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PHYSIQUE NUCLÉAIRE
NUCLEAR PHYSICS

Equipe FIIRST
Faisceaux ISOL, Ions Radioactifs et Structure

Analysis of thin EUV Photoresist Films with MeV Gold Nanoparticles

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Samples studied

imec

Characterization of Photoresist Films

Alexis Franquet, Valentina Spampinato **IMEC**

SIMS Analysis of Thin EUV Photoresist Films
January 2022 Analytical Chemistry 94(5)

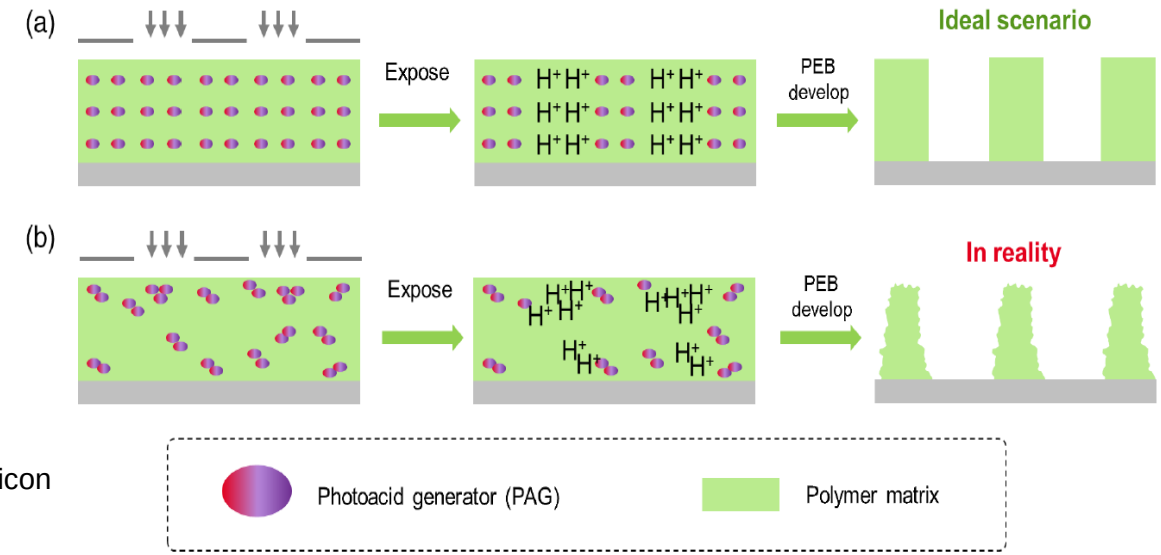


Fig from Hou et al.: Understanding photoacid generator distribution at the nanoscale

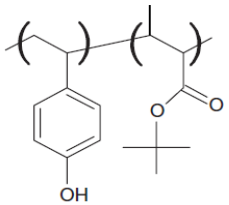
September 2019 Journal of Micro/Nanolithography MEMS and MOEMS 18(03):1

Nanostructured surface <<<<<<<<

Width lines 5 nm
High 35-45 nm.

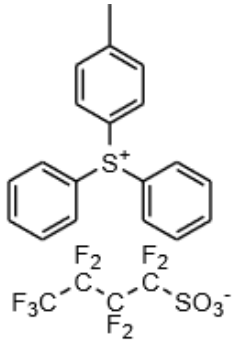
MeV Gold Nanoparticules ToF experiment

Random co-polymer based on pHs-tBuMA



pHS	$C_8H_{14}O_2$	142
tBuMA	C_8H_8O	120
Styrene	C_8H_8	104

Photo-acid generator (ionic PAG)



$C_{19}H_{17}S^+$

277

$C_4F_9SO_3^-$

299

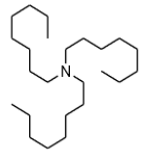
Influence of processing conditions ?

Different Baking
+ EUV exposure

Photo-induced fragmentation

+ Quencher

Tri-octadecyl Amine



$C_{24}H_{51}N$

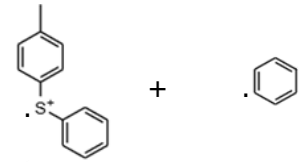
353

+ Surexposure EUV

200x2mJ/cm2 exposed

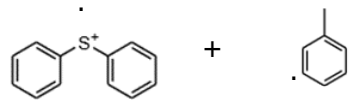
Fragment A

$C_{13}H_{12}S^+$ 200



Fragment B

$C_{12}H_{10}S^+$ 186



Polymer influence ?

Different polymers compositions before exposed

pHS	50	25	10
Styrene	0	25	40
tBuma	50	50	50

Quantitative analysis ?

Different PAG concentrations before exposed

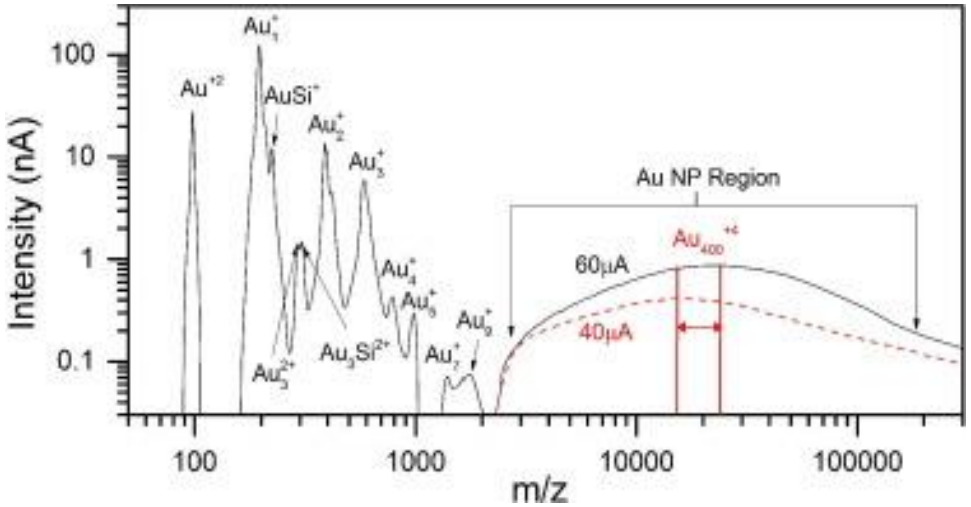
5.0 wt%, 10.0 wt%, 13.0 wt%
17.0 wt%, 26.0 wt% 34.6 wt%
70.0 wt%

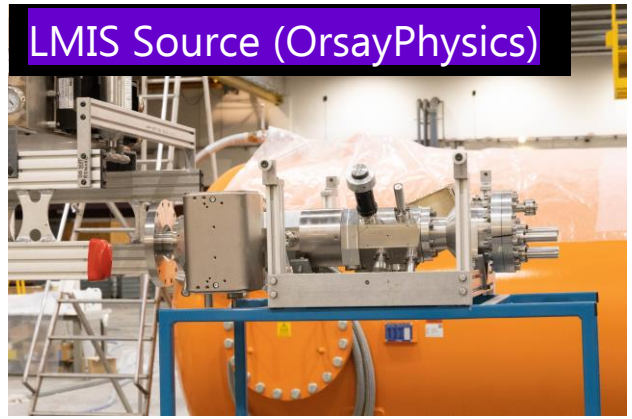
Andromede Facility

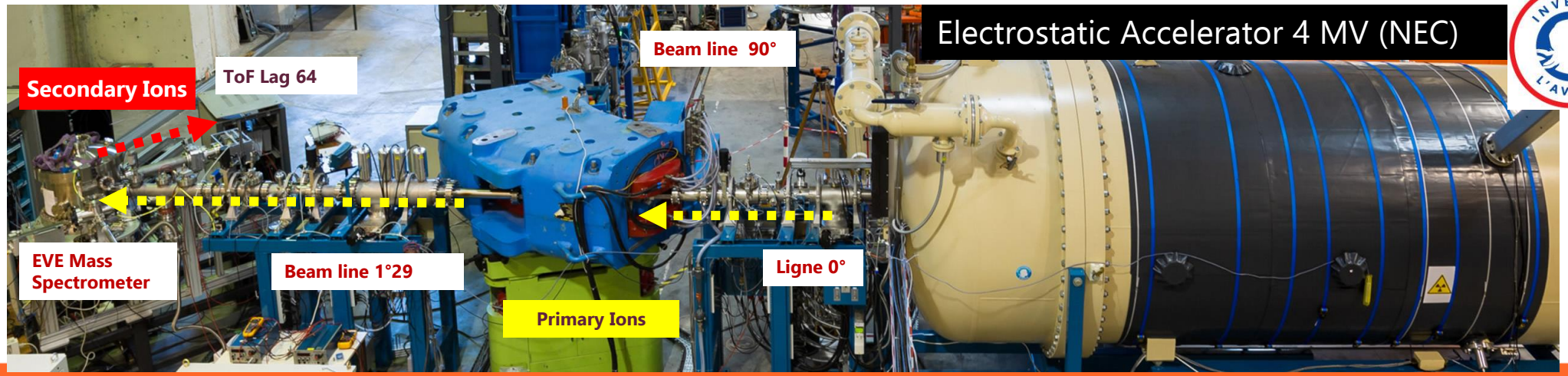
Andromede project:

Surface analysis and modification with probes from hydrogen to nano-particles in the MeV energy range

August 2015
NIM B Beam Interactions with Materials and Atoms 365







Mass Spectrometer EVE

MeV Gold Nanoparticles 12 MeV

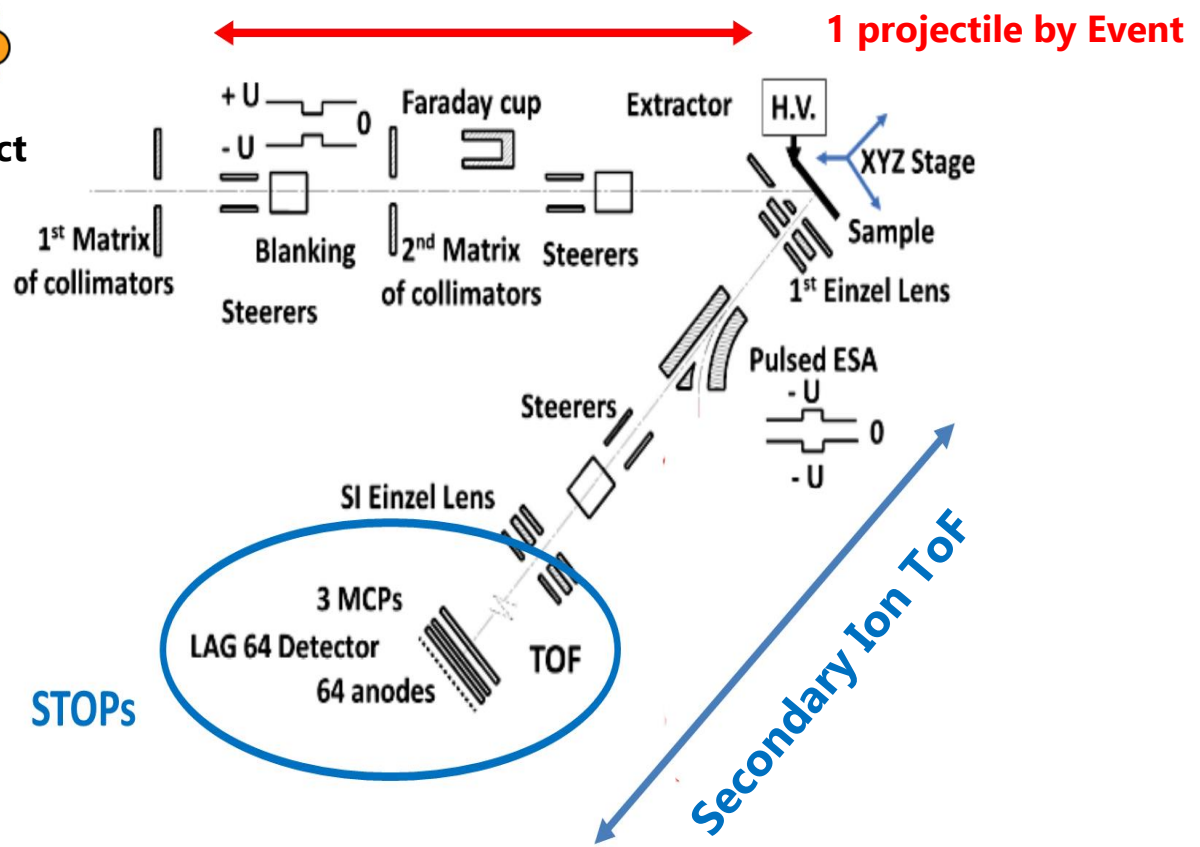
Au_{400}^{4+}

Beam Impact/impact

10^7 impacts for 200 µm

Primary ions

1 projectile by Event



NPs Mev ToF SIMS
Enhanced sputter and secondary ion yields using MeV gold nanoparticle beams delivered by the Andromede facility

July 2020 JVST B: Nanotechnology and Microelectronics 38(4):044008

- High ion multiplicity detection
- Angular distribution measurements
- Impact/impact >>>Correlations

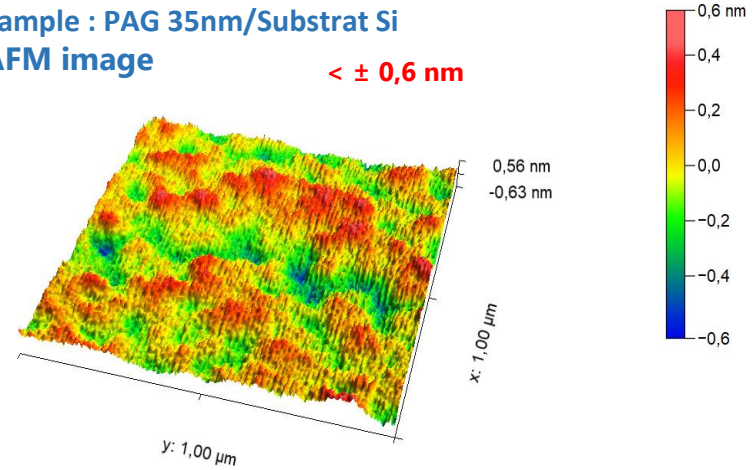
Why use energetic nanoparticles?

High emission yields : Hundreds of secondary ions ejected **under a single primary ion** (impact)

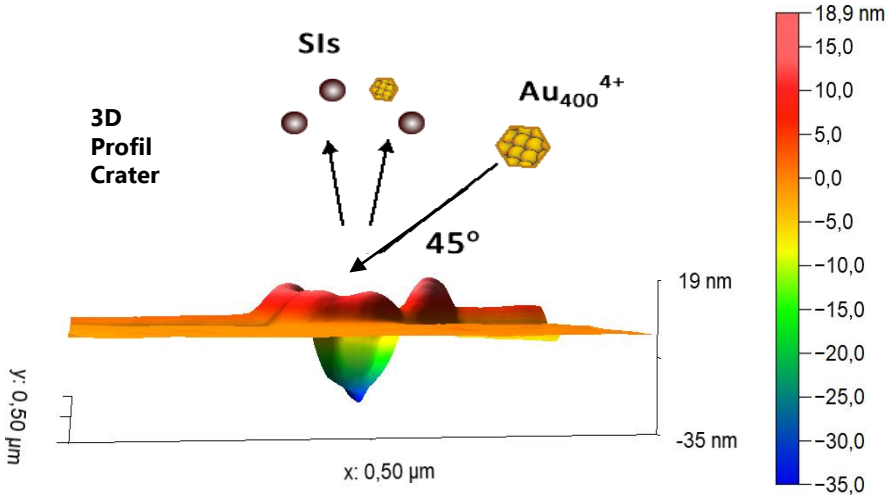
Probe depth : ~ 30nm

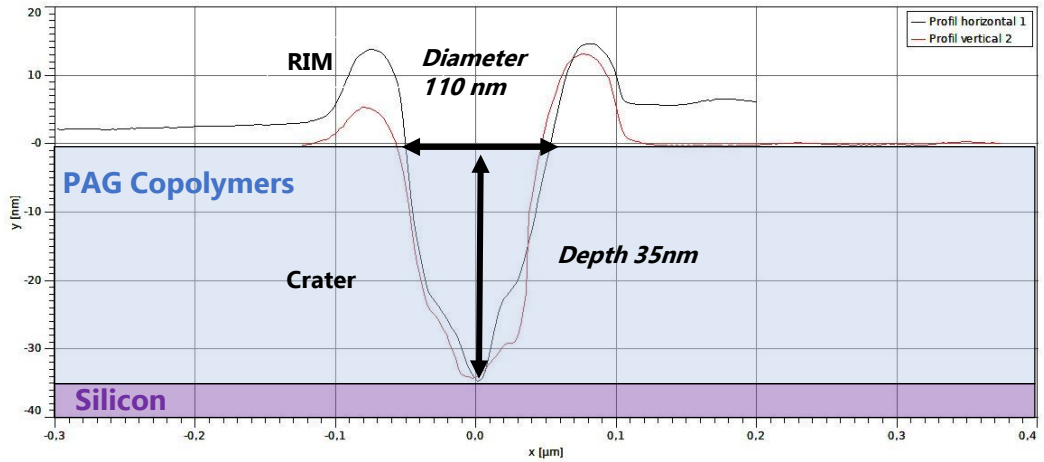
Sample : PAG 35nm/Substrat Si
AFM image

< ± 0,6 nm



Sample : PAG 35nm/Substrat Si
Impact : Au_{400}^{4+}, 12MeV
AFM image

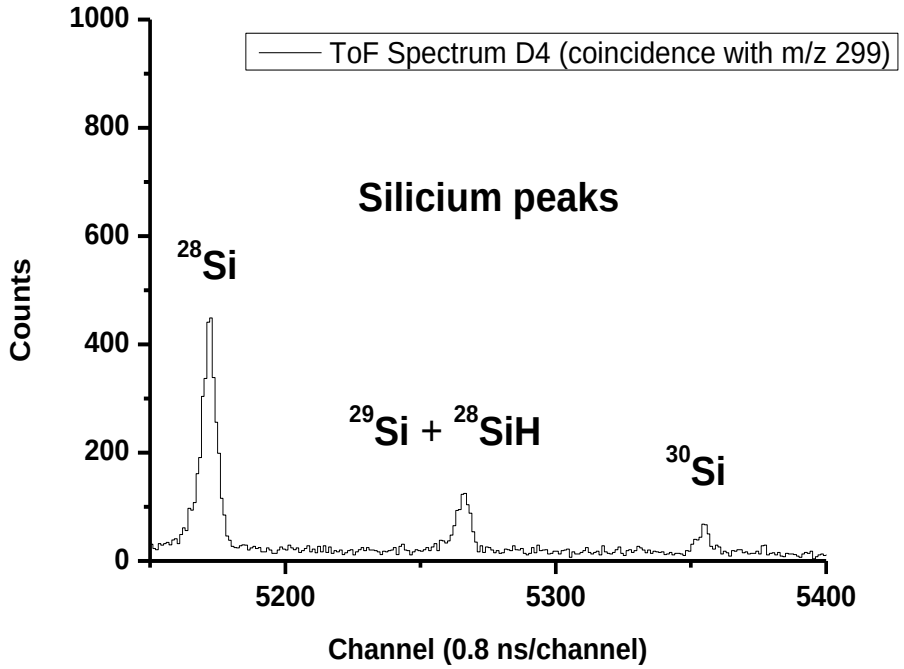




Volume PAG Coemission

Silicon ions are emitted from the crater in correlation with PAG molecular ions !!

The entire crater is involved in ion emission; Depth of ion emission reaches 35 nm.



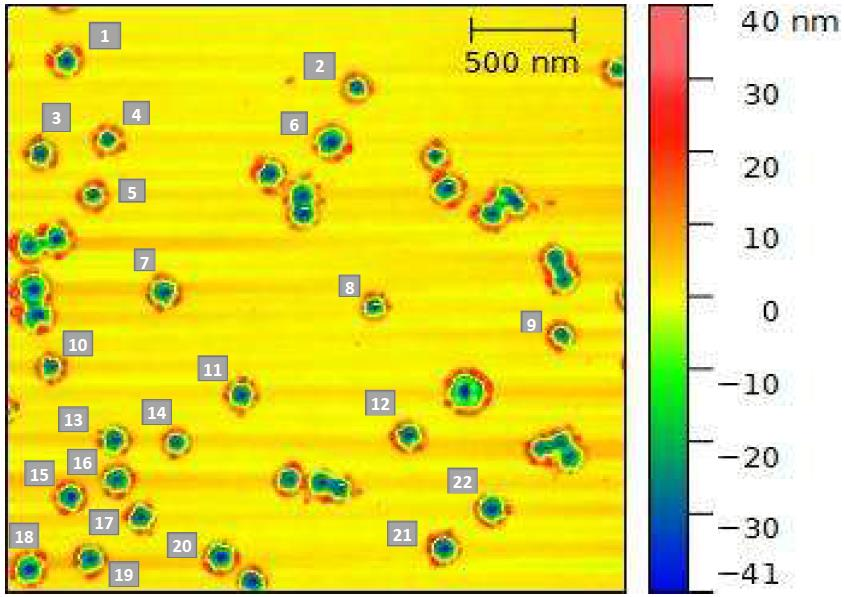
Here, Silicon ions emitted in coincidence with PAG molecules

(volume of emission)

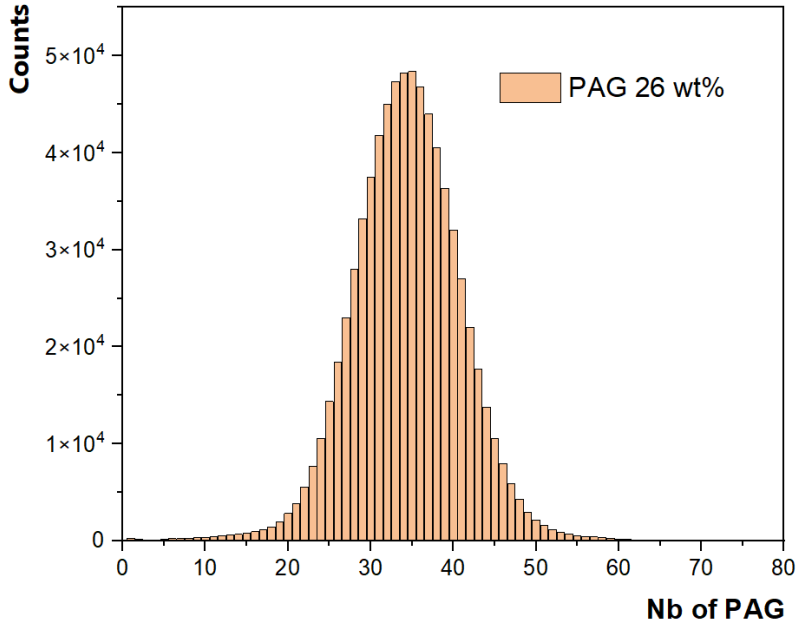
Volume of emission under MeV Gold Nanoparticles

the volume distribution is monodisperse
& correlated with a huge and homogeneous secondary ion emission

All crater volumes are similar
V ~ $10^5 nm^3$/per impact

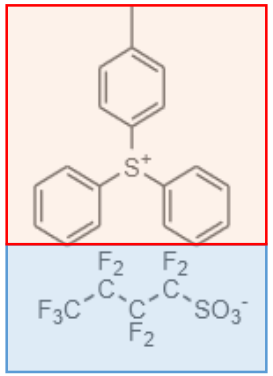


Number of detected intact PAGmolecular ions



Pure Poisson distribution of PAG in polymer

Spectra of Photo-acid generator (ionic PAG)



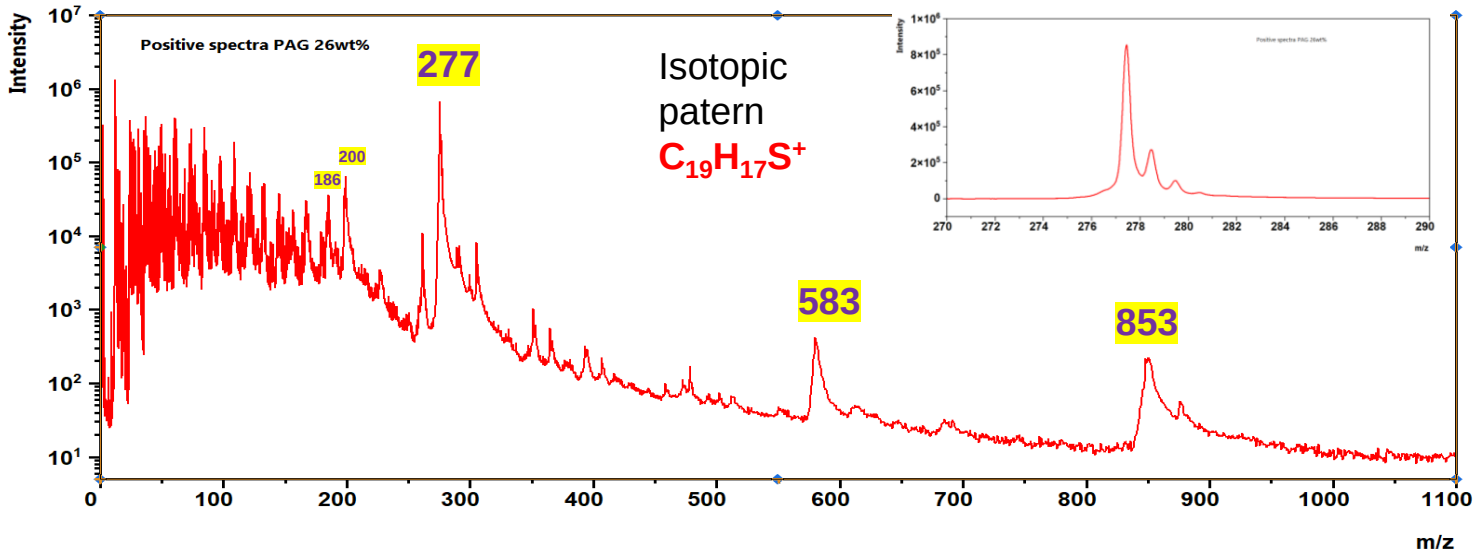
$C_{19}H_{17}S^+$

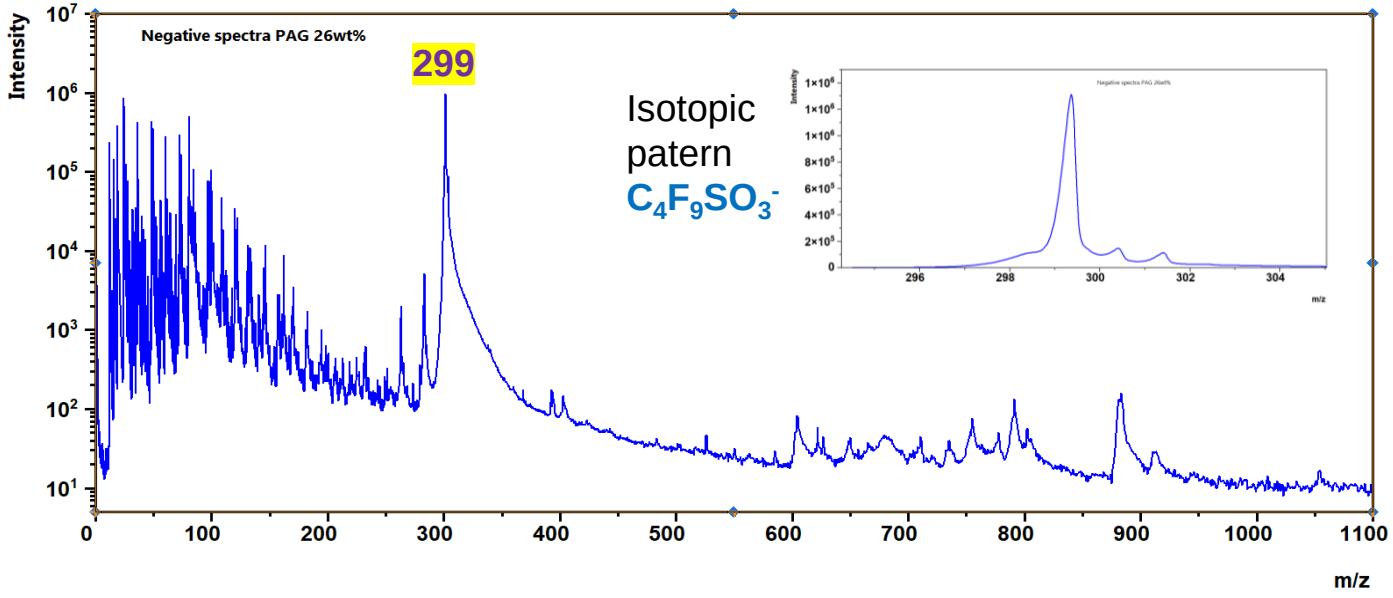
277

$C_4F_9SO_3^-$

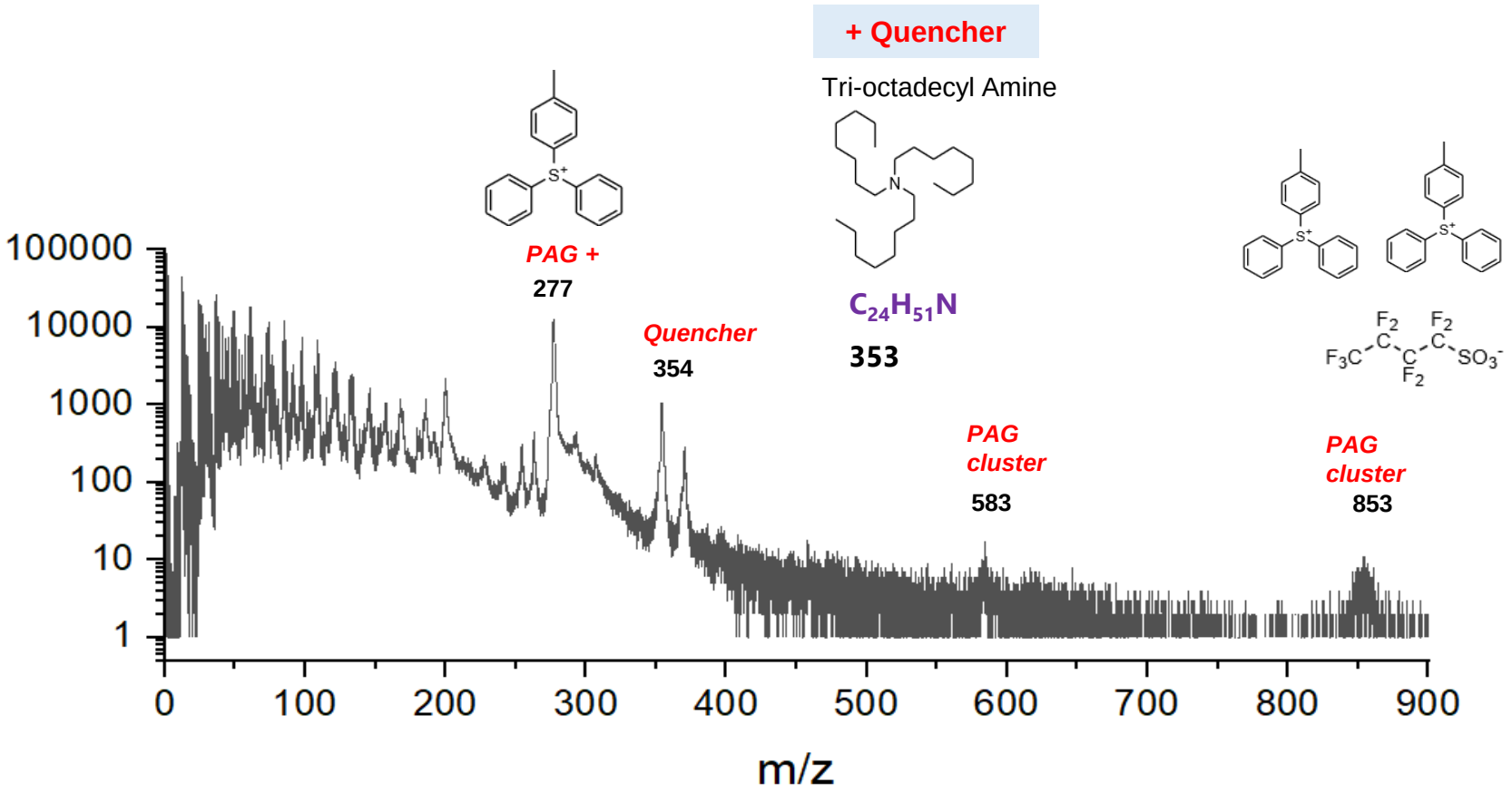
299

PAG aggregates **emission !**
(mass 583 and 853) before exposure





Polymer + PAG + Quencher



ID sample D08

All molecules are present

PAG^+
Quencher
PAG^+ Clusters (583 u, 853u)

Different PAG clusters 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

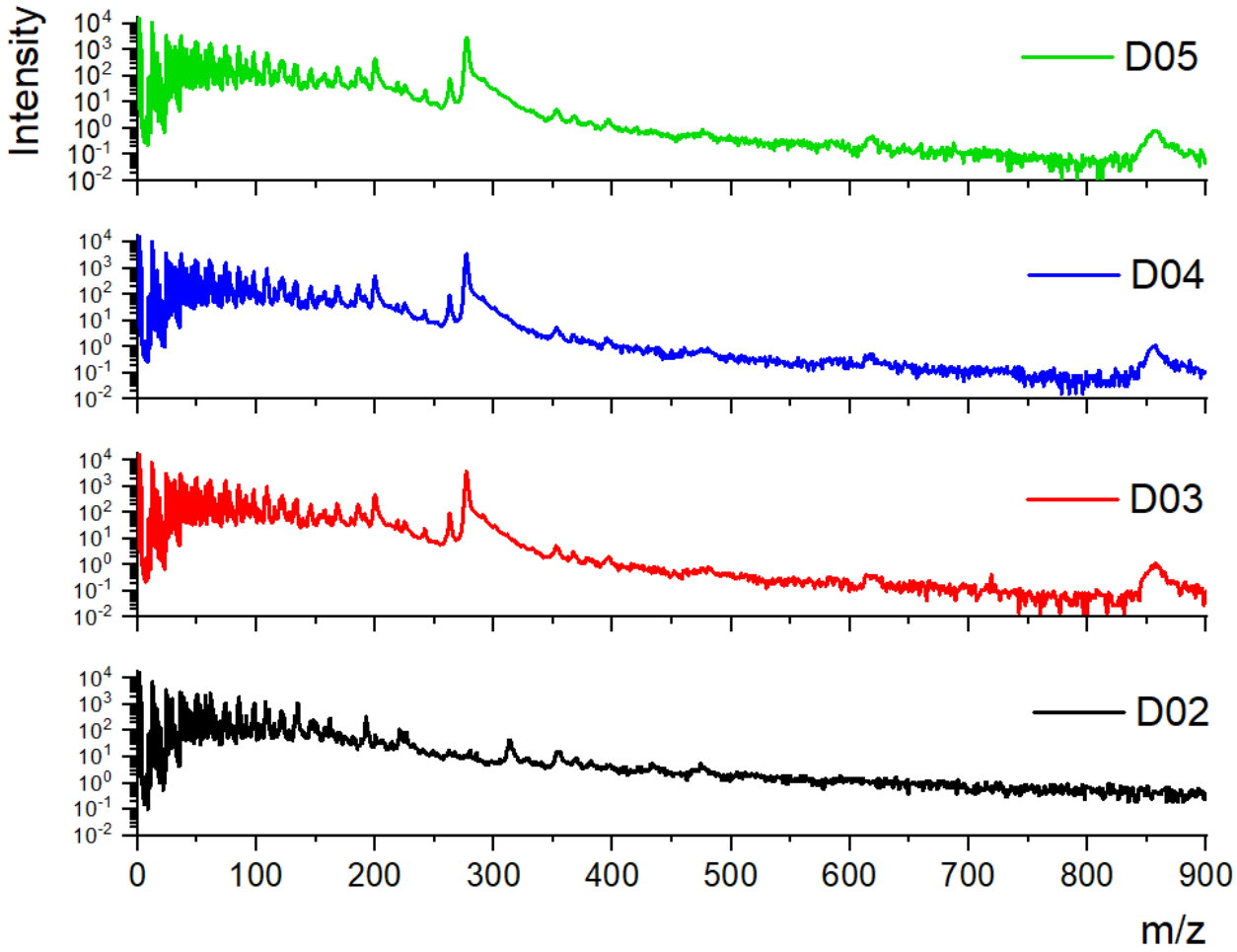
Fragmentation PAG, PAG^+ and PAG cluster

No difference in fingerprint pattern for samples D03, D04 and D05

PAG clusters (853 u) slight decrease as a function of baking temperature

Cluster PAG (853 u)/ PAG^+ (277 u) Ratio at different baking temperature

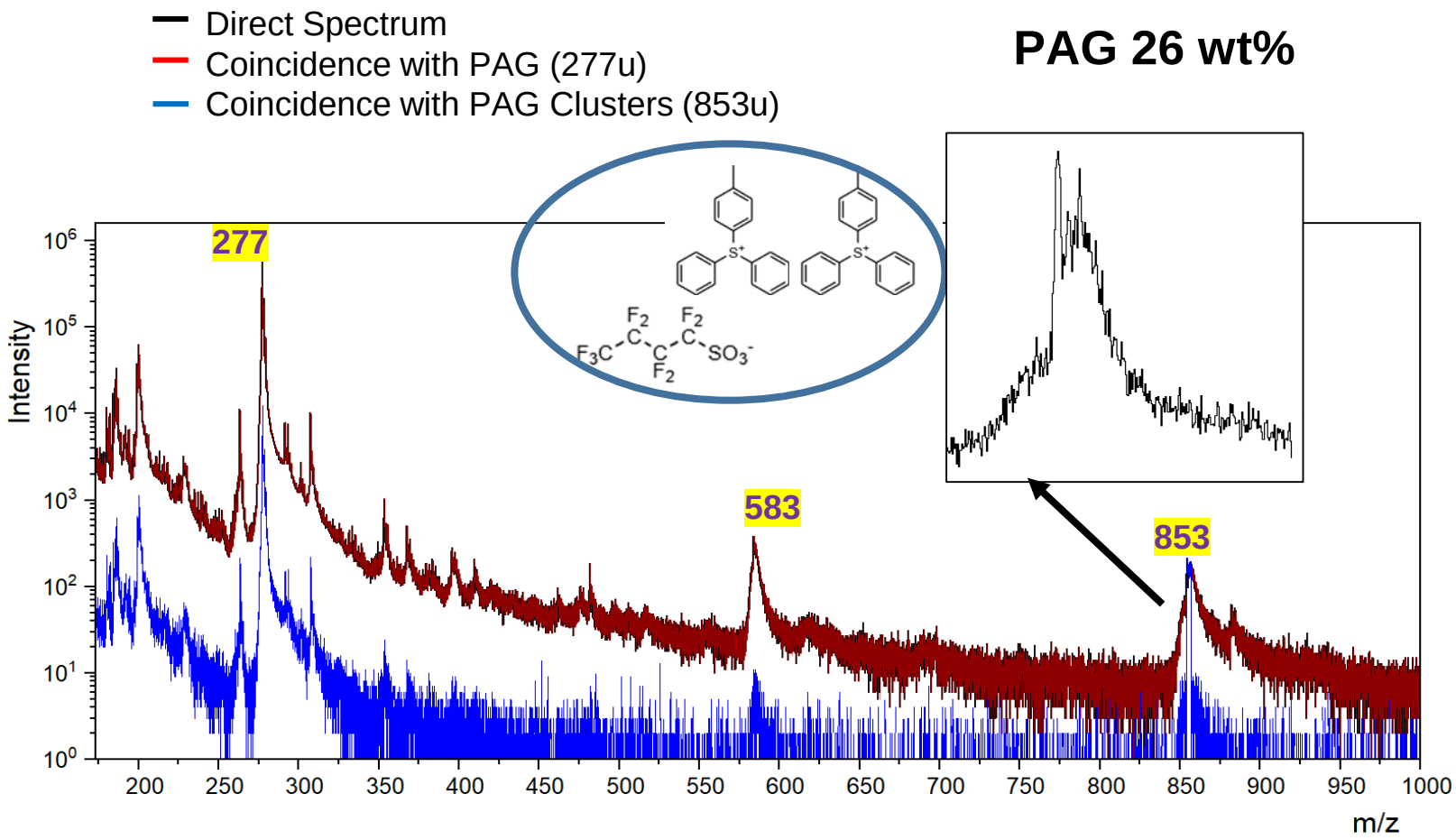
D03	D04	D05
1,36E-02	1,20E-02	7,22E-03



Focus on PAG clusters, PAG+ polymer samples

PAG is homogeneously distributed within the polymer matrix

PAG clusters ions are correlated to all secondary ions (polymer and PAG)



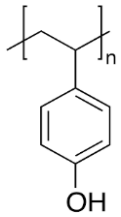
Influence of the PHS /Styrene in the polymer matrix

Random copolymers with Different compositions

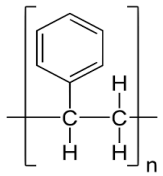
Samples

PAG 17,3 wt%	D07	D08
pHS	25	10
Styrene	**25**	**40**
tBuma	50	50

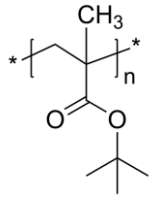
pHS



Styrene

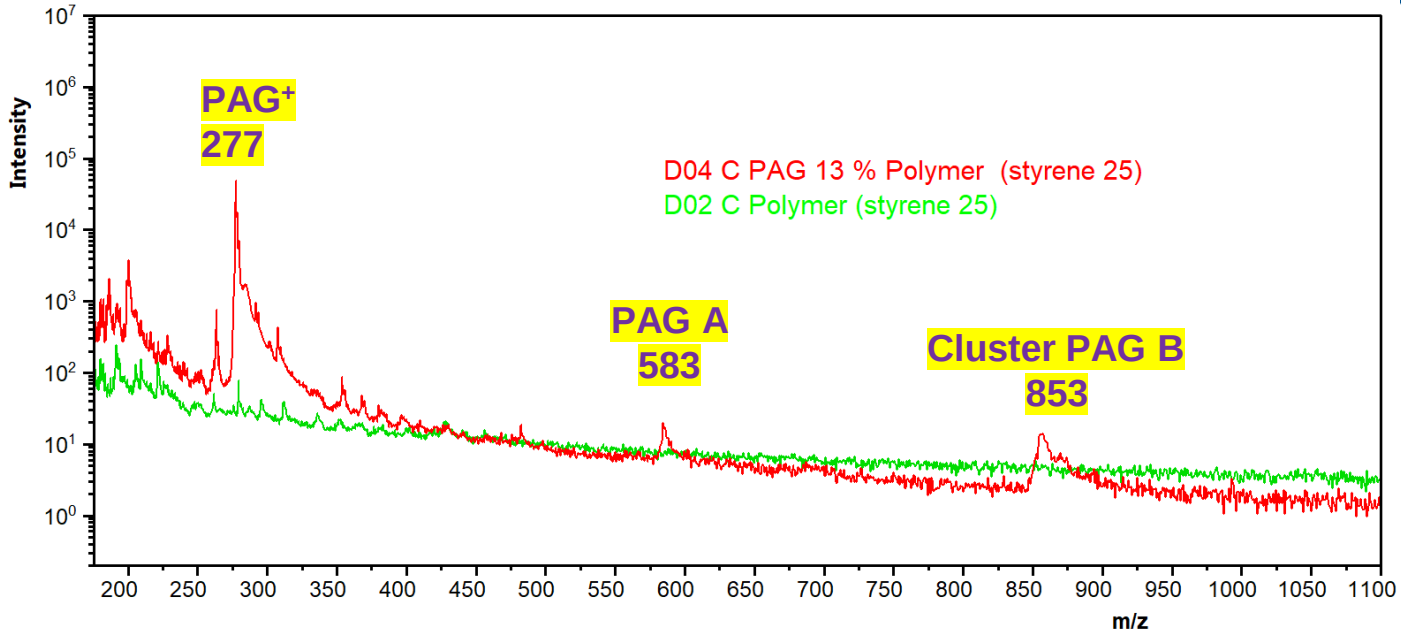


tBuma



No large effect in the aggregation process depending on the copolymer matrix used

Yiel PAG + seems to increase with the presence of styrene



Ratio using PAG + with polymers different (styrene) at PAG 17,3 wt% in photoresist film

PAG 17,3 wt%	PAG A (583) /PAG⁺ (277)	ClusterPAG B (853) /PAG⁺ (277)	Yield PAG ⁺
D07	2,01E-03 ± 0,5E-03	2,10E-03 ± 0,4E-03	**9**
D08	1,60E-03 ± 0,1E-03	1,50E-03 ± 0,15E-03	**17**

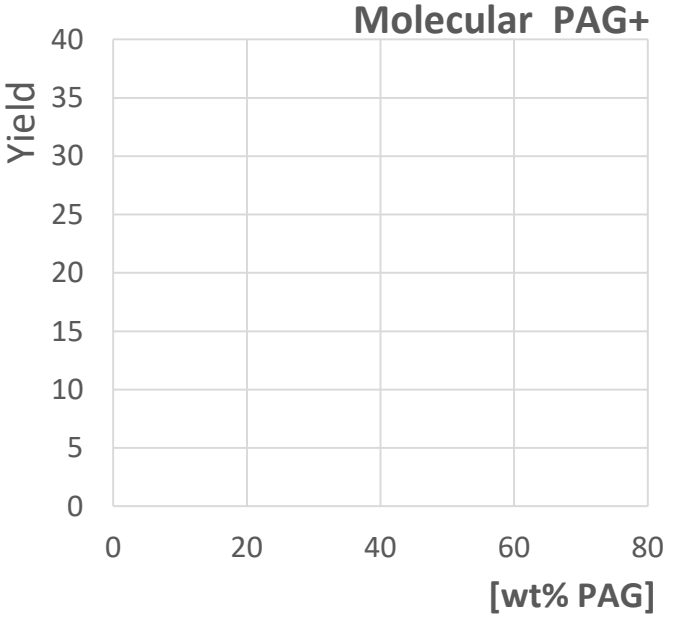
PAG concentration influence on the clusters formation

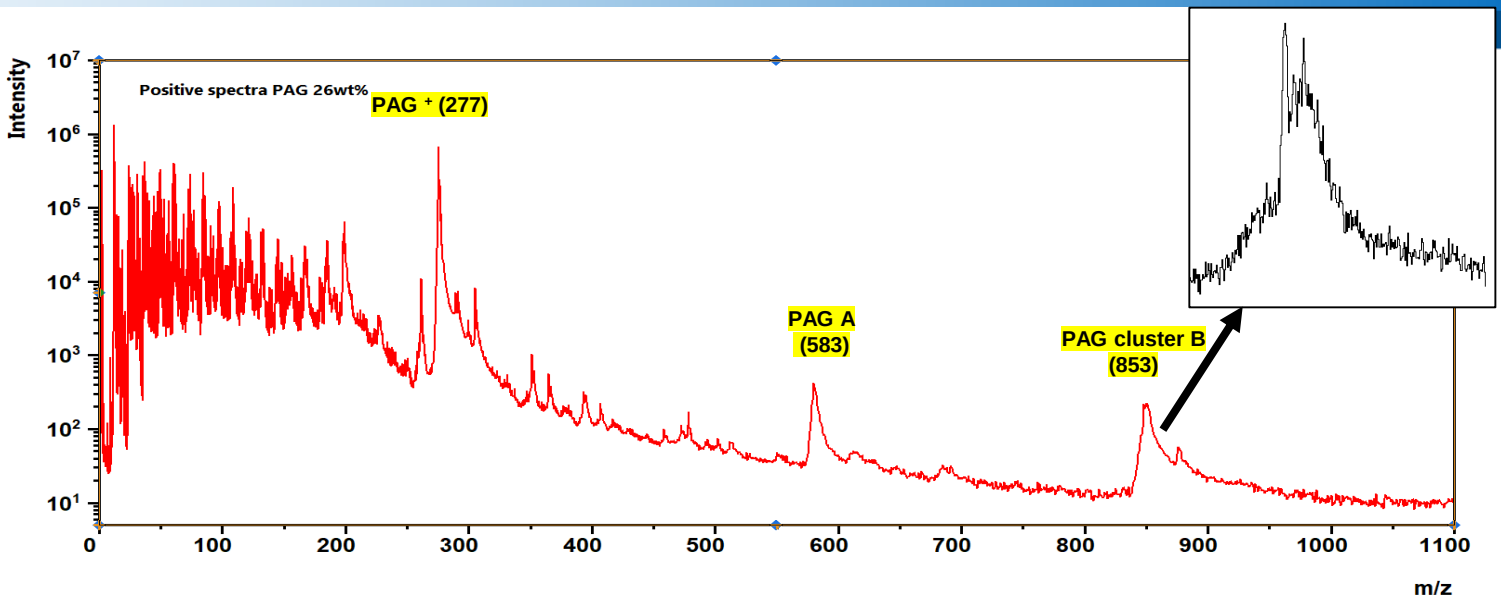
Quantitative analysis ?

Different PAG concentrations

5.0 wt%, 10.0 wt%, 13.0 wt%
17.0 wt%, 26.0 wt% 34.6 wt%
70.0 wt%

Bake: SB120C60"
Thickness: 35nm
No exposure



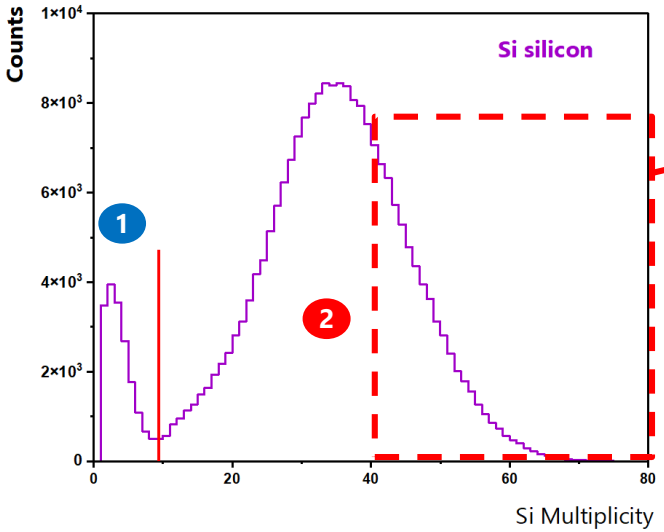


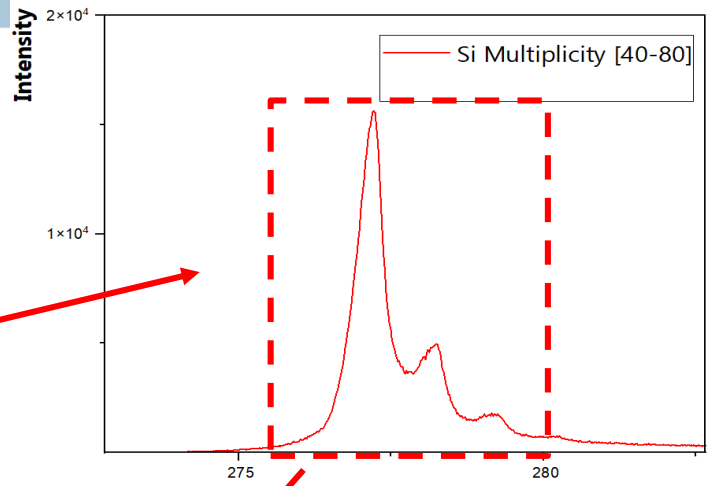
Clusters PAG/PAG + Ratio at different PAG wt% in photoresist film

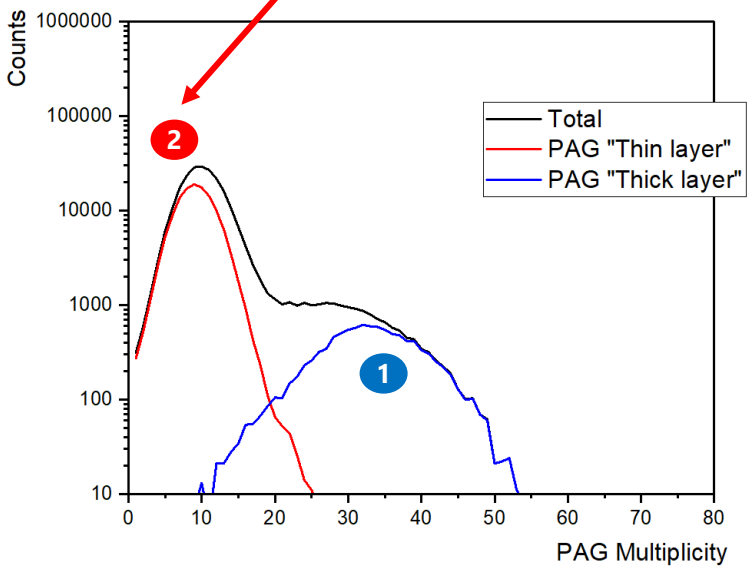
ID Sample	PAG wt %	PAG A (583)/PAG (277) .		PAG Cluster B (853)/PAG (277) .		Agg B/PAG A .
#127 D03b	5	3,3E-04		9,1E-04		**2,74**
#228 D02b	10	4,1E-04	±0,80E-04	5,5E-04	±0,20E-04	**2,74**
#230 D04c	13	6,0E-04	±0,20E-04	5,7E-04	±0,15E-04	**2,09**
#231 D04	26	2,5E-03	±0,21E-03	1,9E-03	± 0,18E-03	**0,74**
#334 D06 "Thin"	70	1,3E-02	±0,02E-02	3,6E-03	±0,10E-03	**0,28**
#334 D06 "Thick"	70	2,4E-03	±0,15E-03	1,4E-03	±0,09E-03	**0,58**

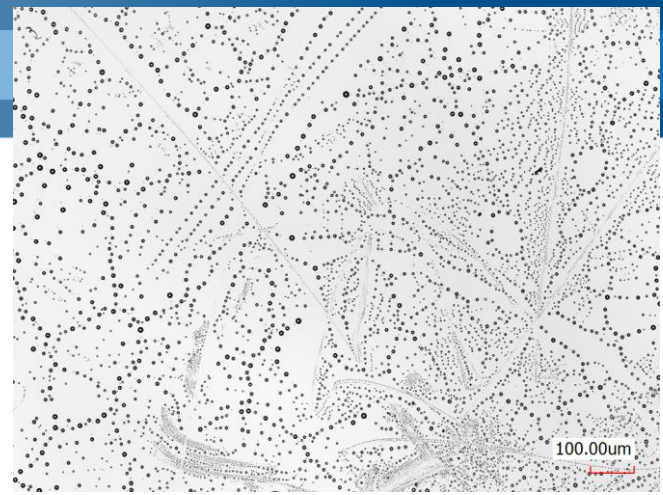
Sample with « µislets » formation (D06 PAG 70 % wt)

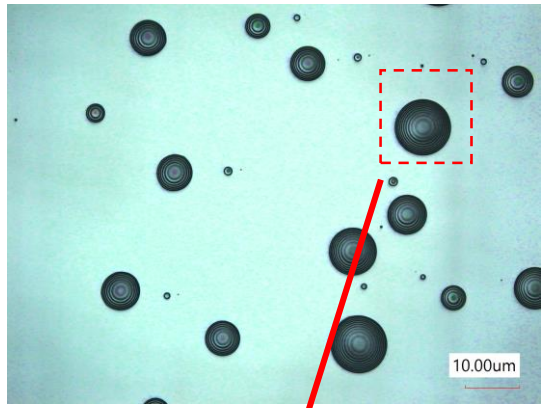
Silicon ion correlation ?

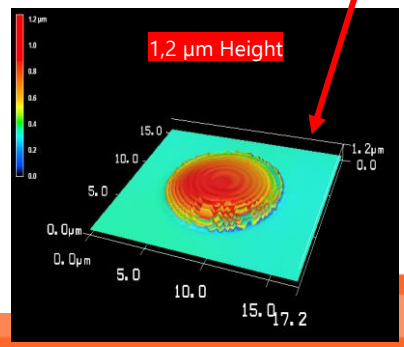












>>>> point of vigilance for analysis (concentration, yield, etc.)

Conclusion

All components of the photoresist film are detected : fragments, molecular peaks and clusters

Total Secondary ion emission is larger than 500 ions per impact. The secondary molecular ion yields are several tens ions per impact, so it is possible to obtain multiplicity distributions. Analysis of these distributions indicate whether the film is homogeneous or not.

Whatever the batch or sample composition (polymer matrix, concentration and temperature effect), the same fingerprint is observed with the presence of PAG clusters. They are directly related to the PAG concentration. However, differences in PAG+ ratios are observed between sample batches.

Correlations show that all impacts are similar (10^7 impacts), so homogeneity of this distribution suggests that clusters are thought to be formed in the solution.

Correlation measurements also show film inhomogeneities (µholes, “µislets”, thickness ....).

Thanks

Thanks to Alexis and Valentina and Danilo De Simone for providing the samples that allowed us to test Andromede capabilities, and for the fruitful exchange and access to their data (IonToF, OrbiTrap).

Thanks to Bruno Mercier (Vide et Surface/IJCLab) and Muriel Thomasset (LMO/ Soleil Synchrotron) for giving us access to their equipment for measuring confocal and AFM images.