

Quantification of EUV Resist Outgassing

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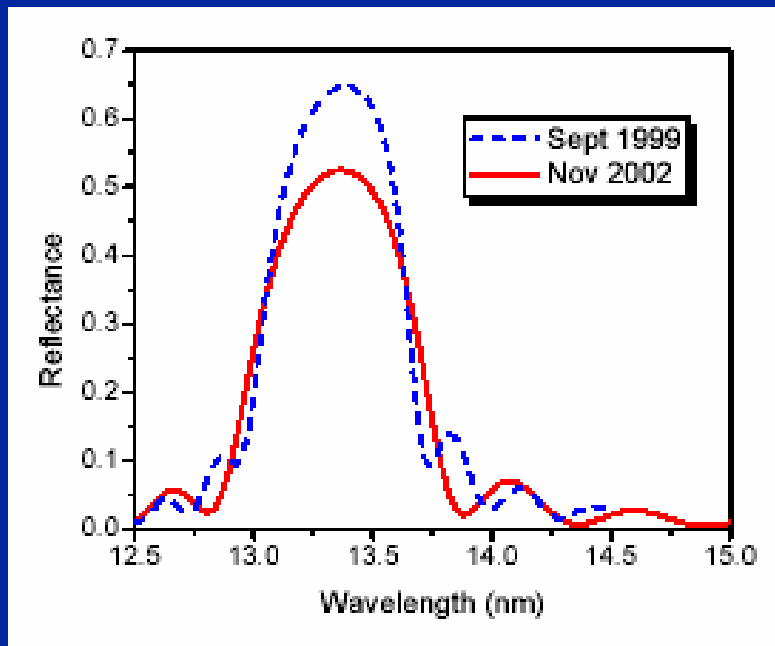
Intel Corporation

Outline

- **Motivation**
- **Experimental Set-up**
- **Quantification techniques**
- **Sources of resist outgassing**
- **Outgassing roadmap**

Motivation

- Resist outgassing in EUV tools can degrade optics. Carbon contamination and non-reversible oxidation will reduce reflectivity of the optics.



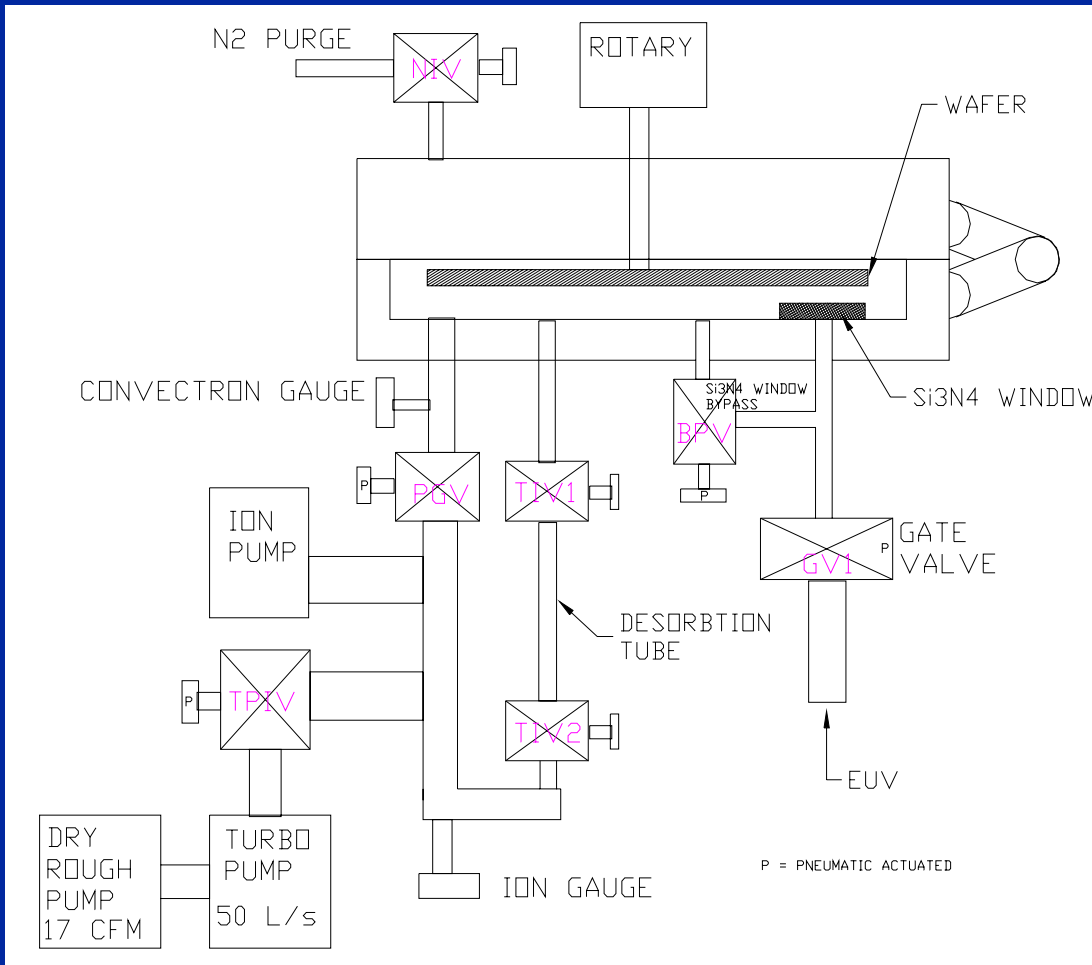
Reflectivity of EUV optics, before and after use in ETS.

From Grunow et. al.,
SPIE 2003, vol 5037,
p.418

- In order to design resists with low outgassing, a better understanding of EUV resist outgassing is needed.

Experimental set-up

Experimental procedure



- Place resist coated wafer in chamber, and pull vacuum.
- Expose resist to EUV.
- Purge chamber with nitrogen into absorption tube.
- Close valve to absorption tube, and remove wafer.
- Repeat with two additional wafers into a single absorption tube to amplify signal.
- Analyze outgassing contaminants using GC/MS.

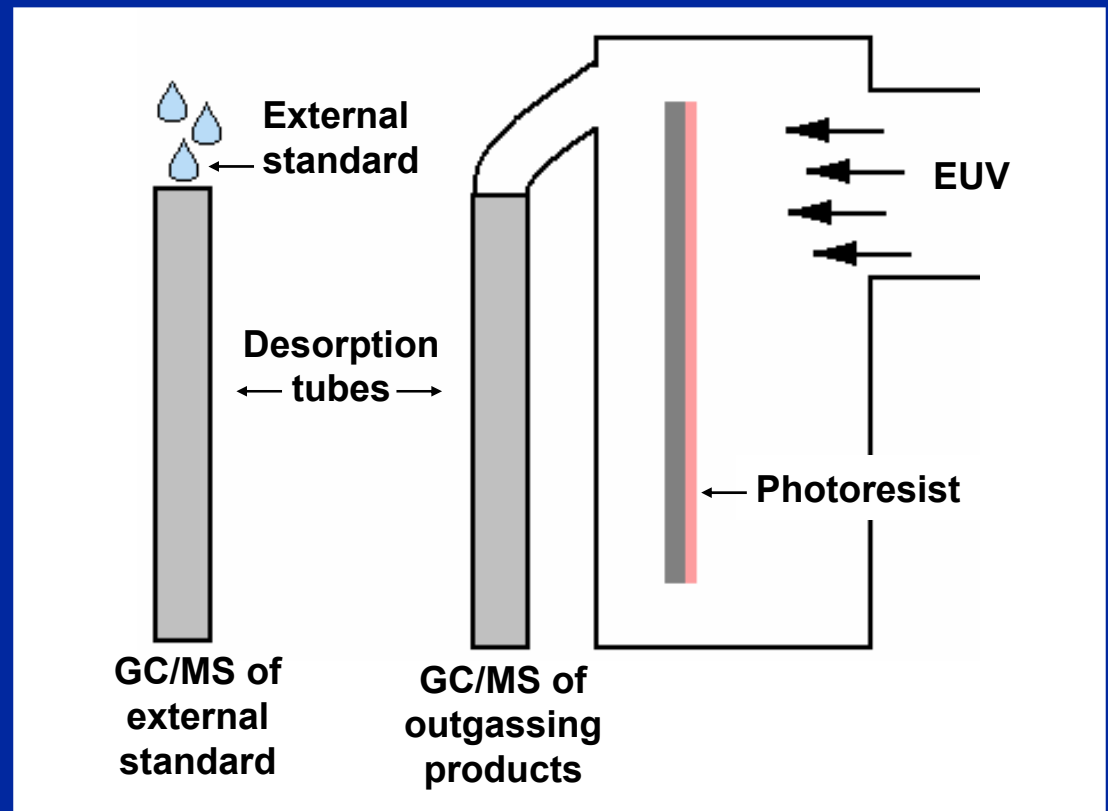
Experimental details

- Desorption tubes are packed with a mixture of Tenax and Carboxen resins.
- Conversion from GC-MS units to molecules is calculated by introducing a known quantity of a chemical into the GC-MS and characterizing the response.

$$\text{Outgassing Conc (molecules/cm}^2\text{)} = \frac{\text{GC-MS response (GC-MS units)} / \text{Conversion Factor (GC-MS units/molecules)}}{\text{Exposed area (cm}^2\text{)}}$$

External standard

A liquid standard is added to empty desorption tube and the response factor is measured. Different desorption tubes are used to measure outgassing of resist.



Advantage

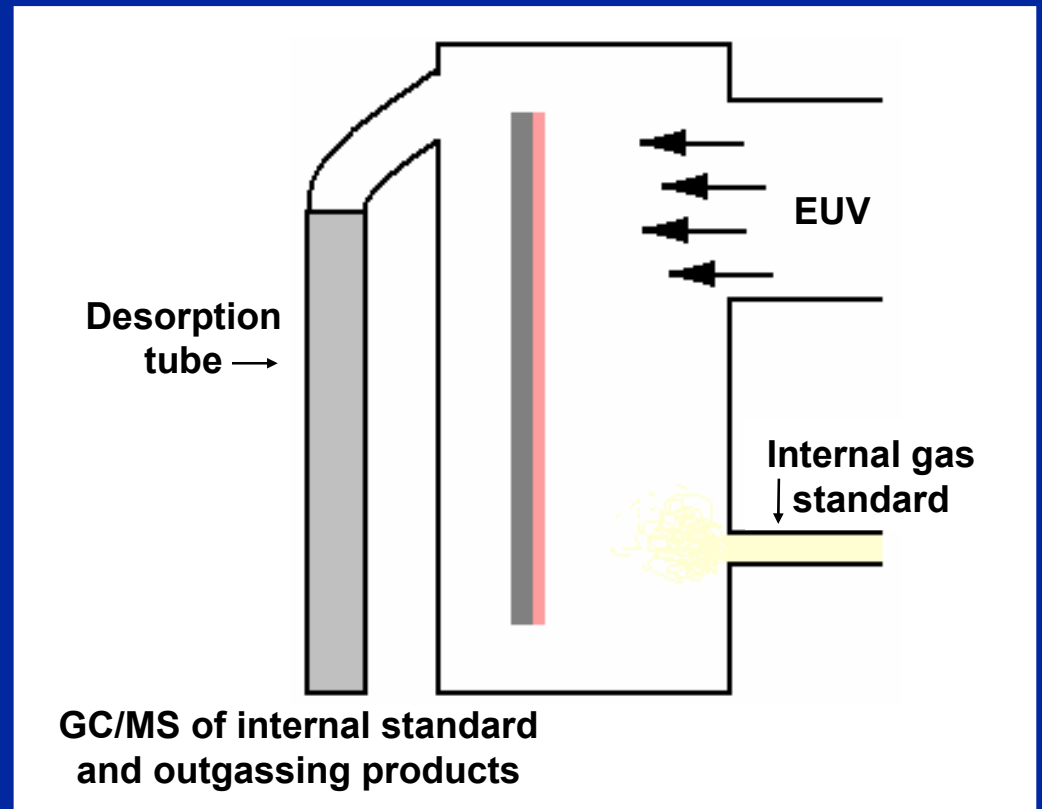
We can calibrate the rate of capture by the desorption tube for different types of molecules.

Disadvantage

We cannot quantify day-to-day differences in repeatability of technique.

Internal standard

A gas standard is added to the outgassing chamber and the response factor is measured. The same tube is used to measure outgassing and response factor.



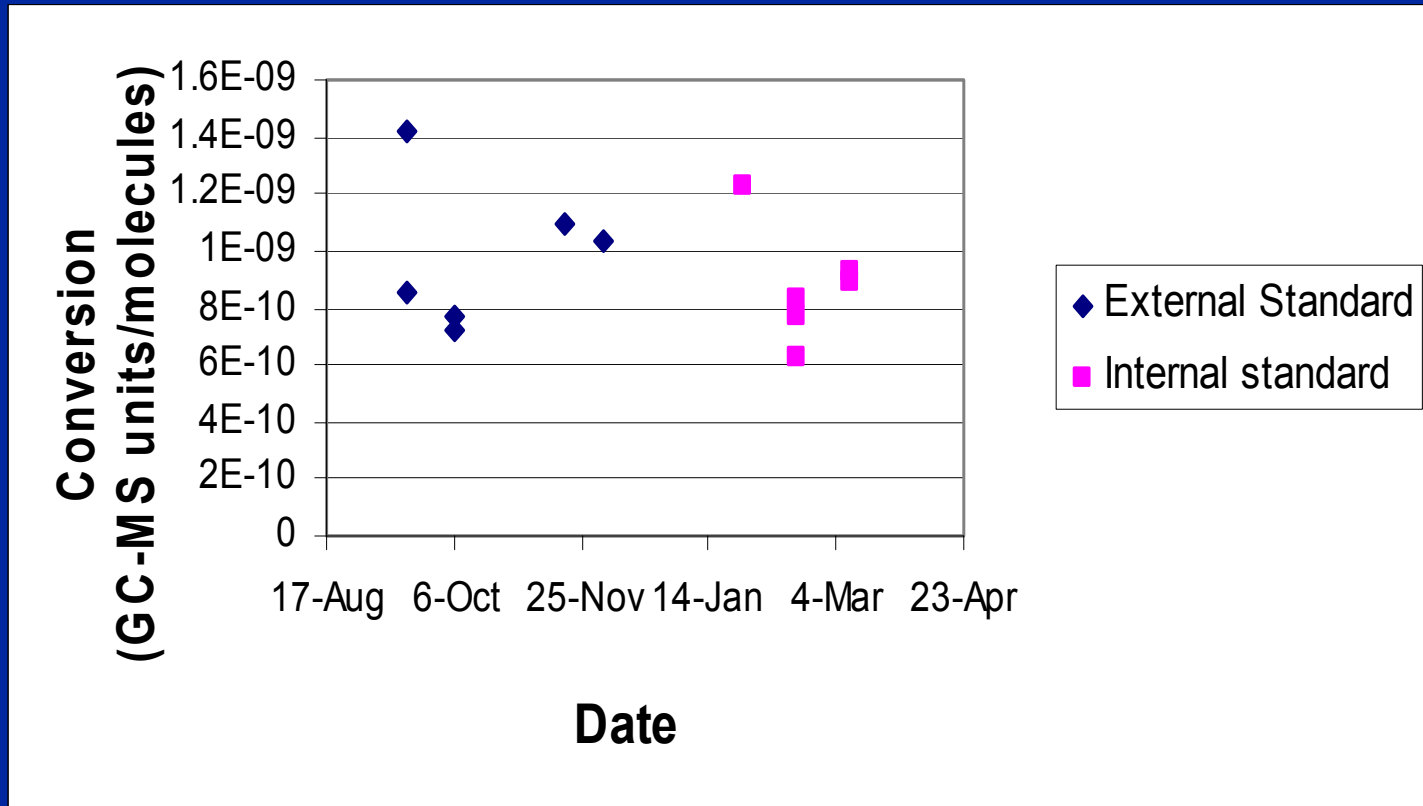
Advantage

We capture day-to-day differences in tools/ desorption tubes.

Disadvantage

If not chosen wisely, standard may mask outgassing response.

Effectiveness of quantification technique



- Very little difference in the conversion factor of toluene for internal and external standards was observed.

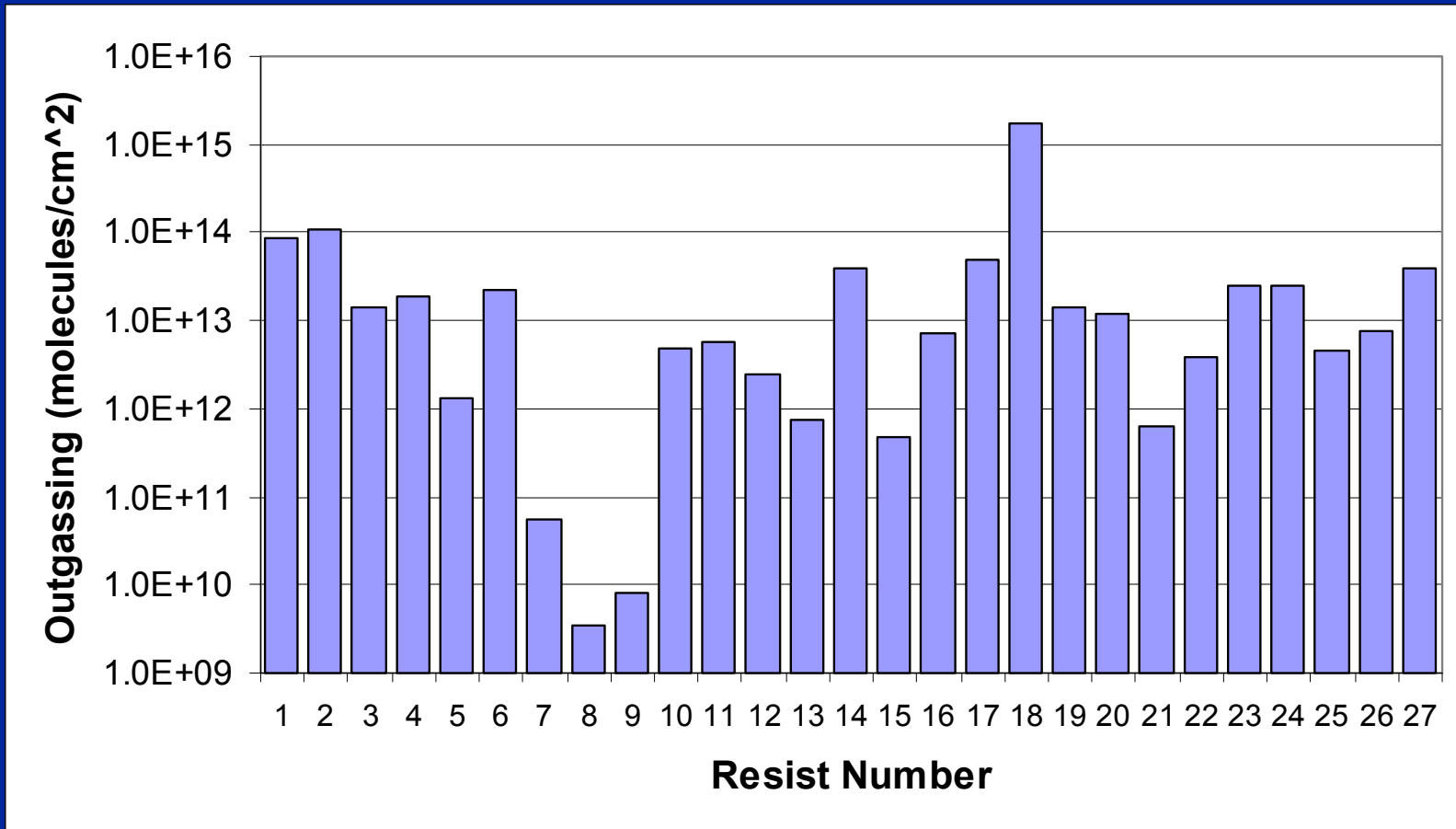
Limit of detection

- Outgassing can be efficiently measured down to levels of 10^{11} molecules/cm². Below this level, noise from GC/MS and background contaminants is problematic.

Background Contamination Introduced by:	Most Common Background Contamination Observed
GC/MS and empty desorption tube	Silanes
Empty outgassing chamber	Hydrocarbons
Internal standard	Acetates

- For each outgassing sample, the empty desorption tube is pre-screened and an empty chamber sample is taken to characterize the background contamination. The background contamination is not included in the final quantification results.

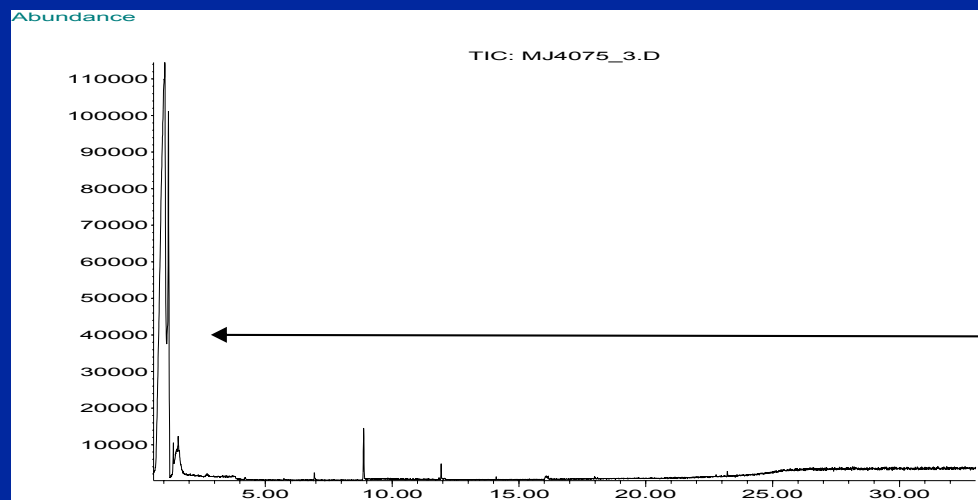
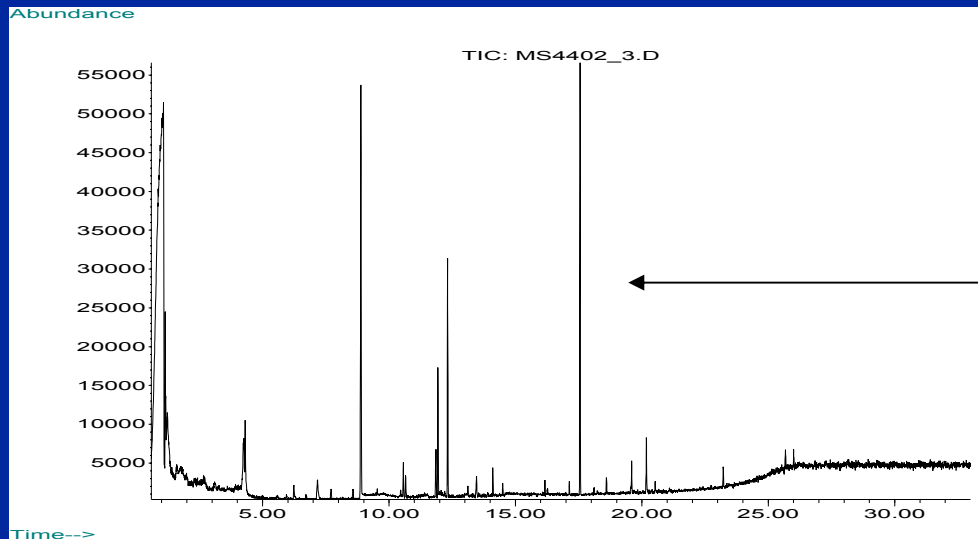
Levels of outgassing



- Resist that have been quantified with outgassing below 10^{11} may not be accurate, since below the detection limit of our technique.

Outgassing results

- Intel has found main sources of outgassing contaminants for EUV resists are PAG fragments and protecting groups.



PAG outgassing

Outgassing results as a function of PAG chemistry:

Ionic PAG A

= $1 \cdot 10^{13}$ molecules/cm²

Non-ionic PAG C

= $6 \cdot 10^{11}$ molecules/cm²

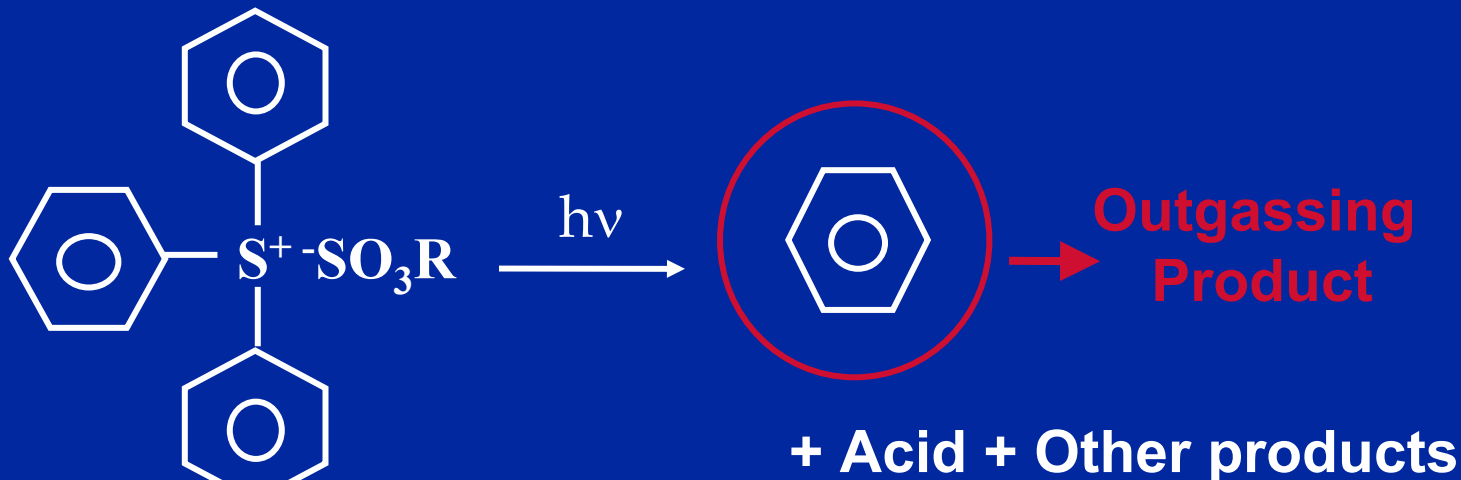
Ionic PAG B

= $6 \cdot 10^{12}$ molecules/cm²

Non-ionic PAG D

= $5 \cdot 10^{10}$ molecules/cm²

Possible outgassing mechanism for an ionic PAG:



Protecting group outgassing

Outgassing results as a function of activation energy (E_{act}) :

Low/medium E_{act} resist E
 $= 4 \cdot 10^{13}$ molecules/cm²

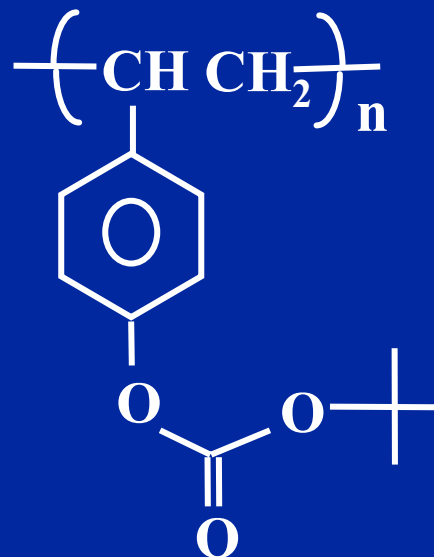
High E_{act} Resist G
 $= 7 \cdot 10^{11}$ molecules/cm²

Low/medium E_{act} resist F
 $= 2 \cdot 10^{13}$ molecules/cm²

High E_{act} Resist H
 $= 5 \cdot 10^{10}$ molecules/cm²

Possible deprotecting group outgassing mechanisms:

*T-boc
 deprotecting
 group (with
 medium
 activation
 energy) will
 outgas in EUV.*



**Outgassing
 Products**

+ Other products

Outgassing roadmap

An outgassing roadmap for EUV resists has been set based upon experimental data and discussions with tool suppliers.

Outgassing limit for Intel MET

$6 * 10^{13}$ molecules/cm²

Outgassing limit for EUV HVM tools

$1 * 10^{10} - 1 * 10^{11}$ molecules/cm²

Resists with non-ionic PAGs and high activation energy resists may be necessary to meet HVM targets.

EUV resist outgassing in vacuum

- **If resists outgas under vacuum, then the time needed to pump down to vacuum may increase and throughput may decrease. Therefore EUV resists must have minimal outgassing when placed in vacuum.**
- **The outgassing data presented in this poster is due to EUV exposure, and more data is needed to understand the effects of vacuum on the outgassing of EUV resists.**

Summary

- A method for quantifying outgassing has been demonstrated using both internal and external standards.
- A roadmap for outgassing has been set for Intel MET and HVM tools.
- The use of non-ionic PAGs and high activation energy resists may be necessary to meet the outgassing targets for HVM.

Acknowledgements

- University of Wisconsin (Dan Malueg, John Wallace)
- Resist suppliers