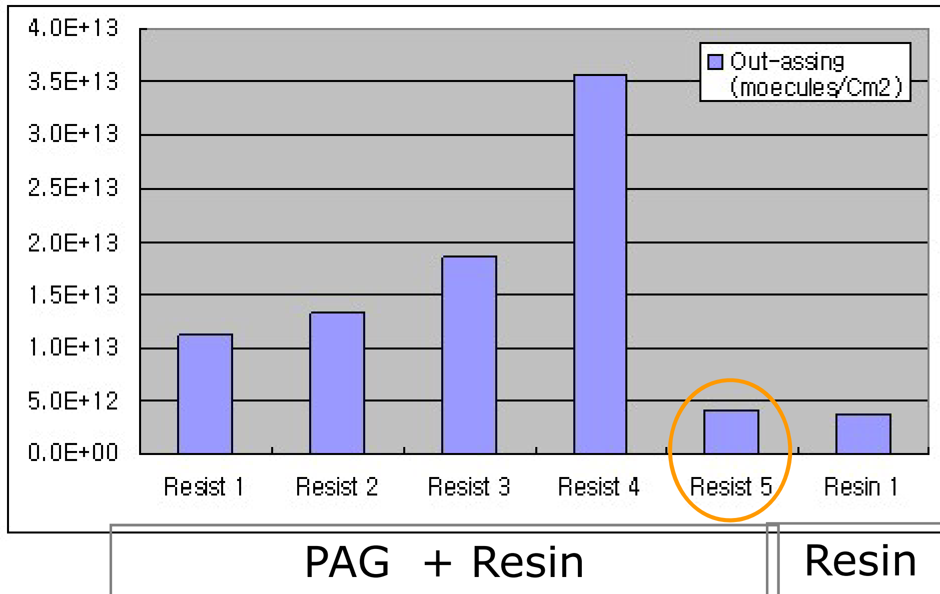
Imidate series

item

difference	sample	factor
Anion difference	#1 vs #2	Anion size
Cation difference	#1 vs #5	Cation structure
Sulfonium vs Iodonium	#2 vs #4	Cation series
Imidate series	#3 vs #1. 2	Imidate vs sulfonate

Changing type of PAG

- Different type of PAG



Best outgassing result (Resist 1)
- tri(4-tert-butyl)phenylsulfonium
+ TFS

Worst outgassing result (Resist 4)
- Iodonium series

Outgassing quantity comparison
- (Anion series variation)
TFS < PFBS < IMIDATE
- (different anion size)
Not effect

	#5	#1	#2	#3	#4
Cation	T(4-tert-butyl)PS	TPS	TPS	TPS	BPI
Anion	TFS	TFS	IMIDATE	PFBS	PFBS

Increase of outgassing quantity

Summary

- EUV outgassing : source of optics contamination
- EUV PR evaluation system was constructed at the Pohang Accelerater Laboratory (PAL)
  : EUV source – synchrotron
  detection – QMS
- Resist outgassing analysis
  - outgassing factors
    : resist thickness. soft bake temperature. type of PAG
  - changing type of PAG
    : tri(4-tert-butyl)phenylsulfonium trifluoromethanesulfonate (best outgassing result)
    Iodonium series (worst)
    Anion size (NOT effect)
  - Outgassing segments from the resist were mainly caused by PAG decomposition