Comparison of EUV resist out-gassing under continuous vs pulsed illumination

J. Simon[1], P. Michallon[1], B. Dal'Zotto[1], A. Jouve[1], L. Rumiz[2], P. Lacovig[2]

1.CEA/DRT/LETI -17 rue des Martyrs -38054 Grenoble, France
2. Sincrotrone Trieste S.C.p.A, S.S. 14 Km 163.5, in Area Science Park I - 34012 Basovizza - Trieste Italy

julia.simon@cea.fr

A stand-alone experimental set-up has been designed to study EUV resist out-gassing at CEA-LETI. The main features fitted on the vacuum chamber are a Z-pinch discharge plasma source, a load lock to introduce resist coated wafers or multilayered mirrors, a mass spectrometer and chemical species inlets. In particular, the calibration module and protocol will be described.
Sematech round robin resist was exposed on this out-gassing tool. The results obtained will be compared with the test performed on the Beamline 6.2L of the Elettra Synchrotron Light Source to try and establish if the EUV illumination type, pulsed versus continuous, has an impact.
Moreover, discussion on how far out-gassing results are comparable from one experiment to the other will be presented.

1.Stand alone experimental Set-up

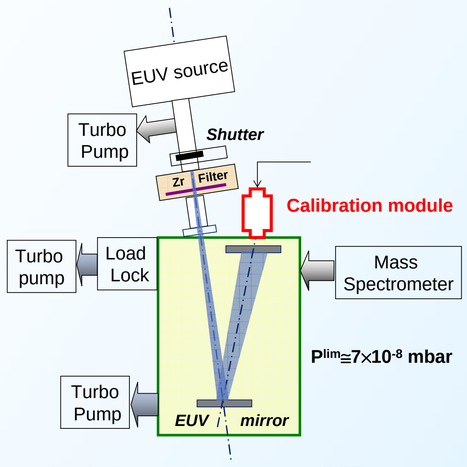


Fig. 1 : Schematic presentation of LETI stand alone out-gassing tool

EUV source :

Z-pinch discharge plasma source from Energetics
At 13.5 nm (2% in band) power on sample = 2 µW/cm²

2. Mass spectrometer Calibration

Partial pressure (P_i) calibration

$$I_{ion}^{MS} = I_e \cdot G_i \cdot \sigma_i \cdot \frac{n_i}{V} = \alpha_i \cdot \frac{P_i}{k_B T}$$ and $$\dot{n}_i = \frac{P_i}{S_i}$$ to obtain out-gassing rate $\dot{n}_i$ (molecules/cm².s)

Where S_i=effective pumping speed

Where I_e=electron source current
G_i=MS ion transmission efficiency
σ_i=Electron Impact ionization cross section
n_i/V=molecule density
α_i=calibration factor

Flow rate calibration

$$I_{ion}^{MS} = \beta_i \cdot \dot{n}_i$$

Direct out-gassing rate
Pumping speed is integrated in the calibration factor

Flow rate calibration chosen

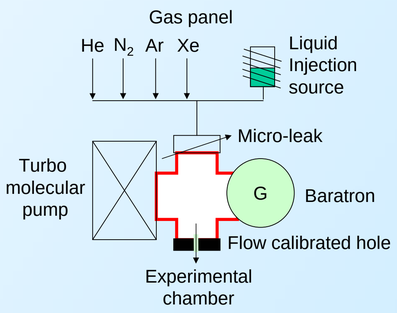


Fig. 2 : Mass Spectrometer calibration module

Flow rate Calibration module : Gas panel and liquid contaminant injection

Gas injection and Vaporization system
for liquid contaminants injection
for MS calibration &/or optics contamination

Flow calibrated hole gives injected flow through equation :

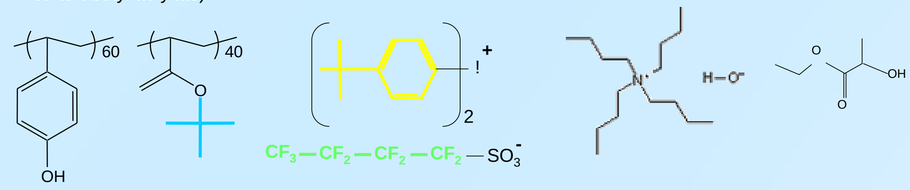
$$\dot{n}_i(molecules/s) = 7.811\times10^{15} \cdot \left(\frac{P_i(mbar)}{2047.815}\right) \cdot \sqrt{\frac{29}{M_{wi}}} \cdot (52.11)^2$$

Where P_i is the partial pressure upstream the calibrated hole
M_{wi} is the molecular weight of the molecule

3. Experimental Protocol

Round robin Resist (Formulated by MIT-LL)

94 % 60:40 poly(4-hydroxystyrene-co-tert-butyl acrylate)
5% t-butylphenyl iodonium 1-butanesulfonate
1% tetrabutylammonium hydroxide
Ethyl lactate (solvent)



4000 rpm spin coated to reach 132 nm thick film SB=140℃/60s, PEB=130℃/90s Dev=0.26 N TMAH/40s

Dose to clear=5.52 mJ/cm² determined on the tool

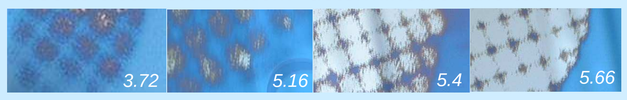


Fig. 3 : Detail pictures of exposed zone with varying dose (mJ/cm²)

Measurement Protocol @ LETI

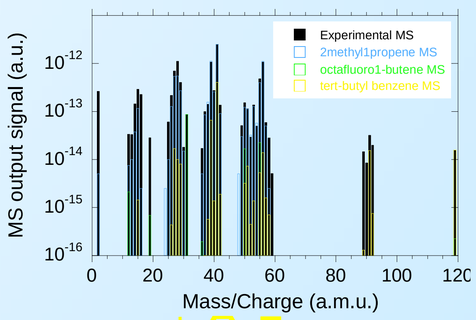
0-200 amu range covered using 1 wafer per 15 mass (15 mass acquisition in 7s)
Background spectrum taken EUV source ON - Zr filter state controlled through 132 mass
Resist exposed at 1.3×Eclear in 1 hour (Low EUV flux condition) - Exposed area= 69.4 cm2 (4.7 cm ∅)
2 hours in vacuum prior exposure

4. Sematech Round Robin out-gassing test results

Mass spectrum of RR resist

Experimental Mass Spectrum can be decomposed in 3 major components

Relative intensity distribution in good agreement with NIST MS data



No significative out-gassing for mass/charge > 120 amu

Small mass/charge peaks may also come from main chain scission
⇒ explain relative intensity discrepancies with 3 elements decomposition

Fig.4 : Experimental mass spectrum of RR resist

$CF_3-CF_2-CF_2=CF$

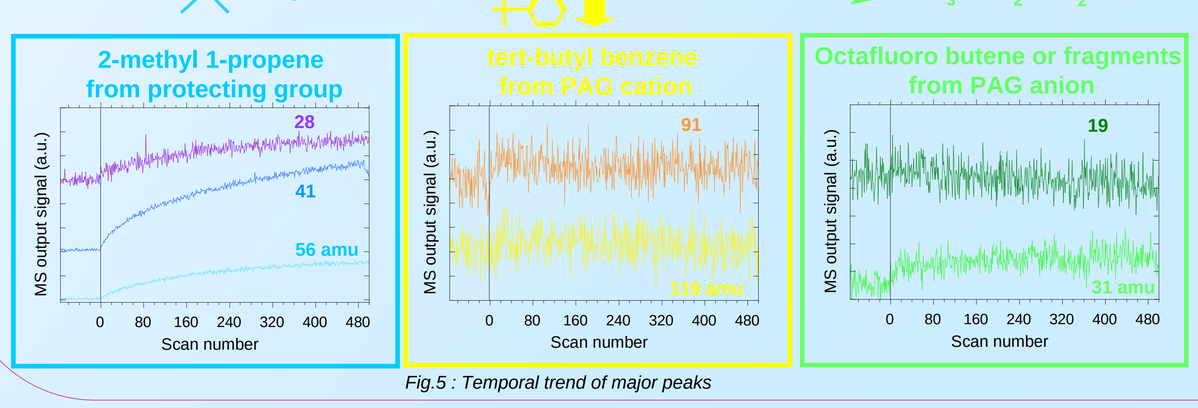


Fig.5 : Temporal trend of major peaks

MS calibration with toluene

(as recommended)

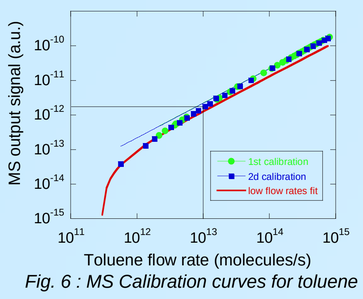


Fig. 6 : MS Calibration curves for toluene

Reproducible non linear response of MS for low flow rates

Non linearity for low flow rates tends to underestimate out-gassing amount ⇒ 2 fits

$$\beta_{91}^{highflow} = 2.2\times10^{-25} \pm 1\%$$
$$\beta_{91}^{lowflow} = -3.77\times10^{-14} + 1.299\times10^{-25}$$

Low flow rate zone limit : Ms output signal < 1.7 × 10⁻¹²

Out-gassing flow rates were estimated reading calibration curve for the major peaks of the 3 out-gassed elements

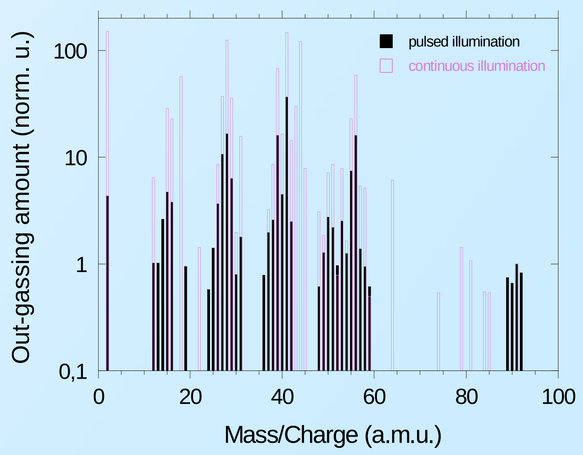
Out-gassed elements	Peaks considered	Total out-gassing in 91 equivalent molecules/cm².s
2-methyl 1-propene	56, 41, 39	**4.1×10^{11}**
tert-butyl benzene	119, 89, 90, 91, 92	**3.1×10^{10}**
Octafluoro butene or fragments	31	**1.4×10^{10}**

Considered peaks are molecular peak (when detected) and major fragmentation peaks of mass/charge > (Molecular ion)/2

Out-gassing is 90% deprotection-related

Using low flow rates fit and all fragmentation peaks of mass/charge > Molecular ion/2, we found total out-gassing amount of **8.8×10^{11}** (91 equivalent) molecules/cm².s

5. Continuous vs pulsed illumination comparison



Measurement Protocol @ Elettra SLS

0-100 amu range covered using 1 fresh region per 3 mass
3 mass acquisition every 1s
Resist exposed at 7.2 mJ/cm² ≅ 1.3×Eclear in 10 s (High EUV flux condition)
Toluene Partial pressure calibration using simulated Effective pumping speed to deduce out-gassing rate
Base pressure=2×10⁻⁸ mbar
48 hours in vacuum prior exposure
Exposed area=1.24 mm²

Fig. 7 : Relative intensity of out-gassing amount measured at LETI and on the Beamline 6.2L of the Elettra Synchrotron Light Source

Major peaks detected identical

Out-gassing amount with continuous illumination up to 3 orders of magnitude higher than pulsed

	Peaks detection comparison		Major peaks total amount out-gassing comparison							
Illumination	Detected / Elettra Undetected / LETI	Detected / LETI Undetected / Elettra	15	28	31	39	41	51	56	91
Synchrotron continuous	18,22,43,44,45 64,74,79,81,84,85		4×10^{13}	1.8×10^{14}	2.2×10^{13}	9.5×10^{13}	2.1×10^{14}	1.2×10^{13}	8.2×10^{13}	1.4×10^{12}
GD Source pulsed		13,14,19,24,25, 36,89,90,92	3.6×10^{10}	1.3×10^{11}	1.4×10^{10}	1.2×10^{11}	2.8×10^{11}	1.7×10^{10}	1.2×10^{11}	7.7×10^{9}

Peaks in red are masked in LETI system by Xe ²⁺ and Xe ³⁺ ions contribution from the source.

6. How far are the results comparable ?

❑ Impact of detector position

Detection prior to walls contact
Strong impact of detector solid angle on quantity detected

Elettra configuration is more sensitive

❑ MS ion source type and settings

I_e=2 mA, E_e=70 eV, E_{ion}=12 eV — **Elettra**
I_e=0.5 mA, E_e=70 eV, E_{ion}=5.5 eV — **LETI**

Impact on MS sensitivity
Impact on ion transmission efficiency
Impact on MS linearity

❑ Impact of effective pumping speed dependence with fragment

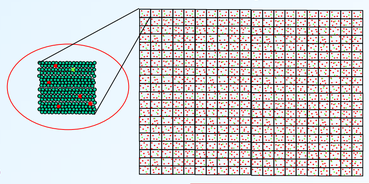
200l/s turbo-molecular pump **(Elettra)** 880l/s turbo-molecular pump **(LETI)**

MS response dependence with ion will differ in the 2 systems

❑ Impact of exposed surface ?

Elettra = 1.24 mm²
LETI = 6940 mm²

Possible statistical effects



An EUV photon has 5600 more chance to excite a PAG or Base molecule in LETI configuration

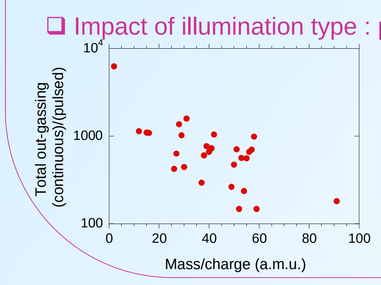
❑ Impact of EUV flux condition ⇒ exposure time ?

Elettra = 0.7 mW/cm² ⇒ 10s exposure
LETI = 2µW/cm² ⇒ 3600s exposure

Possible diffusion time impact on the out-gassing amount

LETI's longer exposure time may result in collecting more fragments

❑ Impact of illumination type : pulsed versus continuous ?



The total out-gassing ratio between continuous and pulsed illumination decreases with ion mass/charge

This behaviour looks more pumping system or MS related (variation of transmission efficiency dependence of the 2 MS), than illumination type related

Too much experimental differences to conclude concerning illumination type impact

Conclusion :

- ✓ A stand alone experimental set-up to measure out-gassing of EUV resist under exposition is implemented at CEA-LETI
- ✓ Mass spectrometer calibration module was described as well as the flow rate calibration protocol chosen
- ✓ The Sematech round robin EUV resist was tested, and total out-gassing amount detected was 4.5 ×10¹¹ molecules/cm².s (up to 8.8 ×10¹¹ depending on the estimation method)
- ✓ 2-methyl 1- propene (from deprotection reaction), tert-butyl benzene (from PAG cation decomposition) and fluorinated fragments (from PAG anion decomposition) were the 3 elements detected
- ✓Out-gassing amount detected on Beamline 6.2L at Elettra synchrotron Light source was found 3 orders of magnitude higher for the same resist
- ✓ Difference of experimental set-up and settings does not allow to conclude concerning illumination type impact on the out-gassing mechanism

Acknowledgments :

This work was partially supported by the More Moore IST project, Resist material was furnished by Sematech (IBM formulation)