L’analyse de composition en 3D par spectrométrie de masse des ions secondaires à temps de vol (TOF-SIMS) – principe, applications et évolutions
**TIME OF FLIGHT MASS SPECTROMETRY**

\[ \text{Kinetic energy} = \frac{1}{2} \text{mass} \times \text{velocity}^2 \]

\[ \text{flight time} = \text{const.} \sqrt{\frac{\text{mass}}{\text{charge}}} \]

Mystery mass spectrum

![Graph showing mass spectrum with musical instruments labeled: Violin, Cello, Double Bass, Piano, Piccolo.](image-url)
« THE FLIGHT OF THE BUMBLE BEE »

Mystery mass spectrum

Number

Mass in kg

0,1  1   10  100  1000
NANO CHARACTERIZATION PLATFORM

8 Centers of Competences

3 institutes

- Mini X-Ray Diffraction (µXRD) Synchr.
- High Resolution Scanning Electron Microscopy (HR-STEM) Holography Tomography
- ToF-SIMS SIMS Atom probe
- Magnetic Resonance Nuclear Magnetic Resonance (RMN) Double Nuclei Polarization (DNP)
- Electron Microscopy
- Ion Beam Analysis
- Surface Analysis
- Specimen Preparation
- X-Ray Analysis
- Scanning Probe
- Optics
- Magnetic Resonance
- Raman spectroscopy
- Ellipsometry
- Spectrophotometry
- Luminescence
- Scanning Probe Optics
- TOF-SIMS SIMS Atom probe
- MXPS X-PEEM Nano-Auger
- FIB-DB Polishing, chemical prep...
OUTLINE

• A brief history of TOF-SIMS and recent evolutions
• Application examples
  • Isotopic analysis
  • Organic materials
  • Correlation with other techniques for improved 3D analysis
• Perspectives
1913 : Thomson mass to charge ratio of Ne and isotopes

1920 : F.W. Aston first mass spectrometer

1949 : Herzog : Ion source by electron impact

1950’s : Honig : SIMS instrument at RCA labs NJ

1960 Castaing & Slodzian/ Herzog & Liebel

1960’s : CAMECA makes 1st magnetic SIMS

1970 : Benninghoven (TOF-SIMS)

2000’s : Cluster sources

2016 : Tandem MS Orbitrap

Geology

Materials

Biology

Semicon

History of Secondary Ion Mass Spectrometry
Principle of Secondary Ion Mass Spectrometry

Primary ions in
1 to 60 keV
Ar\(^+\), Cs\(^+\), O\(_2\)\(^+\), O\(^-\)
Xe\(^+\), Bi\(^+\), Bi\(_3\)\(^{++}\), ...

Secondary ions out
1 to 20000 daltons
H\(^+\), Si\(^+\), ...

C\(_{27}\)H\(_{19}\)N\(_3\)O\(_3\)Al\(^-\)
Principle of Secondary Ion Mass Spectrometry
ToF-SIMS

- Detection of molecules and their fragments
- All Elements and insulators analyzable
- Depth resolution (~1 nm)
- Lateral resolution (~50 nm)
- Detection limit (ppm – ppb)

-flight time = const. $\sqrt{\text{mass/charge}}$

$^1\text{H}^+$ (3 μs) $\rightarrow$ $^{197}\text{Au}^+_1$ (42 μs)

ns time resolution $\frac{m}{\Delta m} = 10000$

m/z daltons

counts
TOF-SIMS DEPTH PROFILING

Pulsed analysis gun

Sputter gun

Analysis Beam pulse

ToF Analysis

Sputter Cycle

1 – 50 ns

5 – 10 µs

1 s

0.5 s pause time

Substrate
Example TOF-SIMS data

Depth profile

Analysis primary ion beam (Bi)

Secondary ions x,y,z,mass

Successive ion images

3D render

Tube-wall based on GaN/InAlN MQWs

C. Durand et al/ Nanoletters 2017, 17, 3347
### Isotopes

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Protons</th>
<th>Neutrons</th>
<th>Mass</th>
<th>Spin</th>
<th>Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{28}\text{Si}$</td>
<td>14</td>
<td>14</td>
<td>27.976</td>
<td>0+</td>
<td>92.223</td>
</tr>
<tr>
<td>$^{29}\text{Si}$</td>
<td>14</td>
<td>15</td>
<td>28.976</td>
<td>1/2+</td>
<td>4.685</td>
</tr>
<tr>
<td>$^{30}\text{Si}$</td>
<td>14</td>
<td>16</td>
<td>29.973</td>
<td>0+</td>
<td>3.092</td>
</tr>
</tbody>
</table>

Need to avoid spin of 29 Si for Quantum computing applications (Si Qbits)
Isotopes – Si 28

99.992% $^{28}$Si CVD-grown epilayer on 300 mm substrates
large scale integration of silicon spin qubits

Monoatomic vs Cluster sputtering

- Introduction of cluster sputtering in 2000’s enables molecular depth profiling

\[ \text{Monoatomic sputtering: } 500 \text{ eV/atom} \]

\[ \text{Cluster sputtering: } 1 \text{ eV/atom} \]

Fragmentation of molecules

Ejection of intact molecules

This opens up the fields of organic electronics, chemistry and biology
Monoatomic vs Cluster sputtering

Monoatomic sputtering
500 eV/atom

Cluster sputtering 1 eV/atom
TOF-SIMS of OLEDs

Tris(8-hydroxyquinoline)aluminum (Alq₃)

Fresh

TOF-SIMS depth profile: molecular composition and degradation
TOF-SIMS OF OLEDS

TOF-SIMS depth profile of molecular composition of complete OLED stack

Graph showing the normalized intensity of various elements as a function of sputter time.
THE NEED FOR SURFACE TOPOGRAPHY DATA
NATURAL EXAMPLES OF EROSION RATE DIFFERENCES
Sputter rate > Sputter rate

- Initial sample
  - Initial topography

- Sample during depth-profile
  - Evolved topography

TOF-SIMS 3D RECONSTRUCTION ARTEFACTS

NEED TO CORRELATE THE TOF-SIMS DATA WITH TOPOGRAPHICAL INFORMATION (AFM, confocal microscopy, etc)
COMBINED TOF-SIMS AFM METHODOLOGY

TOPOGRAPHICAL + CHEMICAL INFORMATION FROM SAME AREA
An x, y and z coordinate for every voxel!

GaAs/SiO₂ test sample

GaAs sputters twice as fast as SiO₂
COMBINED TOF-SIMS AND AFM PROTOCOL

OVERLAY
ToF-SIMS and AFM

SPUTTER RATE MAP

DEVELOPMENT OF A COMBINED TOF-SIMS AND AFM PROTOCOL

Next step – combine with other AFM modes: piezoresponse, resistance, …..
CROSS SECTIONS FOR LARGER OBJECTS
FIB-TOF-SIMS TOMOGRAPHY

Deeply buried
Heterogeneous
Air-sensitive

Analysis primary ion beam (Bi)  Secondary ions x,y,z,mass

Scanned primary ion beam

Successive ion images

FIB

Secondary ions x,y,z,mass

FIB-TOF-SIMS « slice and view »

3D render of Cu in through-silicon-via

20 µm
COMBINING X-RAY AND TOF-SIMS TOMOGRAPHY

X-ray computed nanotomography (CNT) then TOF-SIMS on the same object.
CORRELATIVE MICROSCOPY

X-ray tomography

Morphology from X-ray CNT

Composition from FIB TOF-SIMS

solid oxide fuel cell

ToF-SIMS

10 µm

LSC
LSCF
LSCF/CGO
CGO
8YSZ
Ni+3YSZ

O₂ electrode
Barrier layer
Electrolyte
H₂ electrode
COMBINED DATA SET

3-D TOF-SIMS AND X-RAY NANOTOMOGRAPHY

La (LSCF/CGO)

Y (YSZ)

Ni (Ni+YSZ -3%Y)

ToF-SIMS  X-ray tomo

10 µm
3-D ELEMENTAL DISTRIBUTION AND PROFILES

SUMMARY AND PERSPECTIVES

• TOF-SIMS is a versatile tool for ultra sensitive 3D composition analysis of both inorganic and organic materials

• Correlation with other characterisation techniques can enhance data sets

• Perspectives
  • Advanced data treatment to exploit the full mass spectrum
  • Improving lateral resolution with new ion sources (cold Cs\(^+\), He\(^+\) ions ..)
  • Improved interpretation of the mass spectrum using tandem MS
  • Easy to use instruments for the clean room
• Plasma Profiling Time Of Flight Mass Spectrometry

Plasma source
Sputtering & ionization

Detection
Orthogonal time of flight mass spectrometer
Use full spectrum, compressed sensing, resolution enhancement, machine learning,...
Slide courtesy of Greg Fisher, Physical electronics
TOF MS-MS – SURFACE CONTAMINATION

ID of two molecules with the same mass!!

Slide courtesy of Greg Fisher, Physical electronics
THANK YOU FOR YOUR ATTENTION

ANR, CARNOT (ATRIUM PROJECT) AND H2020 METRO4-3D FOR FUNDING, SOLIDPOWER S.P.A FOR THE SOFC SAMPLE, CNRS-LTM FOR THE GAAS/SIO2 SAMPLE

The PFNC and Maiglid Moreno, Eric Langer, Agnieszka Priebe, Pierre Bleuet, Gael Goret, Guillaume Audoit, Jerome Laurencin, Arnaud Bordes, Eric De Vito, Nicolas Chevalier, Tanguy Terlier, Franck Bassani, Thierry Baron, Marc Veillerot, François Pierre, Adeline Grenier, Philippe Holliger, Frédéric Laugier, Nicolas Lhermet, Jean-Claude Royer, Emmanuel Nolot, Yann Mazel, Amal Chabli, François Bertin, Agnès Tempez (Horiba), Sébastien Legendre (Horiba), Gregory Fisher (Physical Electronics)