EUV Resist Outgassing Round Robin Results

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Objective

- What level of outgassing from resist is acceptable?
- How should we measure outgassing?
- How should we standardize the methodology?
- Ultimately, how we determine if a resist is safe to use?

Outgassing Specifications

- **Intel's spec for microexposure tools**
  - 6.5x10^{13} molecules/cm^2 (2004)

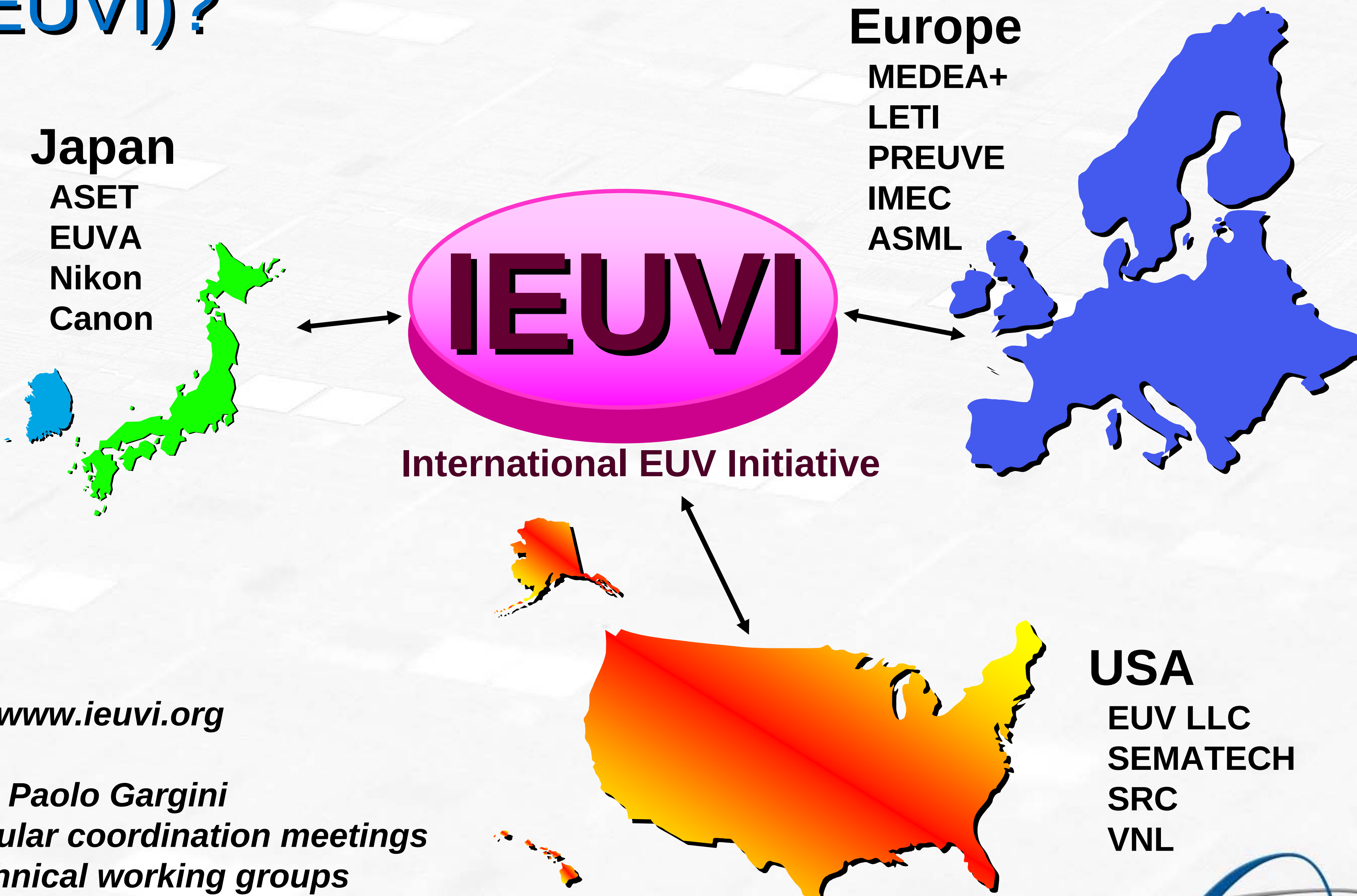
    (Sum of all outgassed species 33-550amu)

- **ASML's new outgassing protocol (July 2006, IEUVI resist TWG meeting)**
  - Expose a multilayer sample and resist in the same chamber
  - Expose the equivalent of one 300 mm wafer
  - The resist passes if it causes ≤ 2% reflectivity loss, or if it can be cleaned to get it back to less than 2% reflectivity loss.

Approach

- The IEUVI resist technical working group (TWG) initiated an EUV resist round robin
- 8 researchers agreed to test a model resist and compared results
- The goal is to compare results and develop standard methodology for resist outgassing
- Model resist was formulated by Massachusetts Institute of Technology, Lincoln Laboratory (MIT LL)

What is the International EUV Initiative (IEUVI)?



IEUVI
http://www.ieuvi.org

Chair: Paolo Gargini
- ***Regular coordination meetings***
- ***Technical working groups***
- ***Benchmarking data exchange***

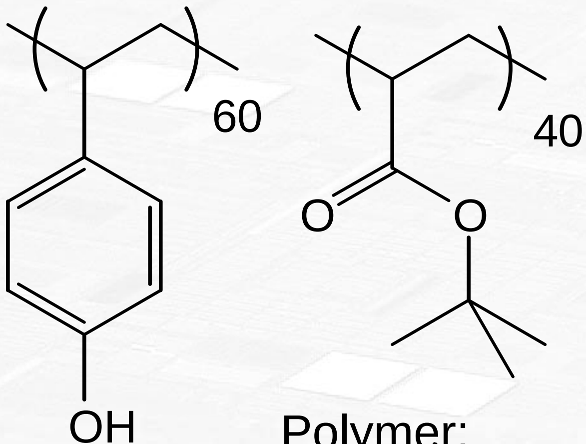
Resist Round Robin Outgassing

- Experimental Details (I)
  - Determine Ezero on each tool
  - Run outgassing test at 1.5X Ezero
  - Record time in vacuum and vacuum level at start of exposure (time in vacuum: 5 hours, 20 minutes, 15 minutes?)
  - For mass spec, record how long it takes to detect a certain mass
  - Use toluene an internal standard
  - Report results in units of molecules/cm^2-sec

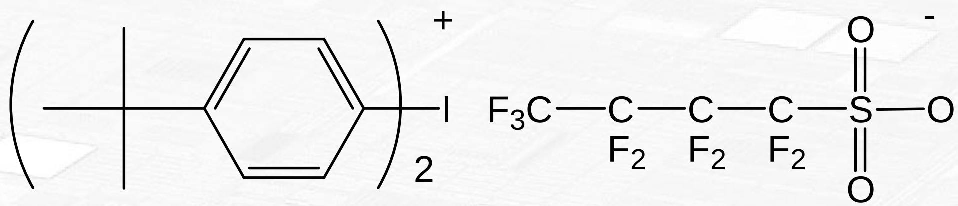
Resist Round Robin Outgassing

- Experimental Details (II)
  - Resist and MSDS shipped by SEMATECH
  - Resist formulated by MIT LL
  - Process:
    - Spin speed: 4000 rpm should yield approximately 125 nm thickness
      Softbake: 140°C for 60 seconds
      Postbake: 130°C for 90 seconds
      Development: use 0.26N TMAH (e.g. LDD26W) for 40 seconds
  - Ezero estimated to be ~3.7 mJ/cm^2 at Wisconsin

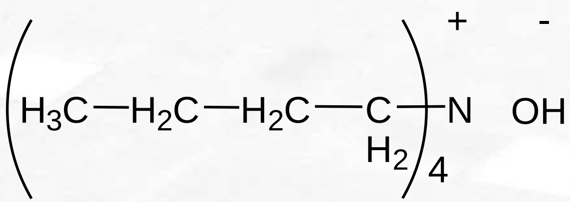
Round Robin Resist Structure
LUVR-99246*



Polymer:
poly(4-hydroxystyrene-co-tert-butyl acrylate)



Photoacid generator:
di(tert-butylphenyl) iodonium -1-butanesulfonate



Base:
tetrabutylammonium hydroxide

Polymer:	0.940
PAG:	0.050
Base:	0.010

Calculated EUV
base 10 absorbance = 2.01 μm^{-1}

*Resist provided by MIT LL, Ted Fedynyshyn

Resist Outgassing Researchers (8)

- **Intel**
  - U. Wisconsin, synchrotron source, desorption tubes
- **Trieste**
  - Synchrotron source, mass spec
- **SEMATECH/U. Wisconsin**
  - Synchrotron source, desorption tubes
- **SEMATECH/U. Albany**
  - Standalone source, mass spec, desorption tubes, witness plate, open frame
- **ASET**
  - Synchrotron source, mass spec
- **CEA/LETI**
  - Standalone source, mass spec, controlled contamination studies
- **BOC Edwards**
  - Standalone source (borrowed), mass spec
- **University of Hyogo**
  - Synchrotron source, mass spec

Methods of Measurement

- **Accumulation method (Wisconsin)**
  - • Total amount of outgassing molecules collected on desorption media
  - + Species can be separated by gas chromatography (GC), identified by mass spectroscopy (MS)
  - – Collection efficiency is dependent on media
- **Pressure rise method**
  - • Outgassing measured by pressure rise and pumping speed
  - + Rate determined by pressure rise and pumping speed
  - – Need to calibrate pressure gauge
- **Summing masses using quadrupole mass spec (QCS)**
  - + Can sum masses that are more important to contamination
  - – Need to calibrate QMS
  - – QMS sensitivity depends on mass number

Converting Measured Outgassing to Estimated Rate for Production Tool

- The estimated power for a production tool is 0.2W, and the estimated intensity is 0.4W/cm^2 (see appendix for details)

- The conversion factor for converting molecules/cm^2 to molecules/cm^2-sec for production tool is 30 (see appendix for details)

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Outgassing Results (I)

Institute	Source Method	Results		Estimate Rate Molecules/cm² /s @Prod. Tool (0.4 W/cm²)
		Molecules /cm² @5.6 mJ/cm² dose	Molecules/cm²/s @each intensity condition	
Intel Wisconsin	Synchrotron Accumulation method	4.4×10^{11}	2.9×10^{10} 0.33 mW/cm² 33-550 amu*	1.3×10^{13}
SEMATECH Wisconsin	Synchrotron Accumulation method	3.9×10^{13}	2.6×10^{12} 0.33 mW/cm² 35-435 amu*	1.1×10^{15}
ASET	Synchrotron Pressure rise method	1.9×10^{14}	4.5×10^{12} 0.13 mW/cm² 1-200 amu	5.7×10^{15}
Univ. of Hyogo	Synchrotron Pressure rise method	9.4×10^{14}	4.5×10^{13} 35-200 amu	6.7×10^{16}

*Excluding 44 amu (CO_2)

Outgassing Results (II)

Institute	Method	Results		Estimate Rate
		Molecules/ cm^2 @5.6 mJ/cm^2 dose	Molecules/ cm^2/s @each intensity condition	Molecules/cm^2/s @Prod. Tool (0.4 W/cm^2)
SEMATECH U. Albany	Stand-alone source Summing method	$3.3x10^{14}$	1.94×10^{13} 0.9 mW/cm^2 35-200 amu*	9.9×10^{15}
CEA/LETI	Stand-alone source Summing method	$1.2x10^{15}$	$4.5x10^{11}$ 2 $\mu W/cm^2$ 1-200 amu*	3.6x1016
ELETTRA Trieste	Synchrotron Summing method	1.4×10^{16}	1.4×10^{15} 0.72 mW/cm^2 1-100 amu	4.2×10^{17}
BOC Edwards	Stand-alone source Summing method	2.8×10^{14}	5×10^{13} 1 mW/cm^2 35-200amu*	8.3×10^{15}

*Excluding 44 amu (CO_2)

Observations

- All values ranged from 10^{13} to 10^{17} molecules/cm^2-sec for the estimated rates for a production tool

- Within same measurement methods, there are substantial variations

- The median value is 8×10^{15} molecules/cm^2-sec

Comparison of Accumulation Methods

SEMATECH and Intel Results @ Wisconsin

SEMATECH		Intel*	
% Area	Molecule	% Area	Molecule
2	Isobutane		
88	1-Propene, 2-methyl-		
3.4	Acetone		
3.3	Tert-butylbenzene	92	Tert-butylbenzene
3.6	Methylstyrene	7	Methylstyrene
Total =	3.9×10^{13} molecules/cm^2	Total =	4.37×10^{11} molecules/cm^2

***Trace amounts of CO_2, isobutene, and isobutane detected; too low for accurate detection/quantification.**

SEMATECH and Intel Results @ Wisconsin

- Both tests carried out at the University of Wisconsin using thermal desorption tubes and GC/MS
- Exposure conditions were the same, but desorption tubes were different
- Intel's tube resin is more accurate for high boiling points compounds; does not efficiently capture low boiling points compounds.
- GC/MS performed by different laboratories
- Repeatability of the two systems is a factor of 2-6

References:

1) W. Yueh, H.B. Cao, V. Thirmala, H. Choi, "Quantification of EUV Resist Outgassing," *Proc. SPIE*, Vol. 5753, 765, 2005.

2) K. R. Dean, K. Gonsalves, M. Thiyagarajan, "Effects of material design on extreme ultraviolet (EUV) resist outgassing," *Proc. SPIE*, Vol. 6153, 2006.

Conclusions

- Substantial differences were observed between institutions
- Repeatability is within 2-6 for some institutions—this outgassing data helps suppliers improve their resists and protect optics
- SEMATECH and the IEUVI resist TWG will continue to work to standardize the methodology and make recommendations to the community
- Next steps, how to correlate counting molecules methods to direct contamination tests (ASML proposal)

Appendix

Estimation of EUV intensity on wafer in production tool

Method-1 : from the source power of 115 W@IF。

Total reflectivity loss of by 12 multilayer mirror(R=68%) = 0.01

Reflectivity loss by mask (65%)= 0.65

Other loss（50%：not sure)：0.5 →Total：0.35 %

EUV power leaching onto wafer is 0.4 W. IF the exposure area is assumed to be 0.5cm^2, EUV intensity on wafer is 0.8 W/cm^2.

Method-2: from throughput of 100 WpH and resist sensitivity of 5mJ/cm^2

Exposure area=π x(15cm)^2 x 80%(effective area ratio）=565 cm^2

Exposure time=3600s/100x40%(overhead correction）=14.4 s

$$\text{Power} = \frac{5\ \text{mJ/cm}^2}{14.4\ \text{s}} \times 565\ \text{cm}^2 = 0.2\ \text{W}$$

EUV intensity =0.2W/0.5 cm2 = 0.4 W/cm^2

Though there are twice discrepancy, It is not so bad..

Temporary, we adopt 0.2 W for power and 0.4 W/cm2 for intensity.

Nishiyama — ASET — EUV Process Technology

How to convert from molecules/cm^2 to molecules/cm^2/s

If the outgassing amount of molecules, M molecules/cm2 is obtained using resist of ε J/cm2 (Esize), outgassing rate (amount of outgassing molecules in 1s) can be calculated as follows

Exposure time for Esize in EUV intensity of I_{euv} W/cm^2

$= \varepsilon\ (\mathrm{J/cm2}) / I_{euv}\ (\mathrm{W/cm^2}) = \varepsilon / I_{euv}\ (\mathrm{s})$

overhead correction factor (duty ratio) = α

Light-on time in 1 s = α (s)

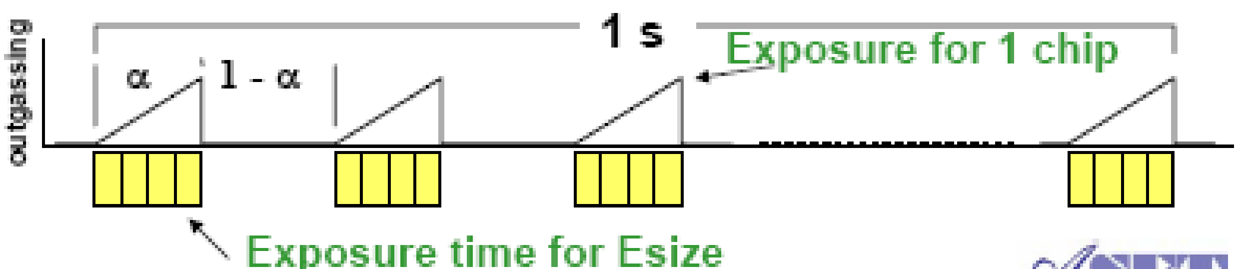
number of irradiations for Esize exposure = αI_{euv} (s) / ε

Outgassing amount in 1 s = M × αI_{euv} (s) / ε

If α=0.4, ε = 5.5 mJ /cm^2, and I_{euv} =0.4 W/cm^2 is assumed,

conversion factor: $\alpha\ I_{euv}(s) / \varepsilon$ = 30

So, 10^{12} molecules/cm^2 in accumulation method corresponds to the outgassing rate of 3 x 10^{13} molecules/cm^2



Nishiyama

ASET
EUV Process Technology

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Published Outgassing Results

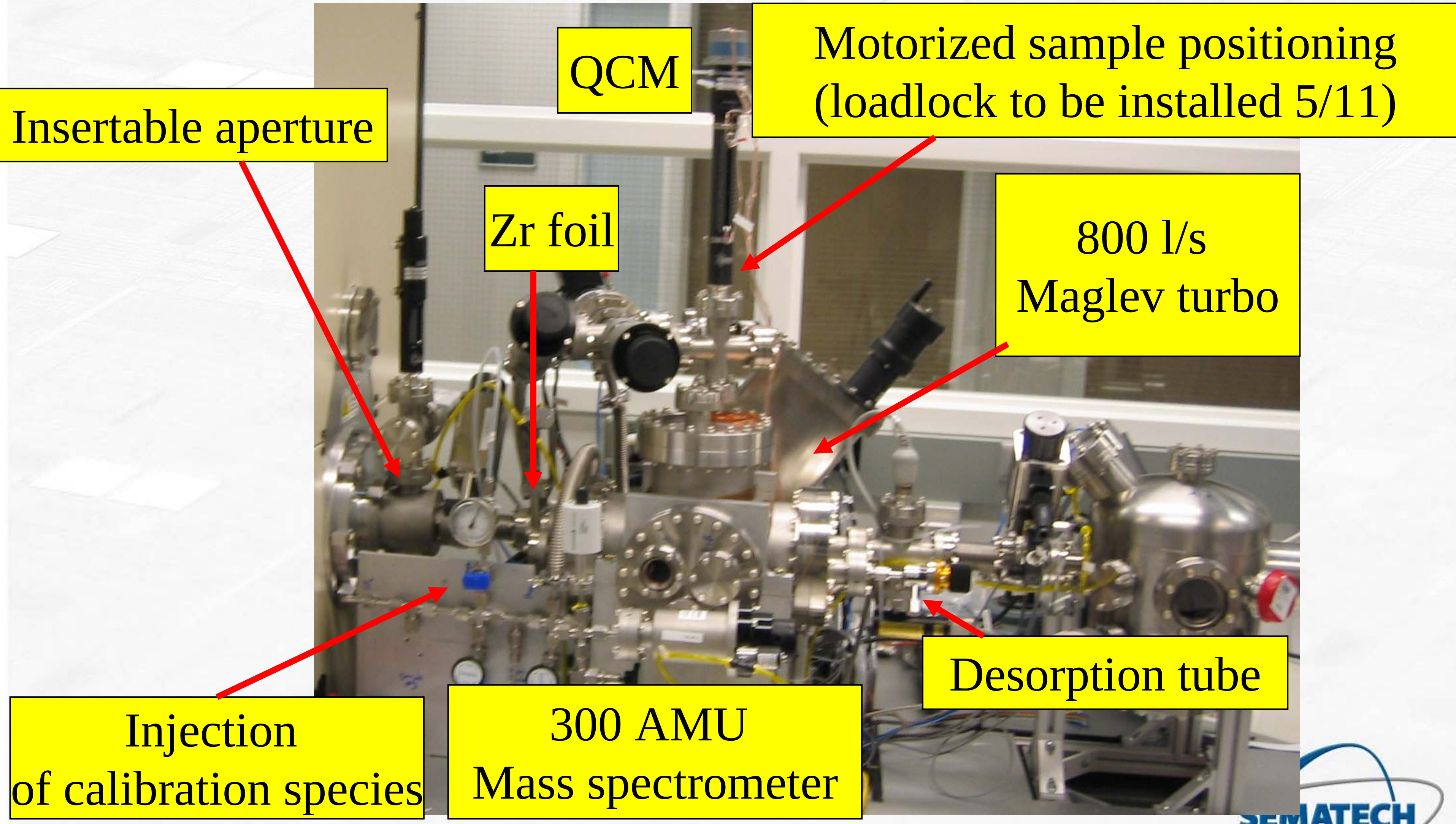
- Most outgassed species are products from acid-catalyzed or photochemical cleavage of protecting groups and decomposition products from the PAG[1]
- Outgassing amount correlates to resist type[2]
  - Low outgassing: DQN and annealing positive CA resist
  - High outgassing: Negative tone CA and non-CA resist
- EUV outgassing is higher than 193 nm or 157 nm outgassing[3]
- Resists with high Ea and non-ionic PAGs show lower outgassing[4]

1) Nealey, P. et al., J. vac. Sci. Technol. B 18(6), Nov/Dec 2000.
2) Watanbe, T., et al., J. vac. Sci. Technol. B 19(3), May/June 2001.
3) Domke, W-D., et al., SPIE, Vol. 5753, 2005.
4) Yueh, W., et al., SPIE, Vol. 5753, 2005.

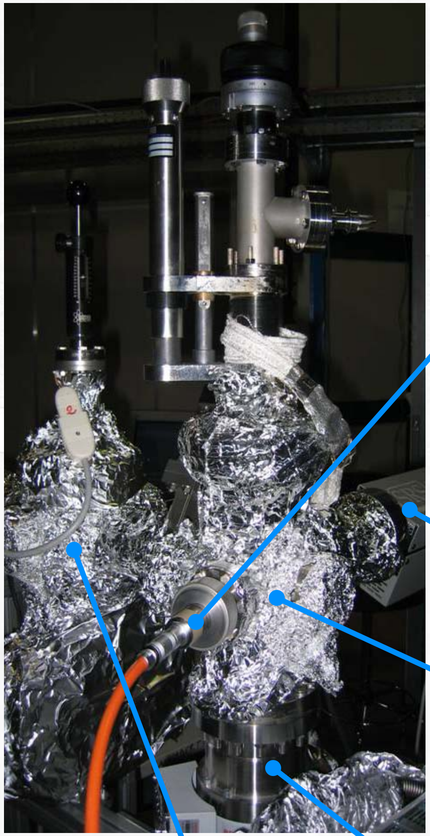
Albany Resist Outgassing System Details

UNIVERSITY AT ALBANY
State University of New York

College of Nanoscale Science and Engineering



Sincrotrone Trieste – Elettra Outgassing Tool



Inverted magnetron pressure gauge

Beam direction

Residual Gas Analyser (RGA)

Main chamber

Mask + photodiode chamber

Nominal 200 l/s (effective: 180 l/s) turbomolecular drag pump

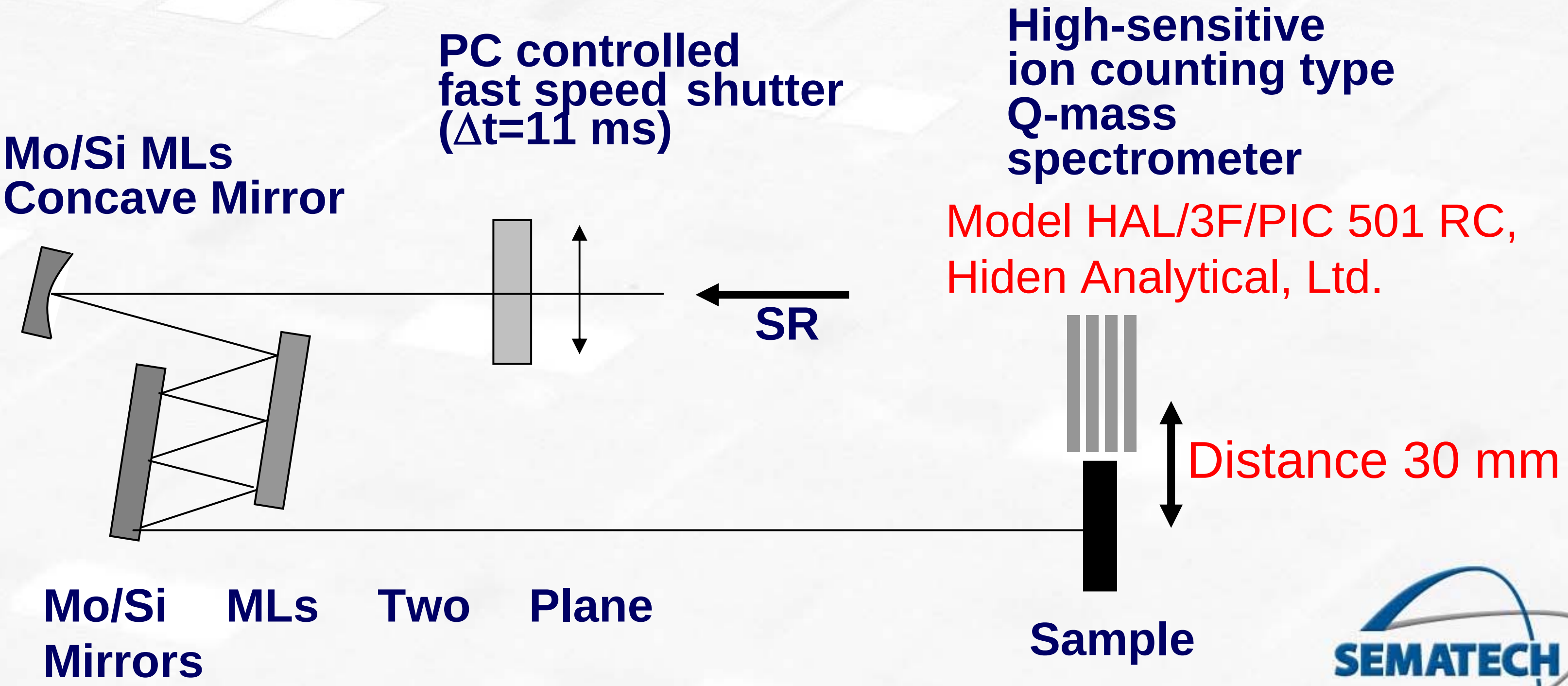
University of Hyogo Outgassing System

1) Measurements of sensitivity
2) Outgas characteristics
3) Chemical reaction analysis

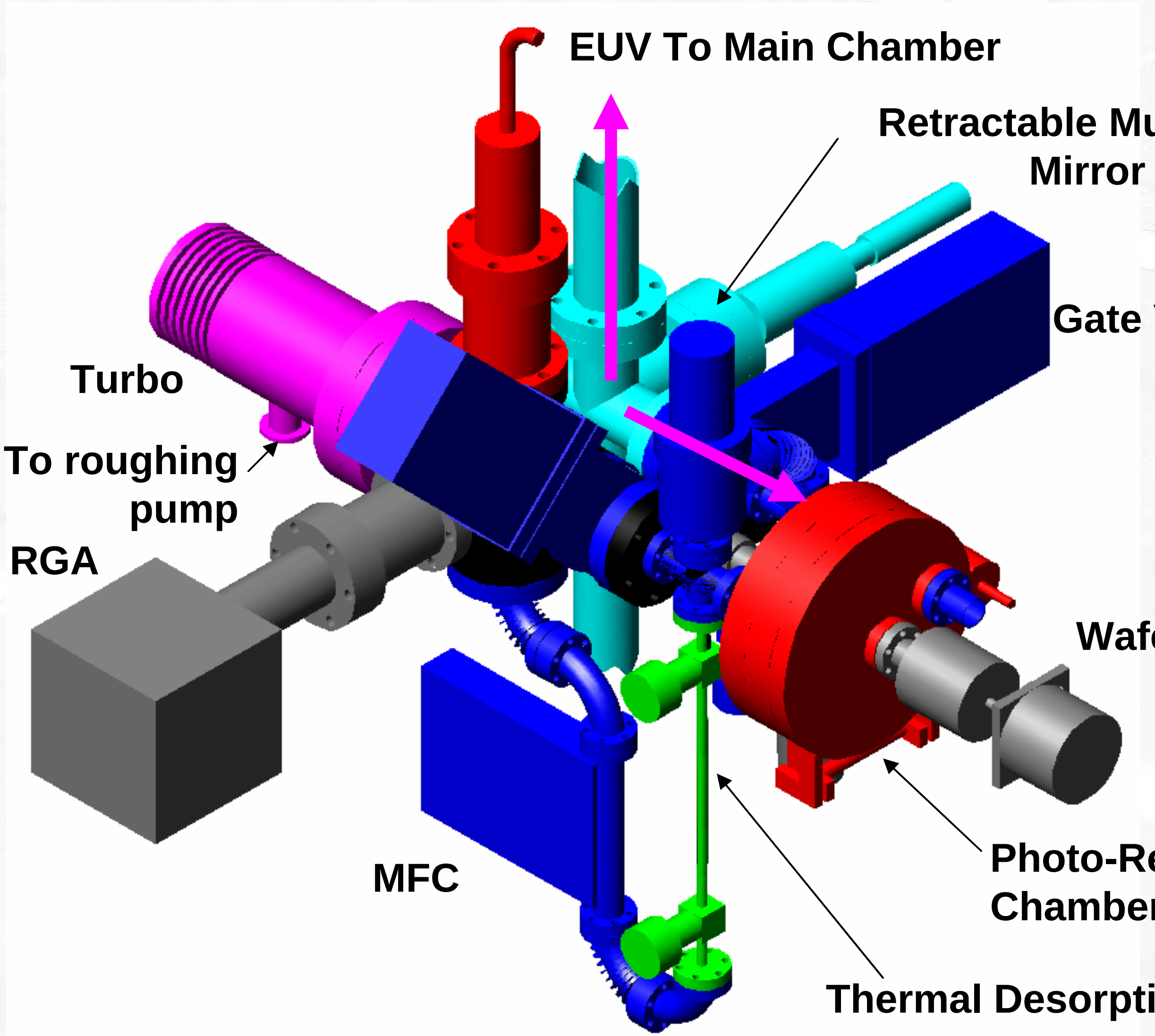
Simulating six-mirror optics

↓

Practical exposure spectrum



Wisconsin EUV Exposure Chamber
Synchrotron Source



LETI Stand Alone Outgassing Tool