Chemical analysis of surfaces and organic thin films by means of SIMS
Secondary ion mass spectrometry (SIMS)
– Static SIMS (SSIMS) vs. dynamic SIMS –

Cu (111) surface 1 ps after the bombardment with a Cu atom having an energy of 5 keV.

Secondary ion mass spectrometry (SIMS) – Units to separate (molecule) ions of different masses –

- ion gun
- desorbed cation → SIMS
- desorbed anion → SIMS
- desorbed neutral particle → SNMS
- shock wave

Quadruple secondary ion mass spectrometer

Sector field secondary ion mass spectrometer
Sector field secondary ion mass spectrometer
– NanoSIMS 50 (Cameca, Paris, France) –

silicon doped with boron,
line width 0.14 µm,
acquisition time: 16 min (ONERA, France)
Static secondary ion mass spectrometry (SSIMS) – Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) –

\[ E_{\text{kin}} = \frac{m}{2} \cdot v^2 = \frac{m}{2} \cdot \left( \frac{s}{t} \right)^2 \]

\[ U = 10 \text{ kV} \]

Ar$^+$ ions

extractor
detector
reflector
tube

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Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

- Pulsed primary ion beam -

- Puls length 59...1888 ps
Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)
– Spectral information –

$$E_{\text{kin}} = \frac{m}{2} \cdot v^2 = \frac{m}{2} \left( \frac{s}{t} \right)^2$$

![ToF-SIMS diagram with molecular formulas and count rates](image_url)
**Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)**

– Excellent mass resolution – PTFE after its treatment in a hydrogen plasma –

| m/z | measured m<sub>m</sub> | calculated m<sub>c</sub> | Δ = |m<sub>m</sub> - m<sub>c</sub>| |
|-----|---------------------|------------------------|-----|-----------------|
| CF<sub>3</sub> + | 68.9873             | 68.9952                | 0.0079         |
| C<sub>5</sub>H<sub>9</sub> + | 69.0695             | 69.0717                | 0.0022         |
| C<sub>2</sub>F<sub>3</sub> + | 80.9888             | 80.9952                | 0.0064         |
| C<sub>6</sub>H<sub>9</sub> + | 81.0645             | 81.0717                | 0.0072         |
| C<sub>2</sub>F<sub>5</sub> + | 118.9858            | 118.9920               | 0.0062         |
| C<sub>6</sub>H<sub>9</sub>F<sub>2</sub> + | 119.0659            | 119.0685               | 0.0026         |

All values were given in [amu]
Fragmentation mechanisms
– e.g. Polymers with aromatic units –

\[
\begin{align*}
\text{CH}_2\text{CH-CH}_3 & \quad \text{CH}_2\text{CH-CH}_3 \\
- \text{H}^+ & - \text{H}^+ \\
\text{C} \equiv \text{CH}_2^{\text{+}} \\
\text{phen} & \\
\text{ethylen} & - 27 \text{ amu} \\
\text{propylene} & - \text{41 amu}
\end{align*}
\]
Fragmentation mechanisms
– e.g. Polymers with aromatic units –

Polystyrene on silver substrate

Poly(4-chlorostyrene)

\[ \Delta m = 14,014 \text{ amu (CH}_2\text{)} \]
Analysis of additives in polymers
– No chance for XPS –

Irganox 259

Irganox 245

Analysis of additives, impurities, modifiers etc.
Application note of ToF-SIMS
– Grafting of styrene and maleic anhydride on polyolefin surfaces –

There are polystyrene sequences
[Sty-Sty-Sty] ?
There are maleic anhydride sequences
[MSA-MSA-MSA] ?
There are hydrolyzed maleic anhydride groups? 
**Imaging-ToF-SIMS**

– Laterally structured poly(γ-benzyl glutamate) –
Imaging-ToF-SIMS
– Laterally structured poly(γ-benzyl glutamate) –
SSIMS is a method oriented to detect and analyse molecules on the surface of samples

- analysis of molecule species [chemical structure and mass of the polymer's repeating units ⇒ type of monomer]
- non-quantitative surface analysis [semi-quantitative surface analysis],
- analysis of end groups Endgruppen ⇒ determination of molar masses and molar mass distributions on surfaces
- analysis of additives, impurities, modifiers etc. [traces can be detected],
- analysis of structural changes caused by surface modification, functionalization, and aging.