Resist outgassing evaluation by gas chromatography mass spectrometry (GC-MS), quadrupole mass spectrometry (QMS) and pressure-rise

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Resist outgassing evaluation method

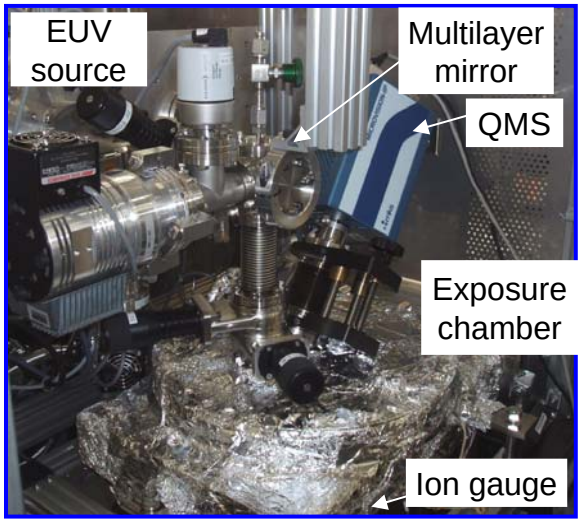
Methods	Description	Evaluation time	Selete
Pressure rise	□ Simple and quick for quantification. ■ Component identification not possible.	2 hours/sample	☺
GC-MS	□ Component identification possible. ■ CO_2 cannot be detected. ■ Low throughput.	1 day/sample	☺
QMS	□ In-situ qualification possible ■ Quantification not possible. ■ Qualification inaccuracy due to fragmentation effect.	2 hours/sample	☺
Witness mirror	□ Contamination level directly observed. ■ Low throughput and high cost.	A few days/sample	😐

□ Advantage & ■ Disadvantage

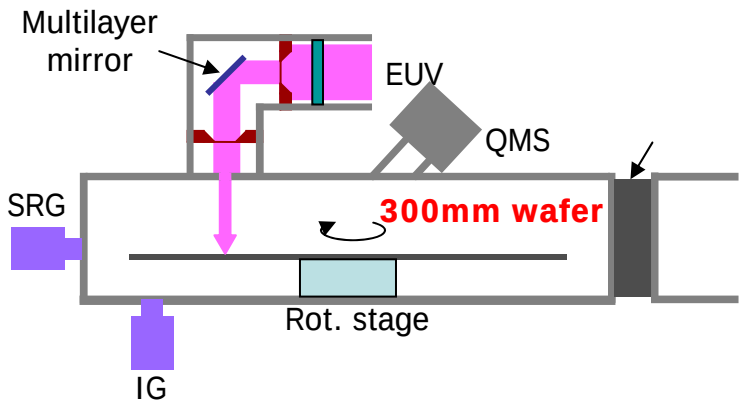
Pressure rise, GC-MS and QMS methods are applied for resist outgassing evaluations.

Evaluation tools for resist outgassing

Pressure rise method

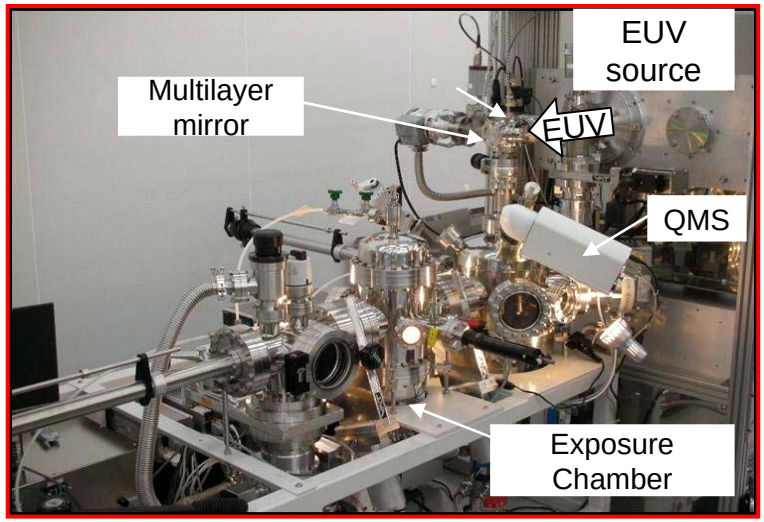


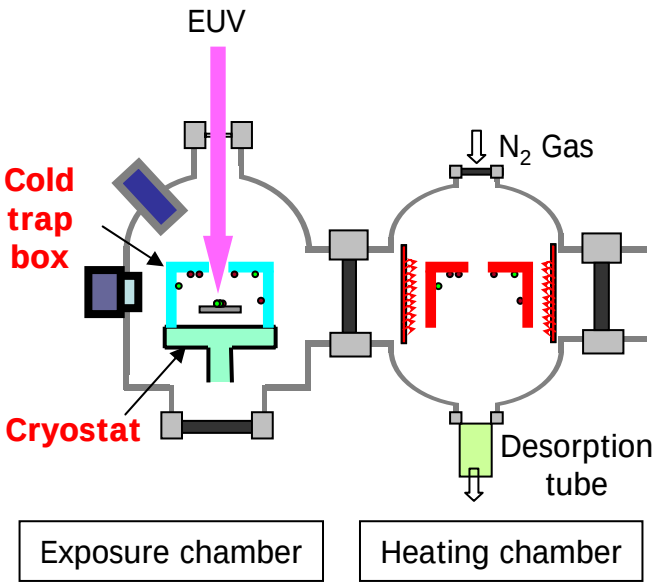
QMS analysis



EUV Source	: EQ-10MR (Energetiq)
Power on Wafer	: 0.03mW/cm^2
Exposure area	: 1.43 cm^2
Base pressure	**: 8x10^{-7} Pa**

GC-MS method

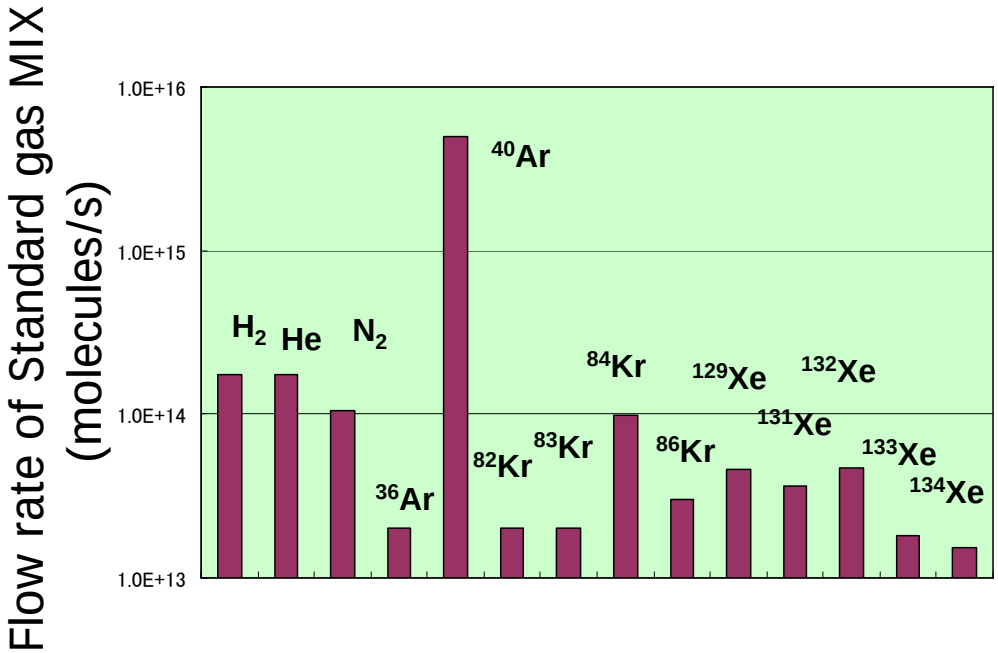




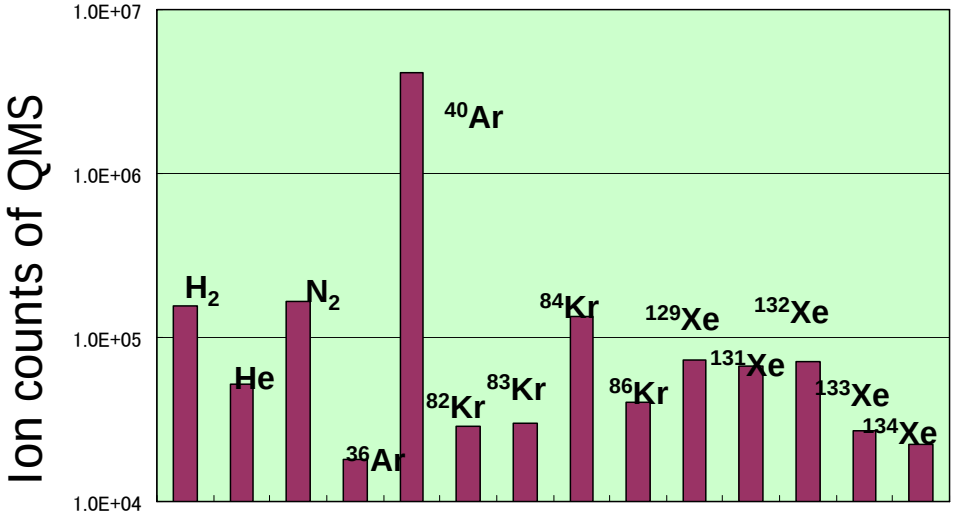
EUV Source	: EQ-10MR (Energetiq)
Power on Wafer	: 0.014mW/cm^2
Exposure area	: 1.09 cm^2
Base pressure	**: 1x10^{-7} Pa**

Calibration: Spinning rotor gauge (SRG) and Standard gas MIX

Ion gauge (IG) calibrated by SRG

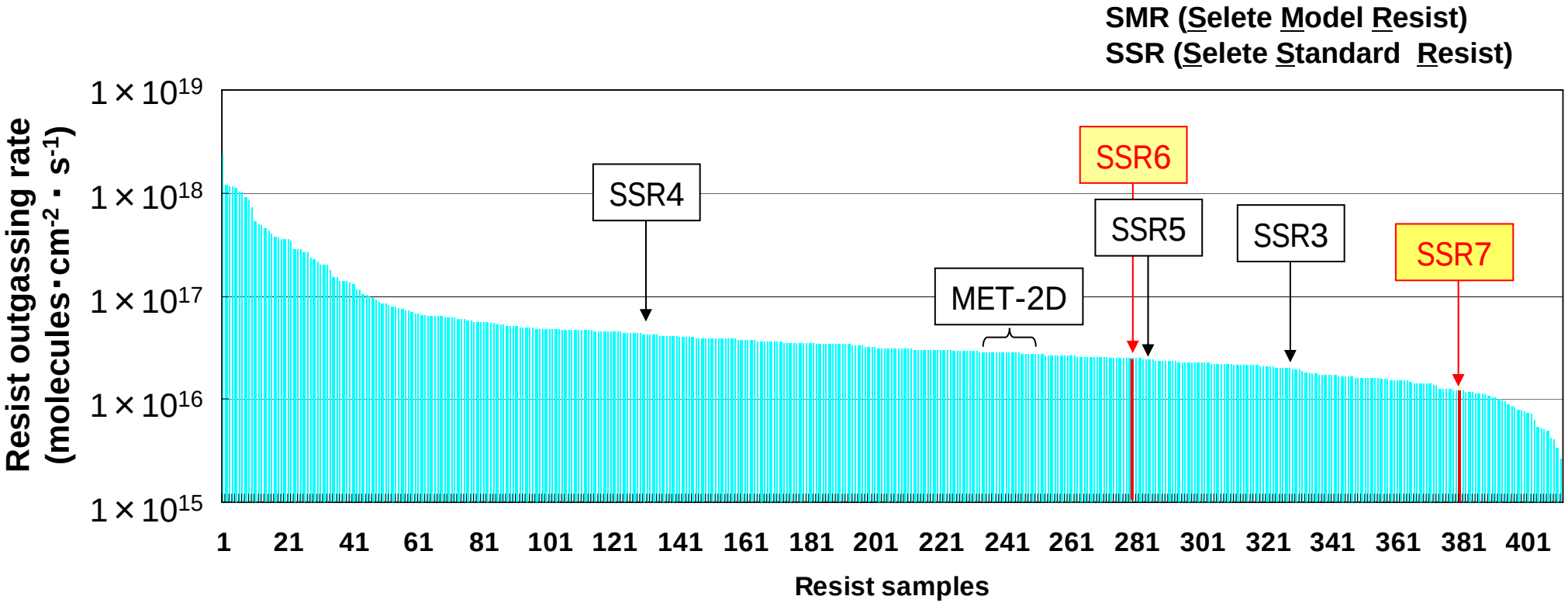


QMS calibrated by Standard gas MIX



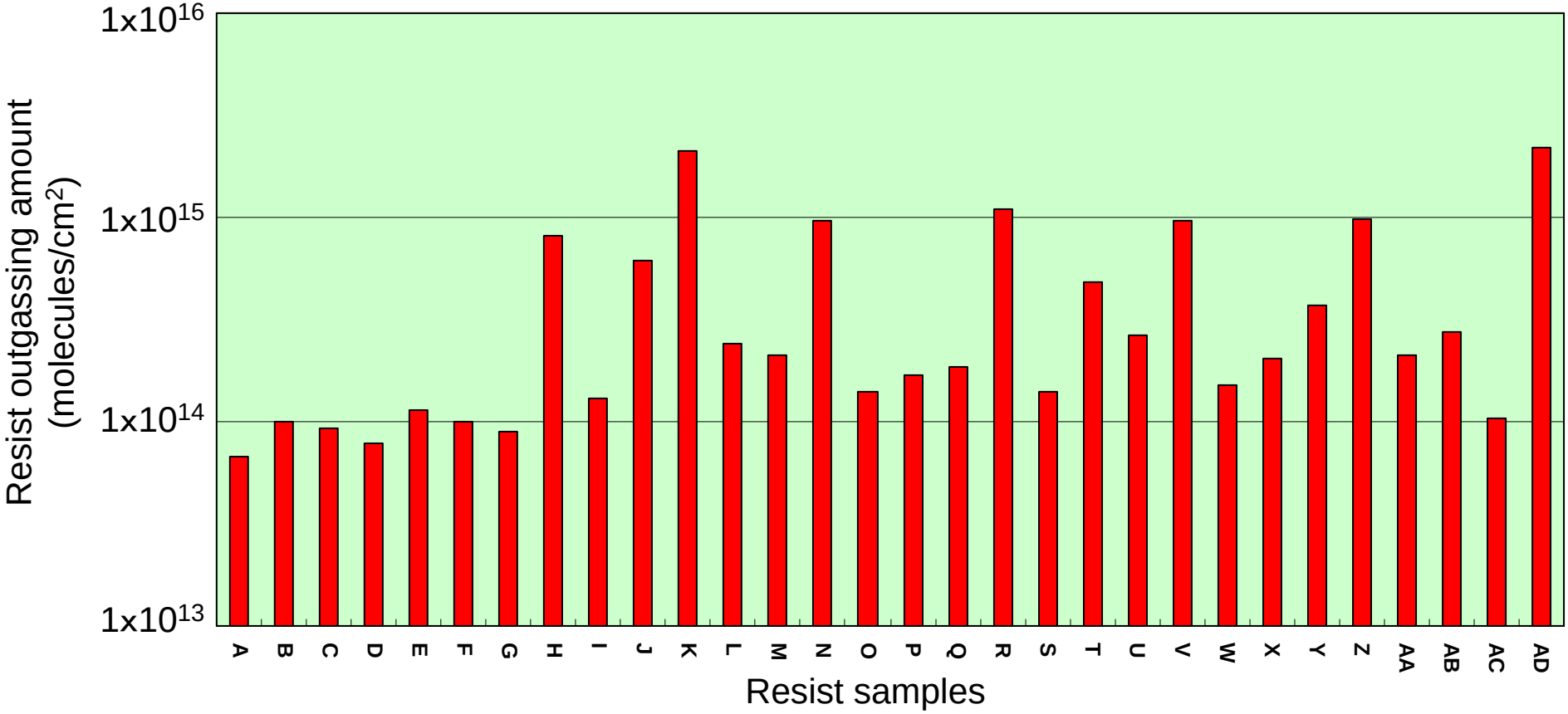
Resist outgassing rate: Pressure rise method

— Calibrated ion gauge (IG) and effective pumping speed —



More than 400 resist samples were evaluated. These are "Quick Screening".

Resist outgassing amount: GC-MS (resists dependency)



More than 30 resist samples were evaluated by GC-MS.

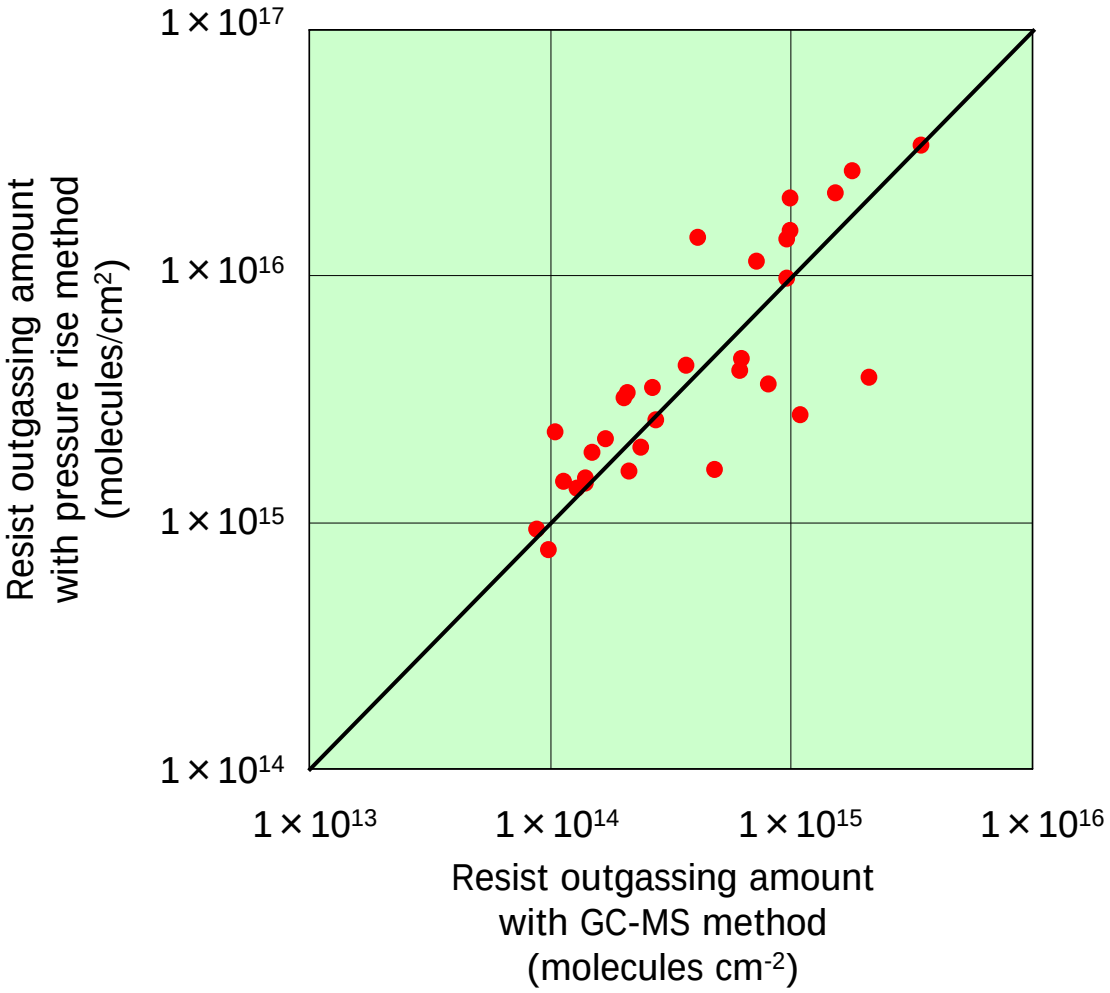
Resist outgassing components: GC-MS (resists dependency)

(unit: %)

Outgassing components	MW	Resist Name																
		A	B	C	D	E	F	G	H	I	J	K	L	M	M	O	P	Q
2,2-dimethyl-Oxirane	54													6				
2-methyl-1-Propene	56	30	50	48	77	36	41		1		0			57	96			2
1-Butyne	56														1			
Acetic acid	60			52					19									
Furan	68					18												
2-methyl-2-Propenal	70		3			7						1			0			
Benzene	78					0		62	21	57	55	7	45	1		84	75	60
Hexanal	100						12	6										
p-Xylene	106	22																
(1,1-dimethylethyl)-Benzene	134				4										2			
2-Adamantanone	150							3		39								
Biphenyl	154								0		1	18	1			4	8	2
Cyclohexene, 1-phenyl-	158											57		1				
Benzene, cyclohexyl-	160											9						
2-Vinyladamantane	162								50				32					
Dibenzothiophene	184					3	14							20				
Diphenyl sulfide	186								9	4	44	9	19			11	17	10
2,4-dimethyl-Heptanedioic acid	188												0					25
Others		48	47		19	36	32	29					4	16				1

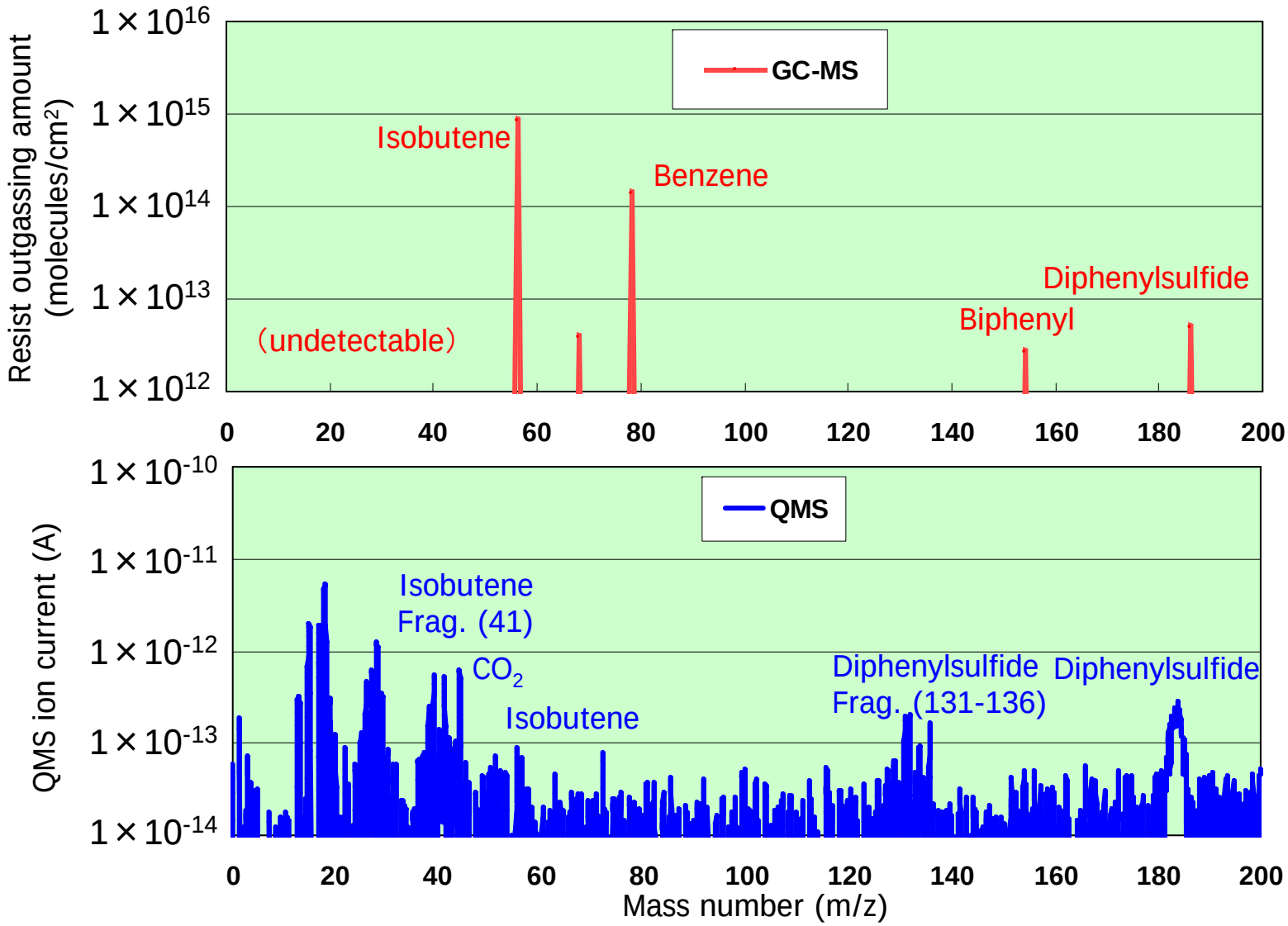
Relatively large molecules (Mw > 100) from resist outgas were detected.

Comparison of methods (Pressure rising vs. GC-MS)



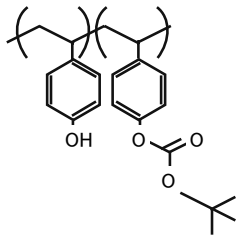
For the Selete evaluation tool, amount obtained through pressure rise method was around 10 times larger than GC-MS.

Comparison of methods (QMS vs. GC-MS)

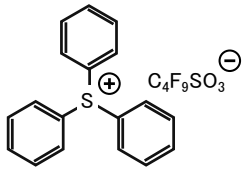


SMR447
(Selete Model Resist)

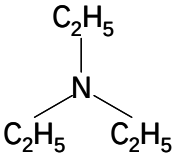
Base resin
& Protecting group



PAG: TPS-PFBS

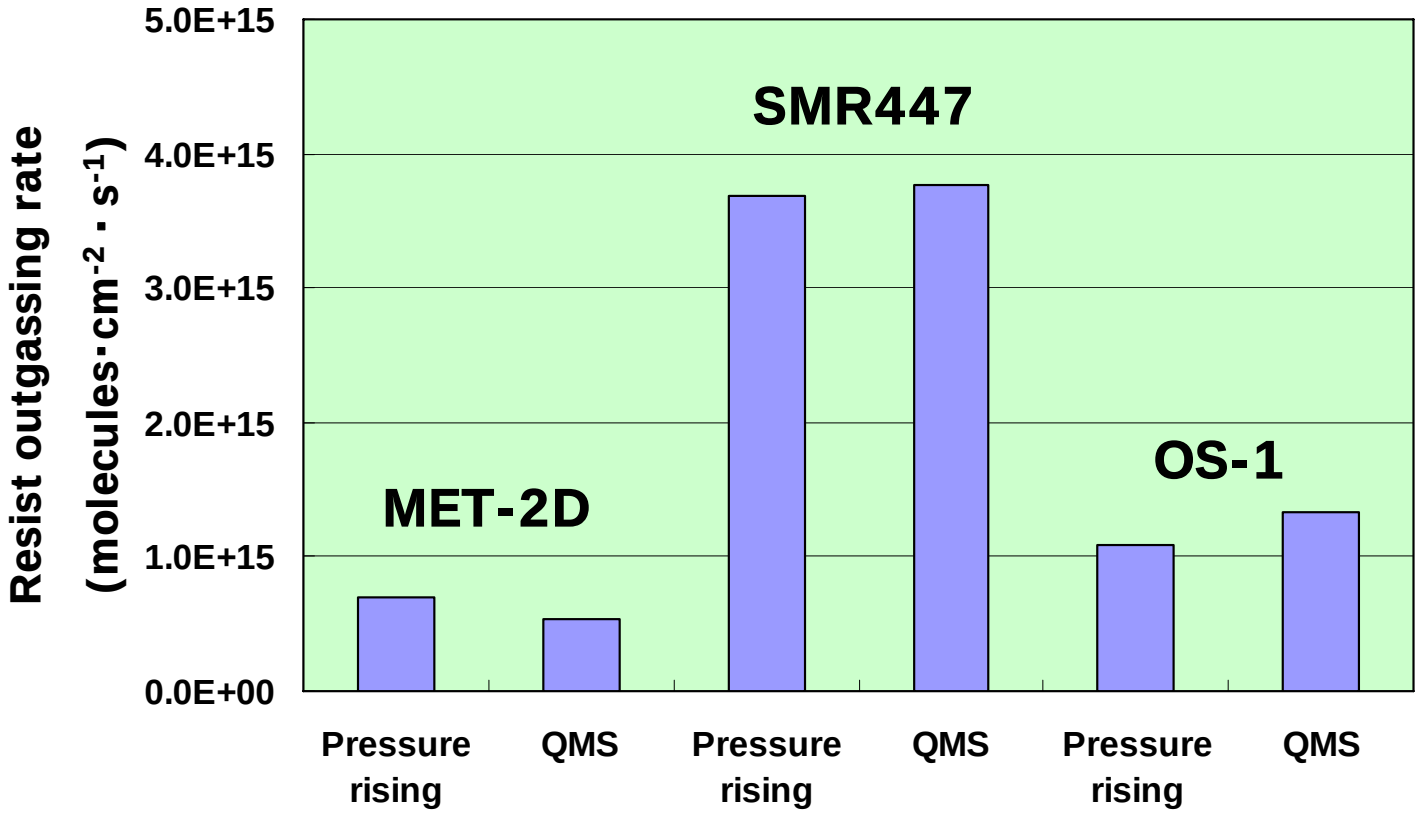


Quencher: TEA



Large difference in the quality of detected mass spectra between GC-MS and QMS results.
QMS method for quantitative analysis is limited by fragmentation.

Comparison of methods (QMS vs. Pressure rising)



Good correlations between QMS and pressure rise methods were obtained (factors < 2).

Selete resist outgassing evaluation procedure

Quantification (Quick Screening)	Pressure rise method Screening of resist samples received for exposure.
Component analysis Quantitative analysis	GC-MS method Improvement of resist samples based on new resist components.
Mechanism analysis	QMS analysis Basic study to improve tools and control methods.

Resist outgassing methods are applied depending on analysis objectives.

Acknowledgements

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