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

- surface analysis
- 2D depth-profiling and 3D analysis
- all elements and isotopes
- 60 nm lateral resolution
- sub-monolayer sensitivity

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.

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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 (see fig. 1). 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 given below.

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
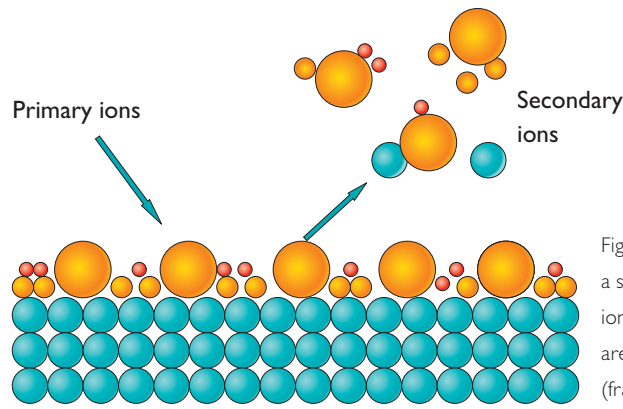

Fig. 1: The principle of static SIMS: a surface is bombarded by (primary) ions. As a result secondary ions are emitted which are elements or (fragments of) molecules.

governed by the chemical composition of the surface. Static SIMS allows for detailed studies of the chemical composition of the outermost atomic layer 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 step in sample processing responsible for contamination. This can be achieved even for small areas allowing for local analysis on e.g.

patterned wafers. The detection of metal trace elements 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. 2a. Detection limits down to 10^7 atoms/cm^2 can be achieved.

The high mass range and advanced cluster ion source (Bi_n^+) makes the TOFSIMS technique suitable to detect complex molecular materials such as polymers and biomaterials with high sensitivity. In fig. 2b, details of a mass spectrum from a C_{60} endgroup on a synthetic polypeptide (poly (g-benzyl-L-glutamate) film is shown.

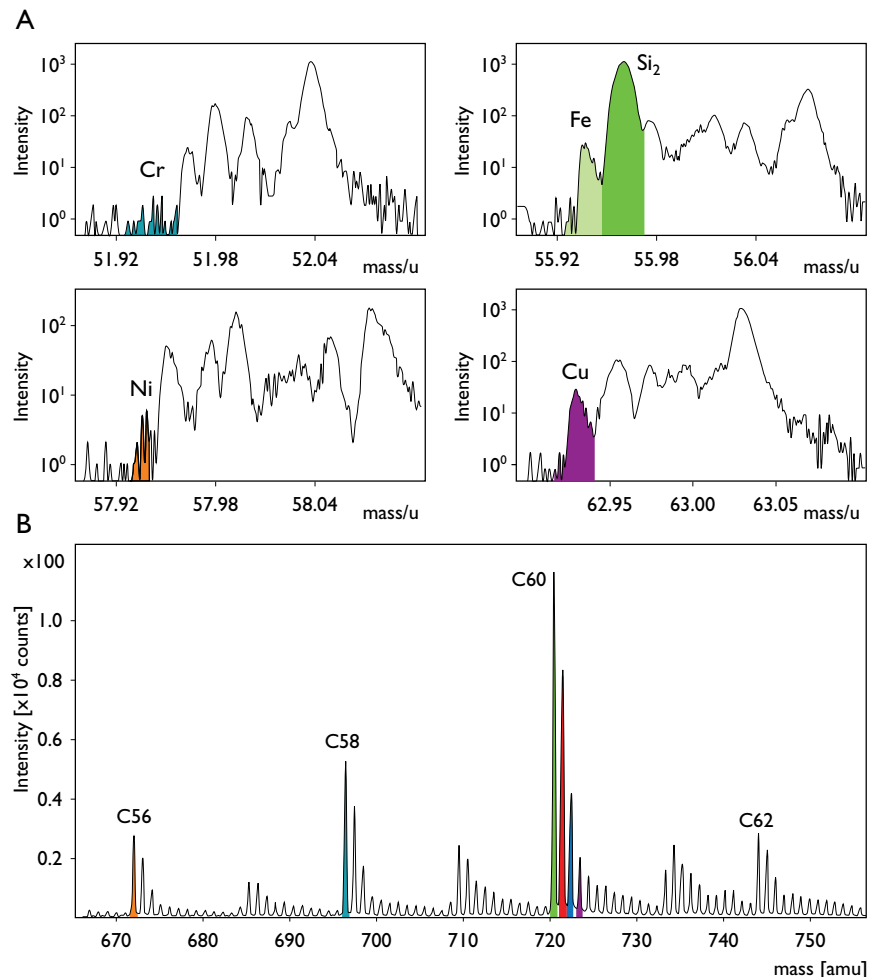Fig. 2: Details of a static SIMS spectrum from a Si surface showing trace metals e.g. Cr, Fe, Ni and Cu (a) and a synthetic polypeptide with a C_{60} end group (b). The peaks at mass 720 amu, 721, 722 and 723 are largely attributed to isotopes of C_{60} fragments. C_{60} end-groups are identified by masses 720 = +/- n*12 ((C_{60}) +/- nC), where n= 1…6.
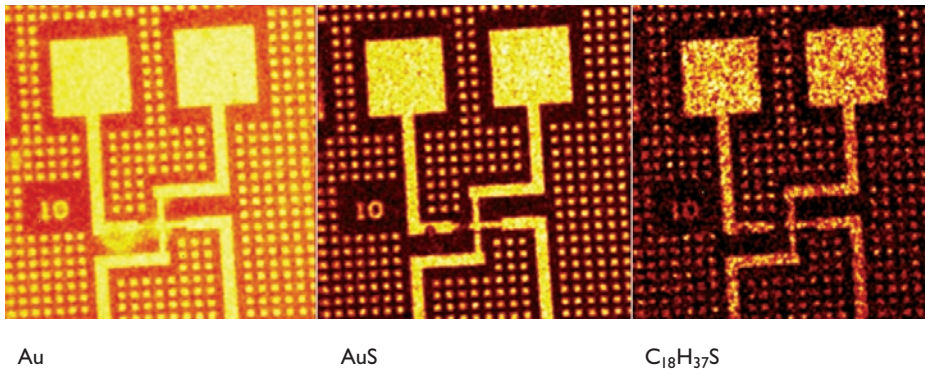
| Au | AuS | $C_{18}H_{37}S$ |

Fig. 3: 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*500 µm².

Static SIMS - Surface imaging

By rastering a finely focused primary ion beam over the sample surface, and collecting a mass spectrum at every pixel point, 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 varying from a few microns down to about 60 nm. Imaging is exploited to 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. 3b, where TOFSIMS is applied to image functionalized self-assembled $C_{18}H_{37}SH$ mono-layers on micro-patterned Au layers. The $C_{18}H_{37}S$ molecules are coupled via Au-S microarrays on gold-coated Si surfaces. 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^-, AuS^- and intact $C_{18}H_{37}S^-$ molecules across the surface is visualized.

Furthermore, there is a huge scope for imaging TOFSIMS for the evaluation of surface modifications on biomedical materials. Fig. 4 shows images of antibodies printed as circles of 150 µm on polystyrene cartridges. The images show the polystyrene, alkali salt from the buffered solution and the amino acid alanine ion signals for different washing steps. Salt crystals of alkali salt cover the printed circles. The TOFSIMS studies show the beneficial contribution of the washing steps.

Dynamic SIMS

Characteristic for dynamic SIMS is the use of a more intense primary ion beam in order to remove much more material. By prolonged exposure of a surface, one can obtain compositional depth profiles. Because of the damage to the sample produced under these sputter conditions, the dynamic mode of operation is suitable for elemental analysis but not for molecular analysis. 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 the sputter gun and the crater bottom is continuously analyzed with a pulsed analysis gun. Such an approach has the advantage of allowing the independent control of the erosion and analysis conditions.
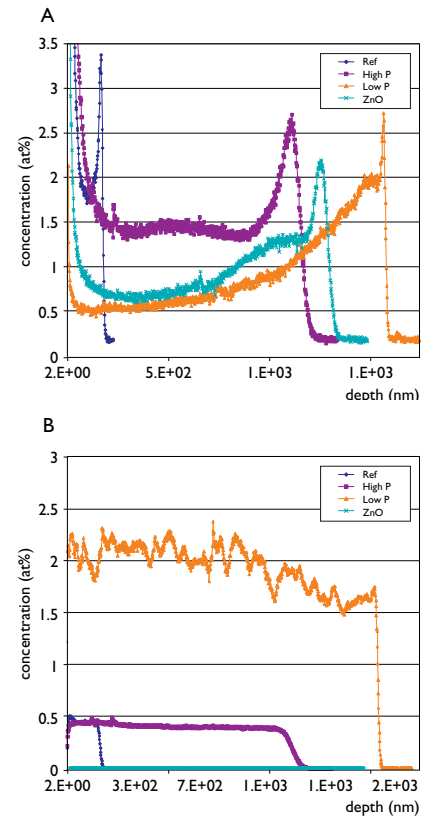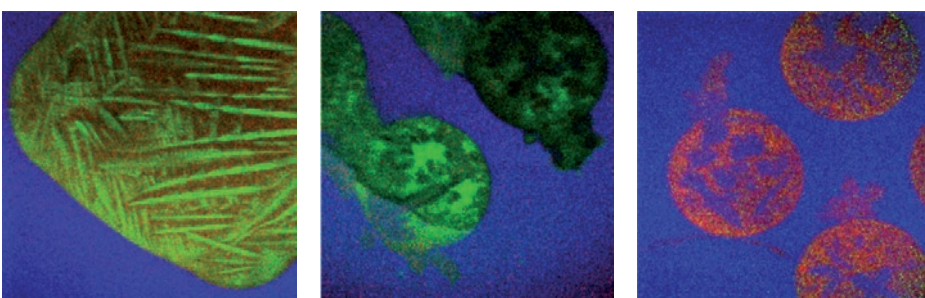

Fig. 5: Overlay of SIMS profiles of differently Al-doped ZnO layers: (a) H-profiles, (b) Al-profiles.

Two-dimensional (2D) depth profiling

Sample profiling by SIMS is widely applied for the characterization of thin layers and multi-layers. By TOFSIMS the entire mass spectrum is stored at each cycle of the depth profile, which is ideal for detecting unknown contaminants at buried interfaces and for studying many elements simultaneously. An example of depth-profiling is shown in fig. 5, where four superimposed hydrogen (fig. 5a) and aluminum (fig. 5b) 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 TOFSIMS profiles are quantified using the known concentrations of a reference sample.

Three-dimensional (3D) Depth profiling

By alternating element mapping and sputtering of the sample, three-dimensional information on the chemical composition is achieved (3D-SIMS). TOFSIMS 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

Fig. 4: TOFSIMS 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*500 µm².

A

Field of view 70.3 x 70.3 μm²

Si   Si

Al

La$_x$Zr$_y$O$_z$

Si

B

Al ⟵ La$_x$Zr$_y$O$_z$ ⟶ Si

intensity [counts]

Time [sec⁻¹]

— Al
— Si
— ZrO$_2$
— LaO

···· Al
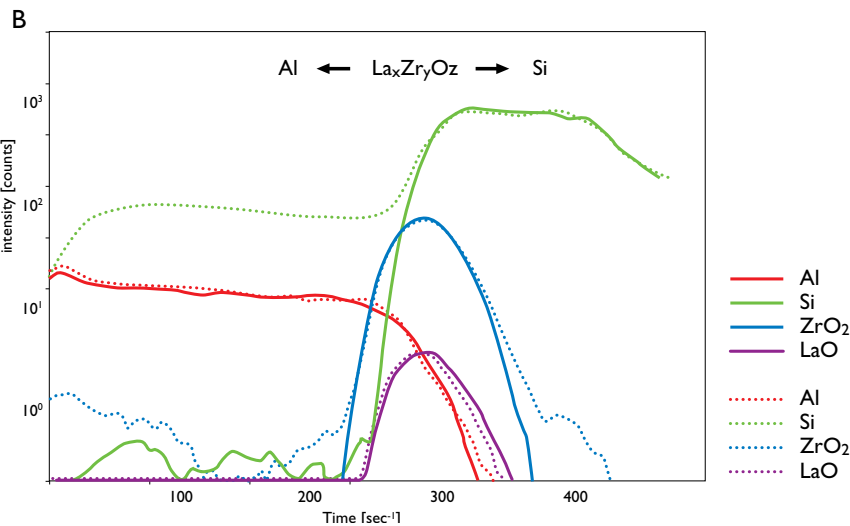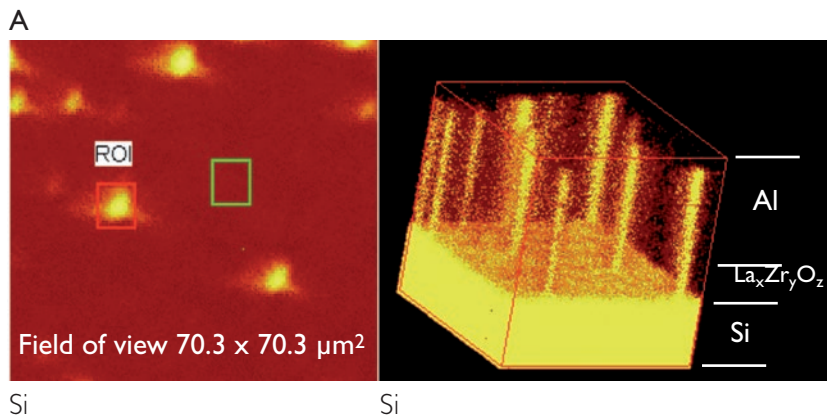···· Si
···· ZrO$_2$
···· LaO

Fig. 6: (a) Mass resolved 3D Si-view of an Al/La$_x$Zr$_y$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). (b) Superimposed depth-profiles obtained from the regions of interest: the red and green square-defined areas from figure 6a are represented by the asterisks and the squares, respectively. The Si profiles (in green) show a large difference in Si diffusion in Al for the two areas.

from any selected area. Various 3D views can be made. In 3D analysis the composition, shape and position can be visualized.

An example where the 3D technique has been applied is the study of out-diffusion of specific elements in Al/La$_x$Zr$_y$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. 6a shows information about the 3D distribution of Si ions.

At the left side of fig. 6a, the corresponding projected image in 2D is shown. The 3D TOFSIMS image (right side) reveals that inhomogeneous out-diffusion of Si occurs via columns from the Si substrate through the dielectric La$_2$O$_3$: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. 6b, revealing enhanced Si-diffusion.

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Characteristics

Sample type
• Solid materials (bulk, thin layers, powder)

Sample sizes
• Ranging from a few mm² up to about 100 cm²

Elemental range
• All elements and isotopes (including H)
• High surface sensitivity (< 1nm)

Lateral resolution
• 60 nm

Signal detected
• Secondary ions (elemental and molecular)

Mass resolution
• 7000 at 29 amu; >10.000 beyond 200 amu

Information depth
• 1 nm, by sputtering up to 1 μm

Detection limits
• 10¹²-10¹⁶ atoms/cm³ (ppb-ppm) in bulk
• < 10¹⁰ at/cm² at surface
• Sub-fmol for molecules

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