ANDROMEDE

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# Characterization of Photoresist Films by Various SIMS Techniques

Alexis Franquet, Valentina Spampinato

18th January 2022 - Paris - France (Virtual)

*"Characterization of Photoresist Films by Various SIMS Techniques"*

# OUTLINE

- FEW WORDS ABOUT IMEC
- MOTIVATION OF THE STUDY & SIMS TECHNIQUES
- EXAMPLES OF RESULTS
- SUMMARY

# IMEC'S MISSION

Imec aims to be the world-leading R&D and innovation hub in nanoelectronics and digital technology.

CLOSE TO
**4,000 SKILLED RESEARCHERS**
FROM OVER 90 NATIONALITIES

A
**TRUSTED PARTNER FOR**
COMPANIES, STARTUPS & ACADEMIA

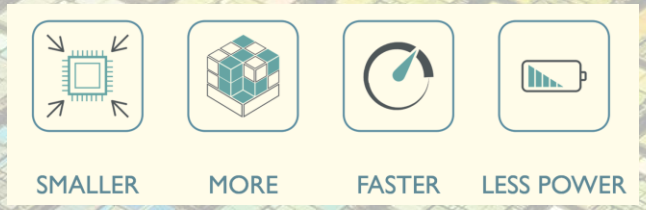
WORLD-CLASS INFRASTRUCTURE
**>12,000 M² CLEANROOM**
CAPACITY

# Electronic devices, the core elements in our society

1980

nowdays

**10, 000 $ present price**
**30 min. talk time**
**~1kg**
**1000 nm technology node**




modern

**500 $ - 1000 $**
**20 h. talk time**
**164 grams**
**>100 MP camera**
**5 nm technology node**

## *Demand cheap, reliable, high-performance devices*

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# Motivation & Objectives

## Fundamental understanding of the chemistry to optimize/design the process

**Random co-polymer**
4-vinylphenol/tert-butyl methacrylate 50/50

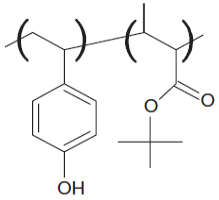
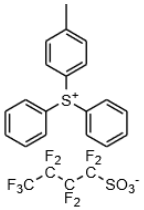
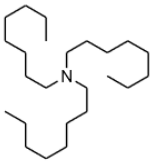
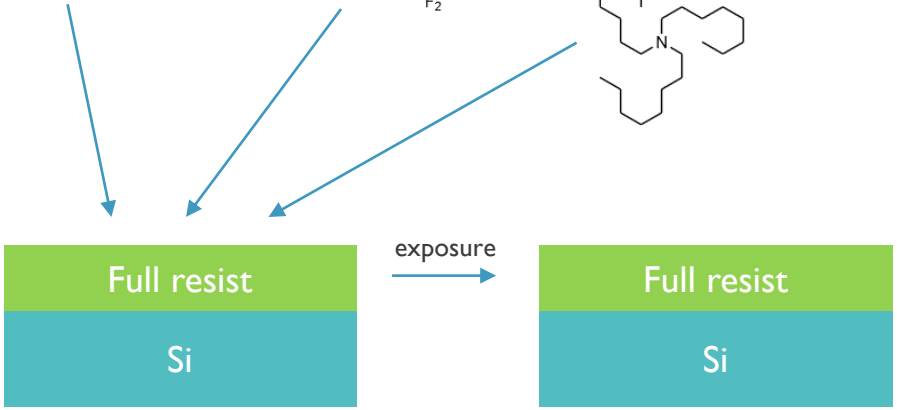



**Photo-acid generator (PAG)**
(4-Methylphenyl)diphenylsulfonium triflate




**Quencher**
Tri-octadecylAmine




**MOLECULAR INFORMATION**
**(in comb with MASS RESOLUTION)**

**DEPTH RESOLUTION**

1. Composition of the PR layer before exposure
   - Distribution of components in depth
   - Lateral distribution of components

   3D / homogeneity

3. Changes/modifications in chemistry

2. Composition of the PR layer after exposure
   - Distribution of components in depth
   - Lateral distribution of components

   3D / homogeneity

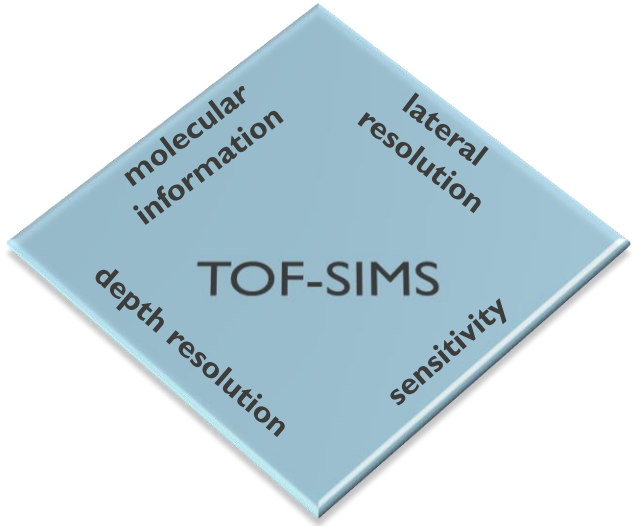
**LATERAL RESOLUTION**

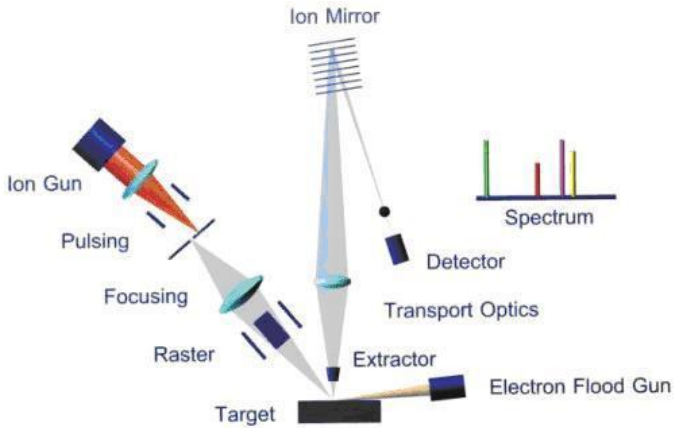
**SENSITIVITY**

# SIMS techniques

**ToF-SIMS*** thanks to its

- **molecular information**,
- **good depth resolution** (1nm/decade),
- **good lateral resolution** (at best 100nm),
- **good sensitivity** (ppm),
- **good mass resolution** (M/DM>10.000), ...




** IONTOF instrument available at imec*

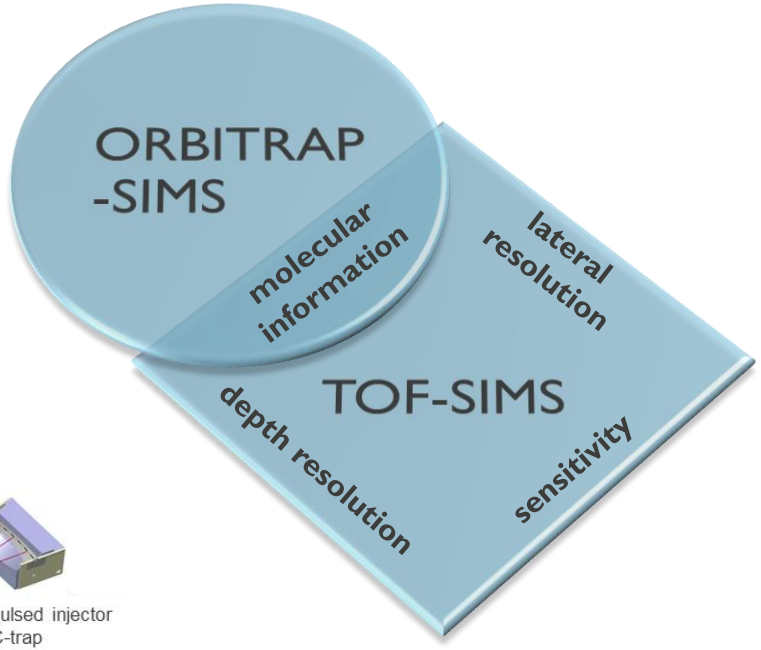


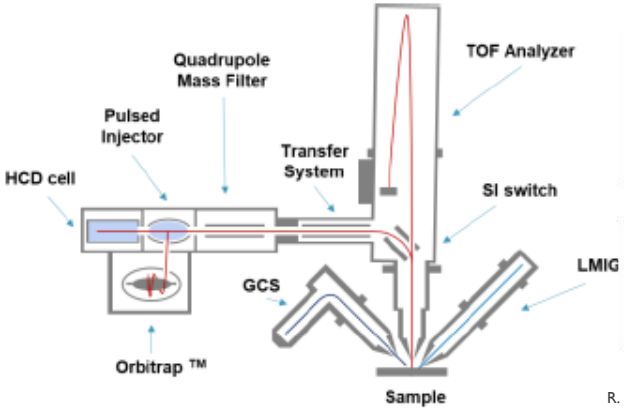
public

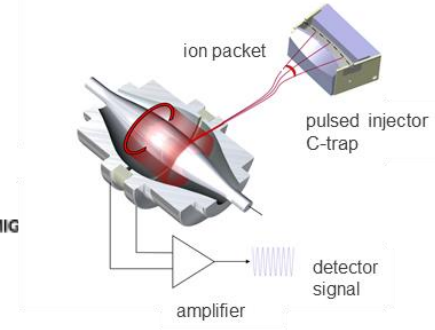
# SIMS techniques

**ORBITRAP-SIMS*** thanks to its

- **molecular information (+MS/MS),**
- **good depth resolution,**
- **good sensitivity** (ppm),
- **excellent mass resolution** (M/DM>240.000), ...
- but **poor lateral resolution** (micron scale)



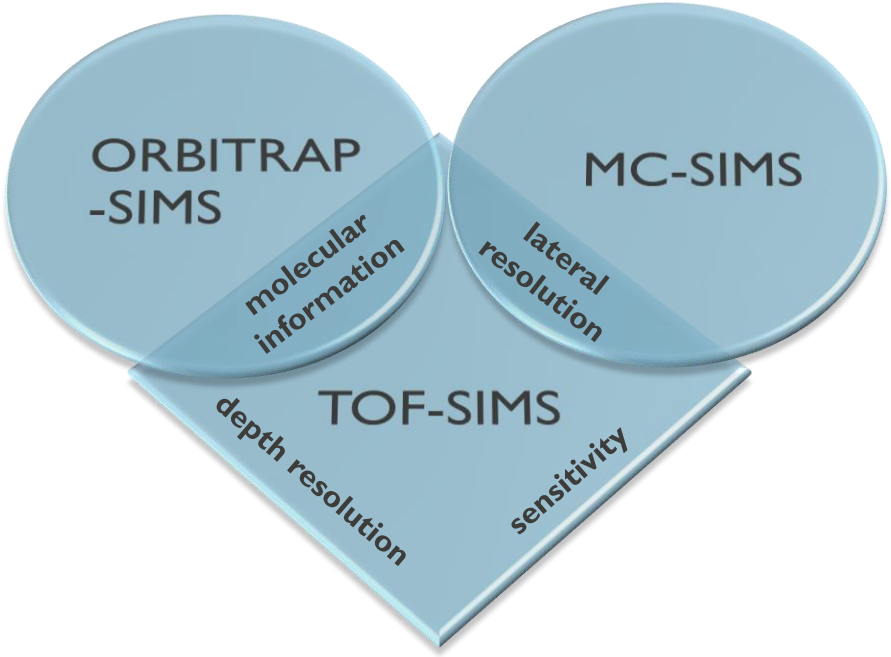

R. A. Zubarev and A. Makarov, Anal. Chem. 2013, 85, 5288−5296

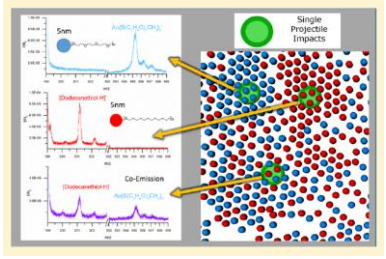
** not available at imec (done at IONTOF, Munster, Germany)*

# SIMS techniques

**MC-SIMS*** (Massive Cluster) thanks to its

- **molecular information,**
- **depth information capability,**
- **good sensitivity,**
- **excellent lateral/spatial resolution (<20nm),** ...
- but **limited mass resolution (M/DM<2000)**



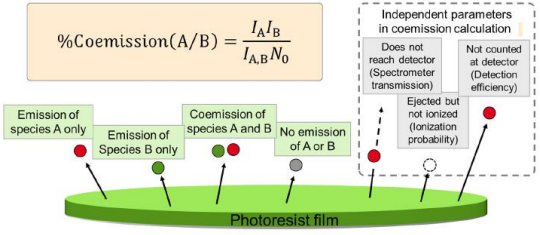




**Fig. 4** A graphical illustration of all possible scenarios during a bombardment event in MC-SIMS. (Inset) Coemission calculation equation of two species A and B.

** not available at imec (done at Université Paris-Saclay, Orsay, Paris)*

X. Hou et al, J. Micro/Nanolith. MEMS MOEMS 18(3) 033502 Jul-Sep 2019



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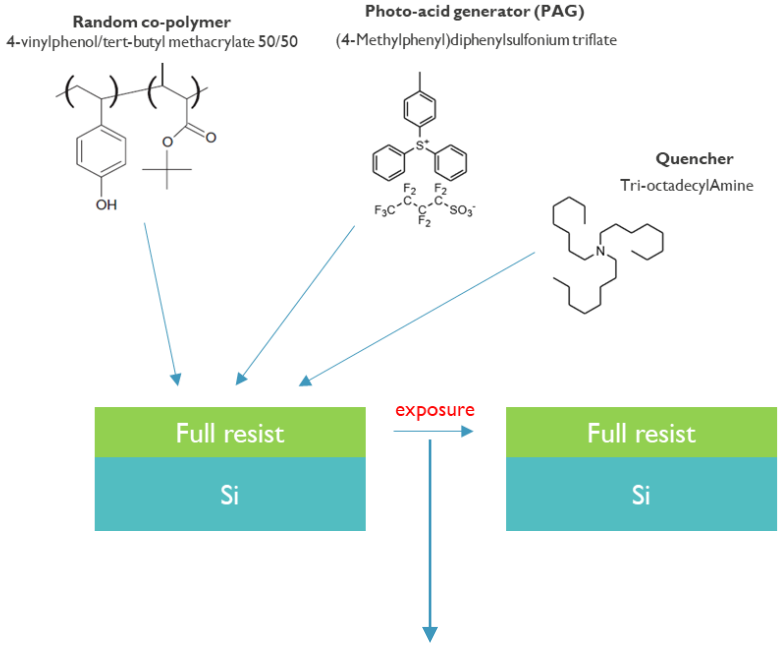
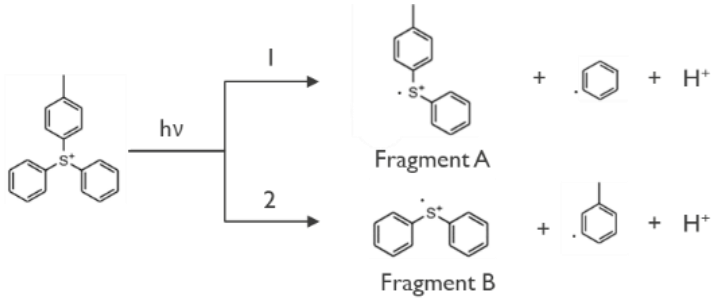
# Samples




From 0 to 2x200 mJ/cm2
(samples from D02 to D08)

Schematic representation of the reactions involved during photo exposure on PAG



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# TOF-SIMS

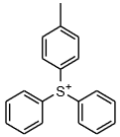
MOLECULAR INFORMATION

DEPTH RESOLUTION

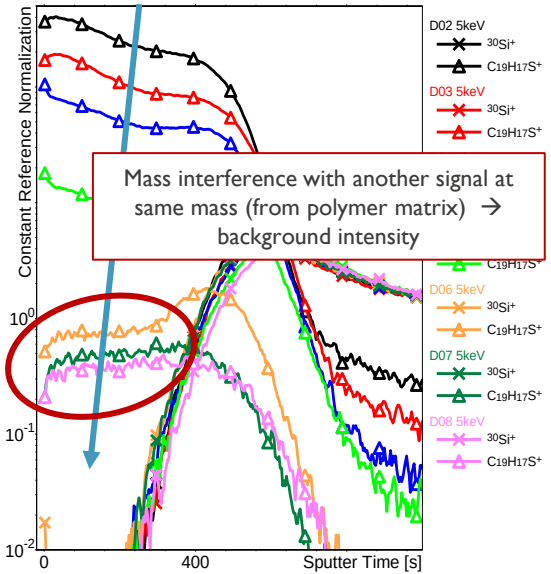
(in comb with MASS RESOLUTION)

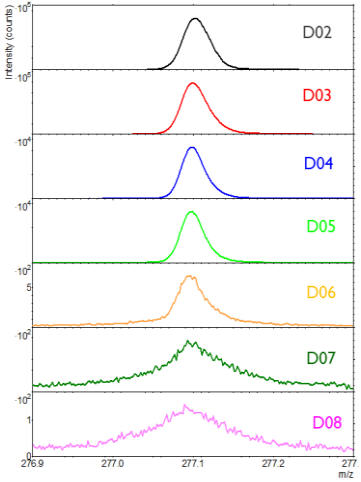
LATERAL RESOLUTION

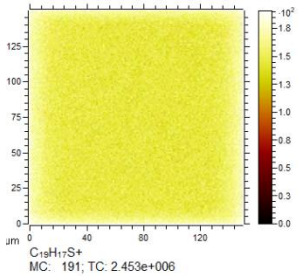
SENSITIVITY



PAG molecular: C19H17S+




| Sample | Exposure (mJ/cm2) |
|---|---|
| D02 | 0 |
| D03 | 10 |
| D04 | 20 |
| D05 | 50 |
| D06 | 100 |
| D07 | 200 |
| D08 | 200x2 |

# ORBITRAP-SIMS

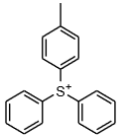
**SIMS analysis of thin EUV photoresist films**
V. Spampinato, A. Franquet, D. De Simone, I. Pollentier, A. Pirkl, H. Oka and P. van der Heide , accepted in Analytical Chemistry

MOLECULAR INFORMATION (in comb with MASS RESOLUTION)

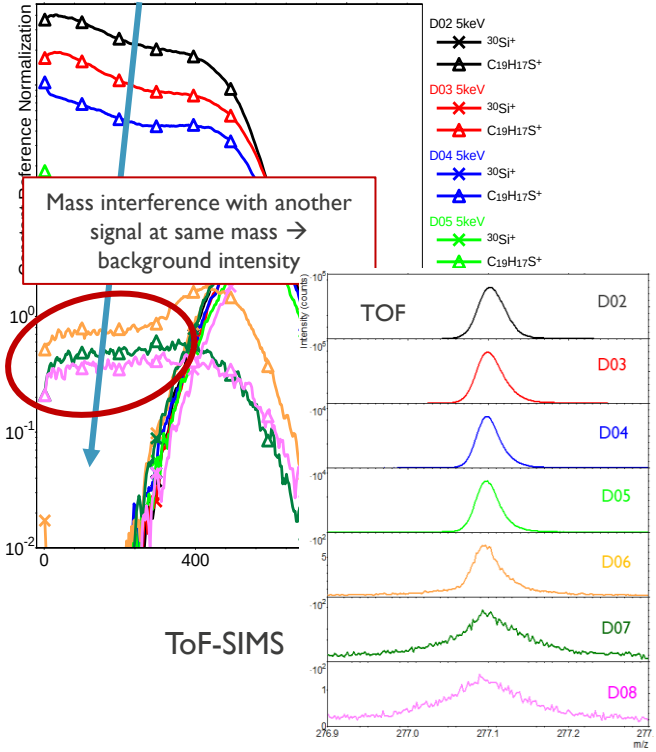
DEPTH RESOLUTION

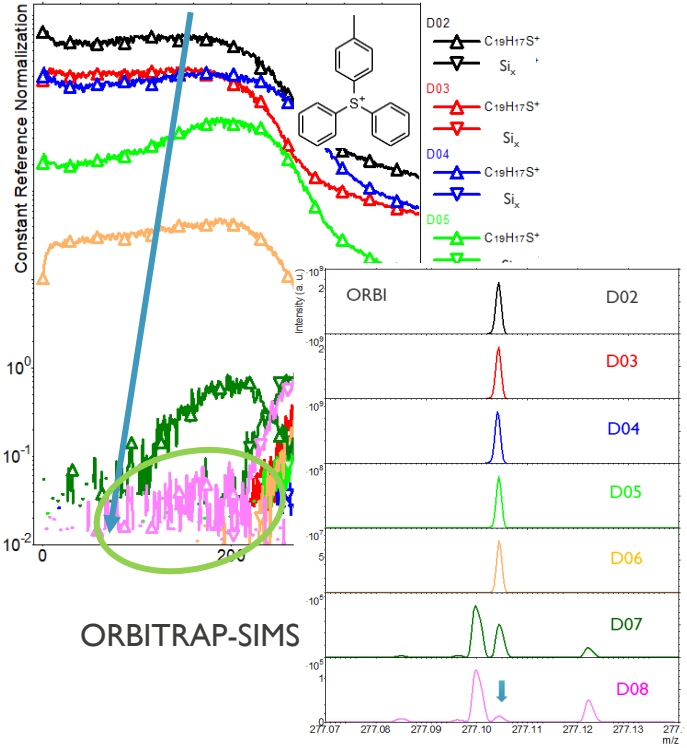
LATERAL RESOLUTION

SENSITIVITY



PAG molecular: C19H17S+




| Sample | Exposure (mJ/cm2) |
|---|---|
| D02 | 0 |
| D03 | 10 |
| D04 | 20 |
| D05 | 50 |
| D06 | 100 |
| D07 | 200 |
| D08 | 200x2 |



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# MC-SIMS

4 samples were selected for which different PAG aggregations might be observed because of various bakes

| Wafer | Bakes | Thickness | Scanner jobs | Comment |
|---|---|---|---|---|
| **D02** | SB90C60" | 35 nm | Coating + SB | Polymer |
| **D03** | No SB | 35 nm | Only coating | Polymer/PAG |
| **D04** | SB90C60" | 35 nm | Coating + SB | Polymer/PAG |
| **D05** | SB130C60" | 35 nm | Coating + SB | Polymer/PAG |

MC-SIMS conditions: Au400 12MeV

Same samples measured with:
ToF-SIMS Ar GCIB 5keV 2000 – Bi1 15keV
Orbi-SIMS Ar GCIB 5keV 2000

**Random co-polymer**
4-vinylphenol/tert-butyl methacrylate 50/50

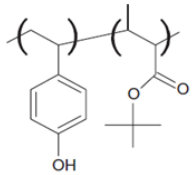
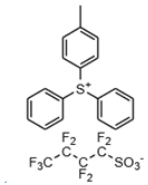



**Photo-acid generator (PAG)**
(4-Methylphenyl)diphenylsulfonium triflate



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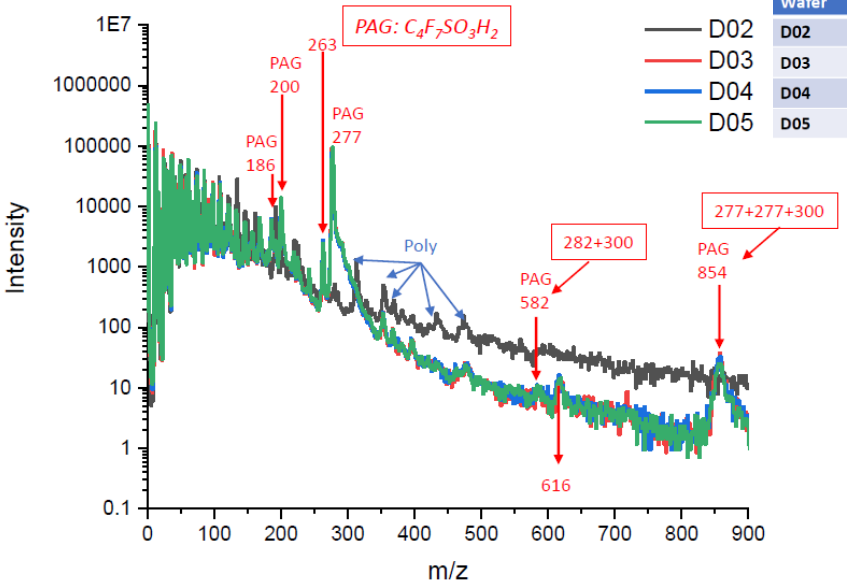
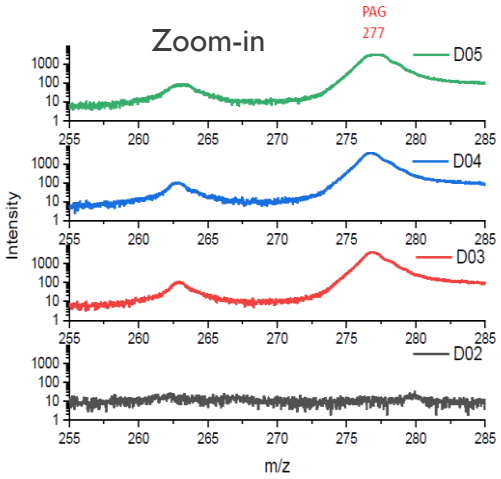
# MC-SIMS / Positive spectra

* Masses of detected peaks are rough estimate → e.g. 854 = between ~850 & ~865

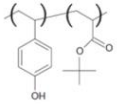



| Wafer | Bakes |
|---|---|
| D02 | SB90C60" |
| D03 | No SB |
| D04 | SB90C60" |
| D05 | SB130C60" |




Possible peak assignments

Random co-polymer 4-vinylphenol/tert-butyl methacrylate 50/50



$C_8H_{14}O_2$: 142
$C_8H_8O$: 120

Photo-acid generator (PAG)

$C_{13}H_{12}S^+$: 200
$C_{12}H_{10}S^+$: 186
$C_{19}H_{17}S^+$: 277
$C_4F_9SO_3^- + H^+$: 300
$C_4F_8SO_3H^- + H^+$: 282
$C_4F_7SO_3H^- + H^+$: 263

- No big difference in term of mass fingerprint pattern and SI yields for samples D03, D04 and D05 (polymer+PAG)
- PAG related signals only visible in D03-D05 and large PAG clusters observed at high masses
- But assignment to be confirmed due to limited mass resolution in MC-SIMS
- Polymer peaks intensity is decreased after PAG deposition → close to the dilution factor (quantitative analysis possible?)
- Similar results obtained in negative polarity



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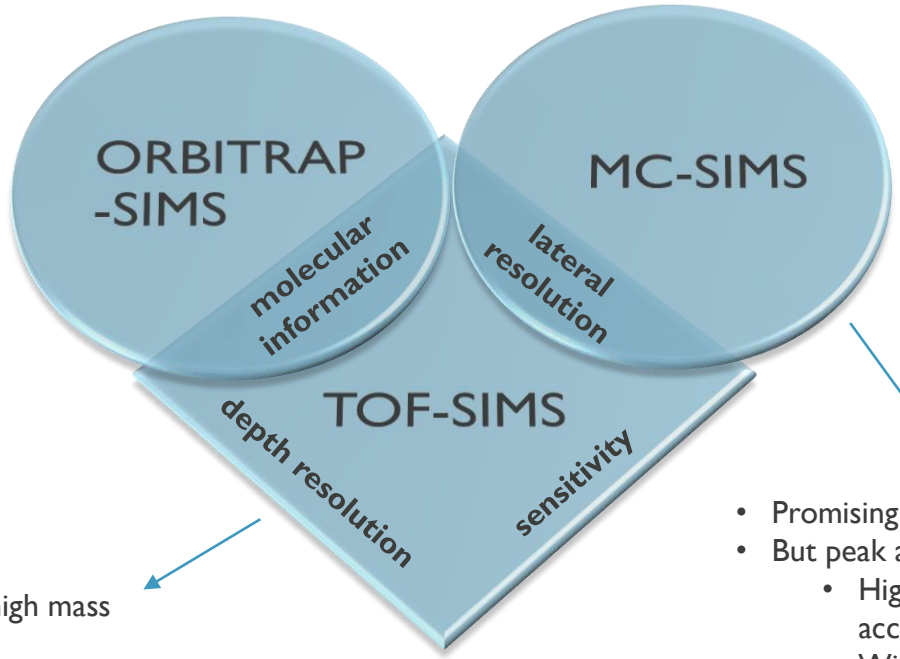
# SUMMARY

## Fundamental understanding of the chemistry to optimize/design the process

- Required when high mass resolution is needed
- PAG aggregation (lateral resolution) can be studied using Self Focusing (SF-SIMS) concept




- Enough for PR systems where high mass resolution is not needed
- PAG aggregation (lateral resolution) can be studied using Self Focusing (SF-SIMS) concept

- Promising results obtained
- But peak assignment needs to be confirmed
  - Higher mass resolution and mass accuracy
  - With the help of ORBITRAP-SIMS
- Quantitative information about the layer composition (no matrix effect?)

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*Acknowledgments:*

*Paul van der Heide, Danilo De Simone (imec)*
*Hironori OKa (FUJIFILM)*
*Alexander Pirkl (IONTOF)*
*Serge Della Negra, Thi Lai, Isabelle Ribaud, Dominique Jacquet (IJCLab, Saclay)*

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# Thank you!