



## APPLICATION NOTE

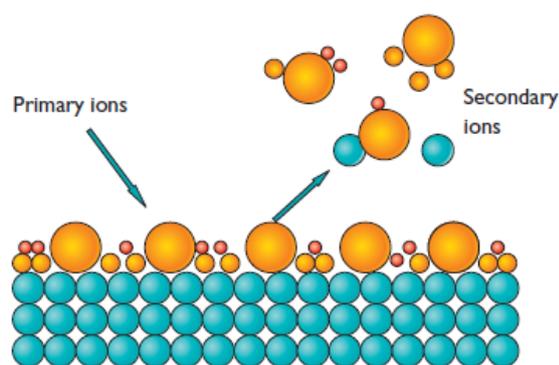
# Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is a technique that is very suitable for surface analysis, metal trace determination, high resolution surface imaging and depth profiling. SIMS can be operated in static and dynamic mode.

Static SIMS provides detailed elemental and molecular information about the outermost monolayer of surfaces. The molecular information enables rapid characterization of both organic and inorganic species present on the surface with a high sensitivity and specificity. Dynamic SIMS provides two-dimensional (2D) depth-profiling as well as full three-dimensional (3D) analysis of thin layers and interfaces.

## Basic principle

TOF-SIMS is the mass analysis of secondary ions emitted from a surface that is bombarded by a pulsed primary ion beam of typically 25 keV (Fig. 1).



*Fig. 1: The principle of static SIMS: a surface is bombarded by (primary) ions. As a result, secondary ions are emitted which are elements or (fragments of) molecules.*

The flux of these primary ions is extremely low. As a result, the surface excitation by particle bombardment leads to the emission of secondary ions characteristic of the chemical composition in the uppermost monolayer. For

each type of molecule, secondary ion emission results in a characteristic set of ionized molecular fragments with well-defined mass spectra. These secondary ions are analyzed with respect to their mass to charge ratio. In a time-of-flight (TOF) mass spectrometer the separation is based on the fact that ions of the same energy that have different masses have different flight times towards the detector.

## Analytical applications

TOF-SIMS is applicable to all types of materials, highly sensitive and able to give molecular information through the detection of molecular ions. High mass resolution and accuracy allows for the identification of inorganic and organic elements and compounds. Because almost all organic molecules give typical fingerprint peaks in the mass spectrum, TOF-SIMS is particularly suited for their identification.

There are different modes of operation: surface spectroscopic microanalysis and imaging, metal trace analysis and depth analysis. Typical examples of TOF-SIMS applications are discussed.

## Static SIMS - Surface spectroscopy

Phenomena such as adhesion, corrosion, adsorption, and wettability are of vital importance in various technological areas like microelectronics, catalysis, polymers and biomaterials. These phenomena are often governed by the chemical composition of the surface. Static SIMS allows for detailed studies of the chemical composition of the outermost monolayer of the specimen.

In its spectroscopic mode of operation, the primary ion beam is used to bombard a relatively large area. As a result, a large amount of material from the outermost monolayer is available for analysis and thus a large number

of secondary ions can be generated. Static SIMS can be effectively applied in failure analysis or can be used to determine the processing stage where contamination is introduced. This can be achieved even for small areas allowing for local analysis on e.g. patterned wafers. The detection of traces of metal contamination is an important analytical task. By using external standards, quantification is possible. Details of a spectrum from a silicon surface, containing trace metals, are shown in Fig. 2. Detection limits down to  $10^7$  atoms/cm<sup>2</sup> can be achieved.

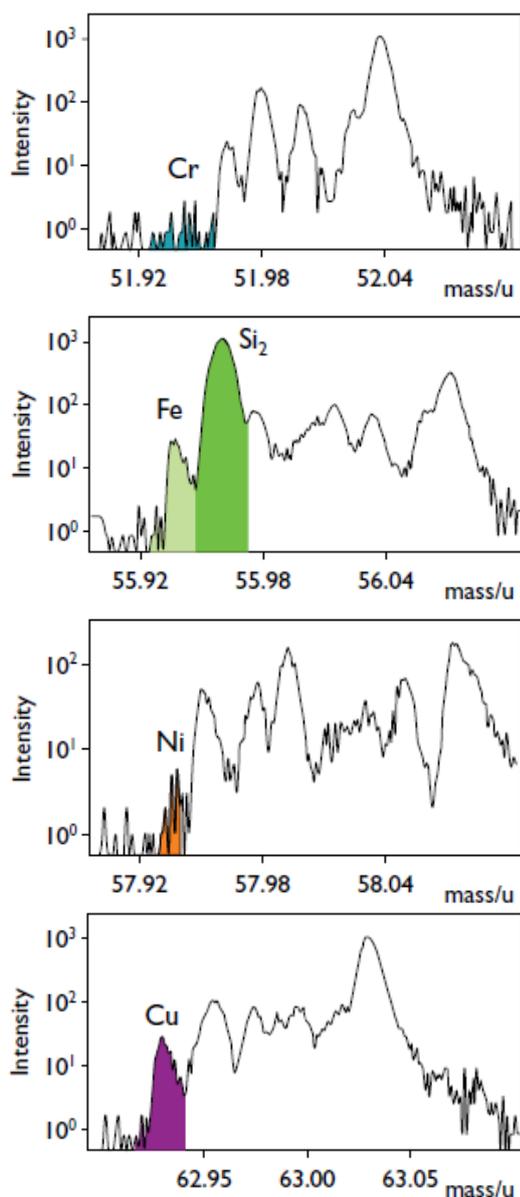


Fig. 2: Details of a static SIMS spectrum from a Si surface showing trace metals e.g. Cr, Fe, Ni and Cu.

The high mass range and advanced cluster ion source ( $Bi_n^+$ ) makes the TOF-SIMS technique suitable to detect complex molecular materials

such as polymers and biomaterials with high sensitivity. In Fig. 3, part of a mass spectrum from a C<sub>60</sub> end group on a synthetic polypeptide (poly(g-benzyl-L-glutamate)) film is shown.

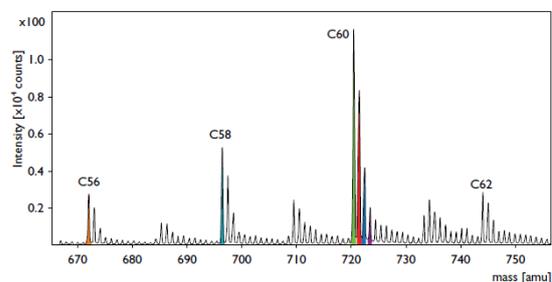


Fig. 3: Part of a static SIMS spectrum from a synthetic polypeptide with a C<sub>60</sub> end group. The peak at mass 720 amu is due to C<sub>60</sub> fragments. Fragments with 2 or 4 C atoms more or less are visible too.

## Static SIMS - Surface imaging

By rastering a finely focused primary ion beam over the sample surface, and collecting mass spectra as a function of position, chemical mapping can be carried out. For any peak in the mass spectrum, an image can be generated, retrospectively. This allows chemical mapping of elements and organic molecules with a lateral resolution down to about 60 nm. Imaging is exploited in different types of applications.

There has been growing interest in chemical modification of surfaces for technical and biochemical systems. An example is presented in Fig. 4, where TOF-SIMS is applied to image functionalized self-assembled monolayers (SAMs) of C<sub>18</sub>H<sub>37</sub>SH molecules on micro-patterned Au layers coated on Si wafers. The C<sub>18</sub>H<sub>37</sub>S molecules are coupled via Au-S bonds to the gold-coated microarrays. In the spectra, the masses of intact molecules and characteristic fragments of alkanethiol SAMs are obtained. Images are recorded by selecting specific peaks from the spectra. The distribution of Au<sup>-</sup>, AuS<sup>-</sup> and intact C<sub>18</sub>H<sub>37</sub>S<sup>-</sup> molecule across the surface is visualized.

Furthermore, there is a huge scope for imaging TOF-SIMS for the evaluation of surface modifications on biomedical materials.

Fig. 5 shows images of antibodies printed as circles of 150 μm on polystyrene cartridges. The images show ion signals of polystyrene, alkali salt from the buffered solution and the amino acid alanine for different washing steps. Salt crystals of alkali salt cover the printed circles. The TOF-SIMS studies show the beneficial contribution of the washing steps.

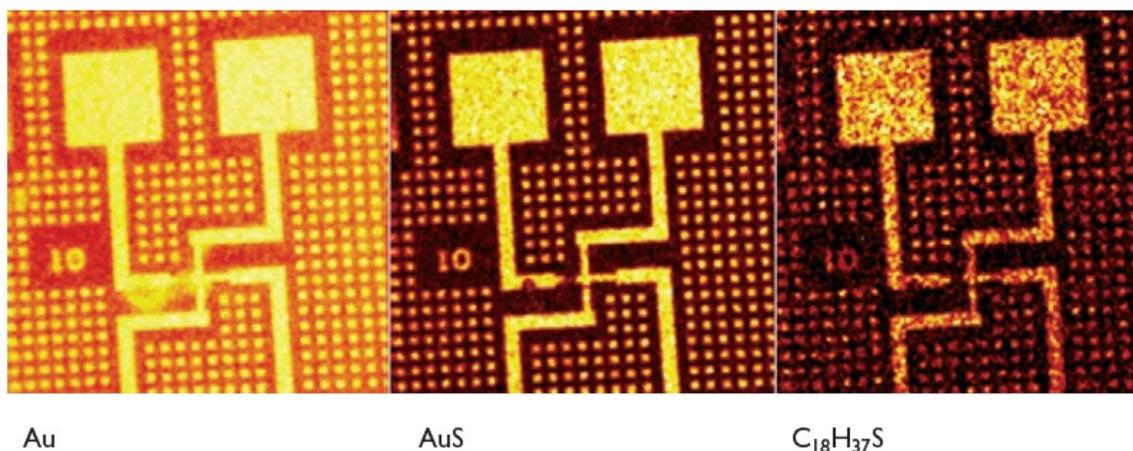


Fig. 4: Secondary ion images of a self-assembled  $C_{18}H_{37}SH$  layer on gold coated Si, showing the distribution of  $Au^-$ ,  $AuS^-$  and  $C_{18}H_{37}S^-$  species. Image area =  $500 \times 500 \mu m^2$ .

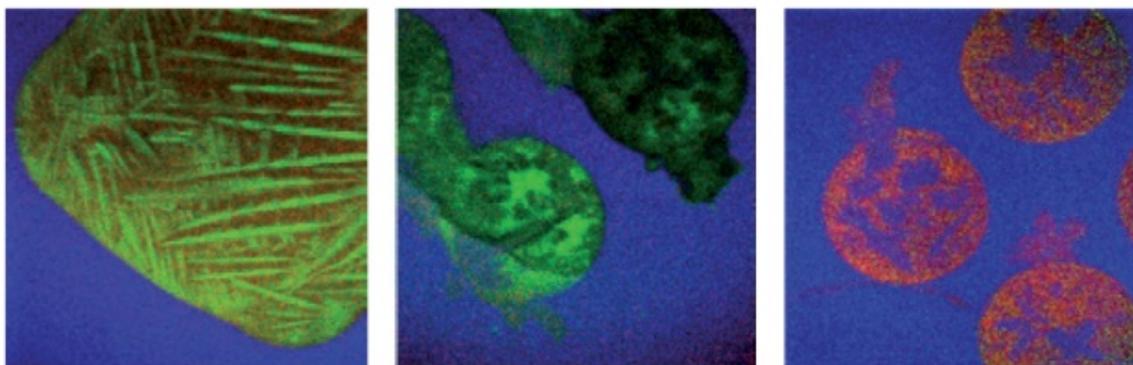


Fig. 5: TOF-SIMS images of printed antibodies on polystyrene (PS) cartridges. Green =  $Na_2Cl$ , blue =  $C_7H_7=$  polystyrene, red =  $C_2H_6N$  (alanine = amino acid in antibody). Left: no wash, middle:  $B(OH)_3$  wash, right: extra  $H_2O$  wash. In the right image the amino acids are clearly visible. Image area =  $500 \times 500 \mu m^2$ .

## Dynamic SIMS - depth profiling

Characteristic for dynamic SIMS is the use of a more intense primary ion beam to remove much more material. By prolonged exposure of a sample, one can obtain compositional depth profiles. Because of the large number of collision cascades in the sample under these sputter conditions, interatomic bonds are broken or re-arranged and the original molecular structure is damaged. Usually, the dynamic mode of operation is only suitable for elemental analysis, not for molecular analysis. SIMS depth profiling with non-TOF instruments is widely applied, e.g. for the characterization of dopant profiles in semiconductors. The main advantage of a TOF-SIMS instrument for depth profiling is the collection of the entire mass spectrum at each cycle of the depth profile, which is ideal for detecting unknown contaminants at buried interfaces and for studying many elements simultaneously, e.g. in (multi-)layers of compound materials.

When dynamic SIMS is performed on a TOF-SIMS instrument, the depth profiles are recorded in the so-called dual beam mode. A crater is etched by cycles of sputtering by an intense ion beam ('sputter gun'). In between these cycles, the crater bottom is analyzed with pulses of the less intense analysis gun, in the same way as used in static SIMS. Such an approach allows independent control of the erosion (through the sputter gun parameters) and analysis conditions (through the analysis gun).

An example of a TOF-SIMS depth-profiling analysis is shown in Fig. 6, where four superimposed hydrogen (Fig. 6a) and aluminum (Fig. 6b) profiles of Al-doped ZnO layers, grown on Si, are depicted. The influence of the precursor gas pressures during deposition is studied. The H- and Al-concentrations in the TOF-SIMS profiles are quantified using the known concentrations of a reference sample.

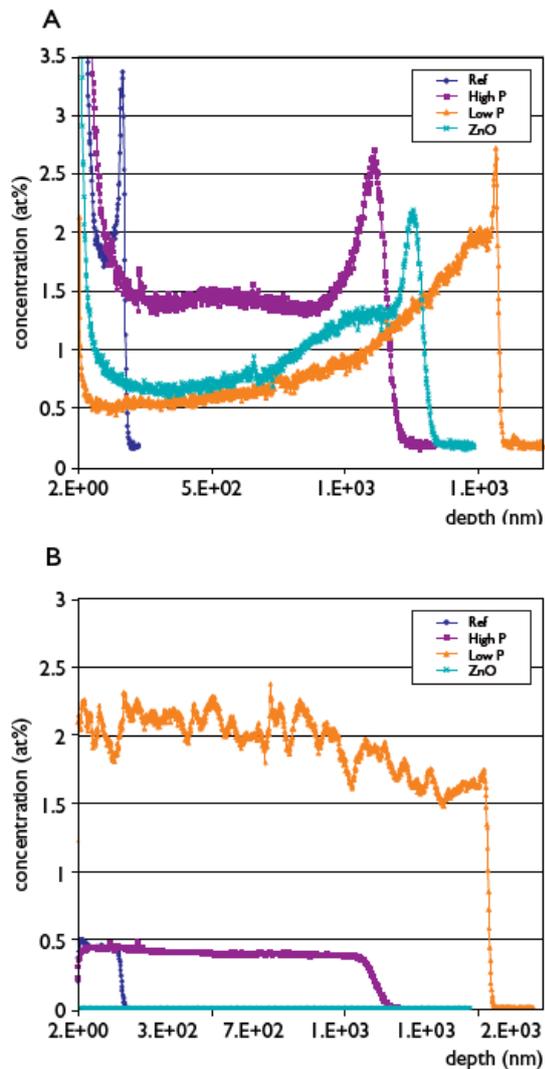


Fig. 6: Overlay of TOF-SIMS depth profiles of (a) H concentration and (b) Al concentration in 4 different Al-doped ZnO layers.

## Dynamic SIMS - 3D profiling

By alternating element mapping and sputtering of the sample, three-dimensional information on the chemical composition is achieved (3D-SIMS). TOF-SIMS provides “retrospective analysis”: data can be explored afterwards to look for complex and unknown structures like defects, phase separations, contaminants at interfaces, particles, and diffusion areas. From the stored data, spectra can be reconstructed from any coordinate, images from any section and depth-profiles from any selected area. Various 3D views can be made. In 3D analysis the composition, shape and position can be visualized.

An example where 3D profiling has been applied is the study of out-diffusion of specific elements in Al /  $\text{La}_x\text{Zr}_y\text{O}_z$  / Si devices after

electrical breakdown. SIMS maps are collected as a function of depth in the sample by sputtering through the structure into the Si substrate. These images are then used to reconstruct volume images (3D images) and depth-profiles (3D depth-profiling).

Fig. 7 shows the 3D distribution of Si ions. At the left side of Fig. 7, the corresponding projected image in 2D is shown.

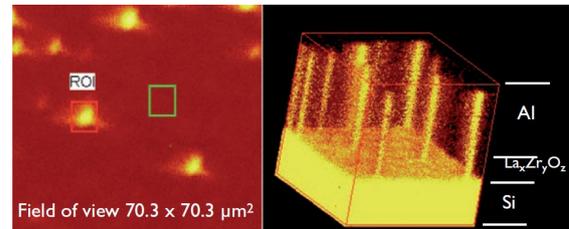


Fig. 7: Mass resolved 3D Si-view of an Al/ $\text{La}_x\text{Zr}_y\text{O}_z$ /Si device structure showing inhomogeneous diffusion of Si into the Al top layer. At the left side the corresponding projection in 2D is visible. Regions of interest (ROIs) are indicated; red square (Si column), green square (reference area).

The 3D TOF-SIMS image (right side) reveals that inhomogeneous out-diffusion of Si occurs via columns from the Si substrate through the dielectric  $\text{La}_2\text{O}_3:\text{ZrO}_2$  films into the Al top layer. SIMS depth-profiles are reconstructed from the images by selecting regions of interest (ROIs). A profile taken in an area, containing such a column (red square), is compared with a profile taken from the surrounding area (green square). The superimposed profiles of some relevant ions are shown in Fig. 8, revealing enhanced Si-diffusion.

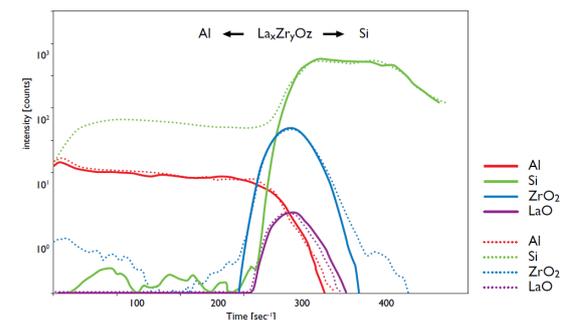


Fig. 8: Superimposed depth-profiles obtained from selected regions of interest: profiles from the red and green squares in Figure 7 are represented by the dotted and solid lines, respectively. The Si profiles (in green) show a large difference in Si diffusion into Al for the two regions.

## Applications

- Surface analysis of organic and inorganic materials.
- Imaging of elements and molecules on surfaces.
- Failure and root cause analysis in case of delamination, blistering, de-wetting, staining, haze, etc.
- Survey depth profiling

## Technical specifications

- *Signal detected:*  
Elemental and molecular ions
- *Elemental range:*  
Full periodic table coverage, plus molecular species
- *Detection limits:*
  - Fraction of a monolayer
  - $10^7 - 10^{10}$  at/cm<sup>2</sup> (metal on semiconductor)
  - Down to 1 ppm bulk concentration in depth profiles
- *Depth resolution:*
  - 1-3 monolayers (static mode)
  - Down to 1 nm (depth profiling)
- *Information depth:*
  - Below 1 nm (static mode)
  - Up to 10  $\mu$ m (depth profiling)
- *Imaging/Mapping:*  
Yes
- *Lateral resolution/Probe size:*  
Down to 0.1  $\mu$ m

## Strengths

- Molecular identification of compounds on a surface.
  - Very high sensitivity and low detection limits.
  - Imaging with  $\sim 0.2$   $\mu$ m resolution.
  - Insulator and conductor analysis.
  - Non-destructive (static mode).
  - Survey depth profiling in all sorts of materials.
  - Quantitative surface coverage and concentration depth profiles for specific materials.
- On specific instruments:*
- Whole wafers up to 200 mm.
  - Molecular depth profiling using an Argon gas cluster ion beams (GCIB).

## Limitations

- Usually not quantitative without standards.
- Samples must be vacuum compatible.
- No molecular information from below the outermost 1–3 monolayer(s).
- Contamination from sample packaging and handling or from previous analyses may impact quality of results.