APPLICATION NOTE

Ion spectroscopy using TOF-SIMS on a Thermo Scientific Helios DualBeam

Secondary Ion Mass Spectroscopy (SIMS)

The ionized particles that are generated by the ion beam milling process can be used for analysis, as they can be identified and quantified. Because these particles come from a very shallow depth, the technique known as Secondary Ion Mass Spectroscopy (SIMS) is considered a surface analysis technique. Discrimination is based on measurement of the time of flight (TOF), once the particles are accelerated into the drift space of the detector. A modern TOF detector is compact and suited to measuring all elements of the periodic table, including all possible isotopes. Various aspects of the technique are described in this application note.

The TOF-SIMS detector

The detector is mounted on one of the ports of the DualBeam chamber. The SIMS detector has its own vacuum chamber, electronic hardware and software, which is operated on the second monitor of the microscope PC. The detector interfaces with the DualBeam in four ways:

1. Information is exchanged between the TOF software and the microscope software via software commands. Examples are the readout of the vacuum level and the start/stop command for the FIB imaging to create a SIMS map.

2. The position of the ion beam for each pixel during a frame collection is coupled via hardware to the SIMS electronics. The SIMS system then follows the FIB scan.

3. For vacuum safety, the system protection is realized by a hardware link. If the chamber vacuum is $> 10^{-4}$ mbar, the TOF valve cannot be opened and voltages to the ion optics extraction system cannot be applied. Similarly, if the microscope chamber is vented, the TOF valve will close and all detector voltages will drop to zero.

4. In operation, the SIMS detector is at a sample distance of 6 mm. It can be moved in and out by software control. The inserted position of the SIMS is used as an interlock for the microscope to prevent simultaneous insertion of the CBS and STEM detector.

In its retracted position the SIMS detector moves 13 mm outward so there are no restrictions for any other DualBeam task.

The detector ion optic extraction system is partially visible on the CCD camera of the microscope, just in front of the final lens of the electron column (Figure 1).

Typical ion currents for SIMS are between 40 and 300 pA. At high ion currents, such as for serial sectioning, it is good practice to retract the SIMS detector to prevent re-deposition of large amounts of material on the ion extraction system.
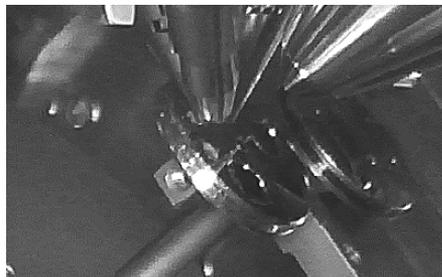

Figure 1. Ion extraction system inserted at 6 mm.

The ion spectrum

Ions will be collected by the extractor of the ion optics of the SIMS detector at around 200 V. One of the characteristics of ion detection is the charge of the ion. The SIMS detector can detect either positive or negative ions. Some ions, such as F and Cl, exist only as negative ions, while others, such as Li, Na and K, exist only as positive ions. Some elements can be detected as either a positive ion or a negative ion. The detection mode for these ions depends mainly on the sample composition. Both detection modes can be used to detect these elements.

It should be noted that the focused ion beam itself is not blanked, and the sample is constantly sputtered. Only the ion beam ejected from the sample surface is pulsed. The timing is fully arranged by the TOF unit, providing a high-voltage pulse to induce an orthogonal movement of the ion group.

At this point, all ions will have the same energy. Due to the different masses, light element such as H will move quickly, and heavy elements such as Au will move slowly. A typical pulse width is 1 us, and a typical detection period is 9 us, adding up to a typical FIB dwell time of 10 us. The cycle is repeated at each dwell time and for each pixel the full TOF spectrum is recorded. A priori knowledge of the sample composition is not needed but is helpful to identify the different mass peaks.

A typical spectrum provides the number of counts per extraction as a function of mass, or more precisely, mass divided by charge. The spectrum cannot be used to derive quantitative information from the sample: peak heights are determined by the amount in the sample but also by the excitation conditions and the matrix effect, i.e. the enhanced or reduced ionization during milling.
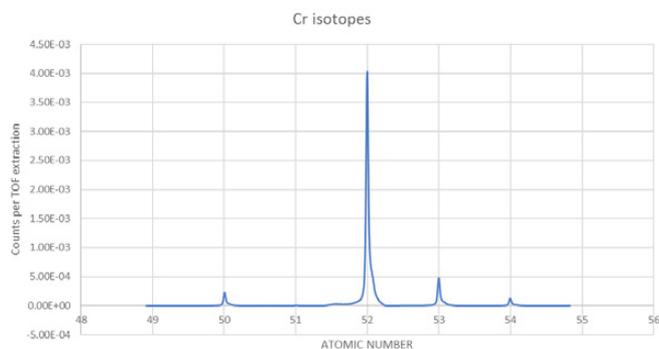

Figure 2. TOF spectrum of Cr foil.

A section of Cr spectrum is shown with the four different isotopes clearly separated (Fig. 2). The most abundant isotope is 52, and in this case, the integrated peak signal is linearly proportional to the actual abundance in the sample. In this way, the isotope ratios can be determined. The result shown compares favorably with results found in literature (Table 1).

Cr Isotope	Abundance Literature	TOF Int Intensity	Abundance from TOF
50	4.35	2.55E-03	4.339
52	83.8	4.93E-02	83.801
53	9.5	5.52E-03	9.393
54	2.37	1.45E+03	2.467

Table 1. For isotopes, this method of calculation is correct because the ionization yield for all Cr isotopes is the same.

Lateral resolution

The lateral resolution of a SIMS signal is largely dependent on the minimum ion beam diameter and the SIMS sensitivity. The BAM L200 sample is used for measuring the resolution. This sample provides a stack of GaAs and AlGaAs layers with known and different widths. It serves as a reference sample, using the aluminum signal at mass 27.
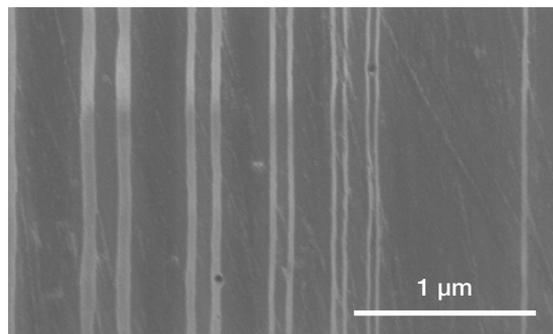

Figure 3. Electron beam image (TLD) of BAM L200. The white line pairs, left to right, refer to P4–P8. The thin line on the right is W8, with a width of 38 nm.

The white lines contain Al, and the dark area is GaAs. The ion beam has been used at 30 kV and 1.1 pA to make an image of the surface (Fig. 4).
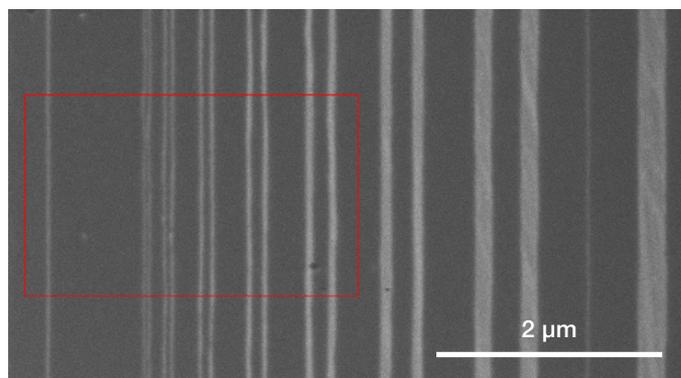

Figure 4. Ion beam image of BAM L200 at 30 kV, 1.1 pA. The area marked in red has been scanned with SIMS to collect the Al signal.

A SIMS map made on this sample has been used to plot the Al signal as a function of the distance on the sample. In this way, it can be seen to what extent the line pairs still are resolved.

From Figure 5, it is concluded that P8 (48.5 nm peak-peak) is well resolved. The lateral resolution is then half the peak-to-peak width, so approximately 25 nm.
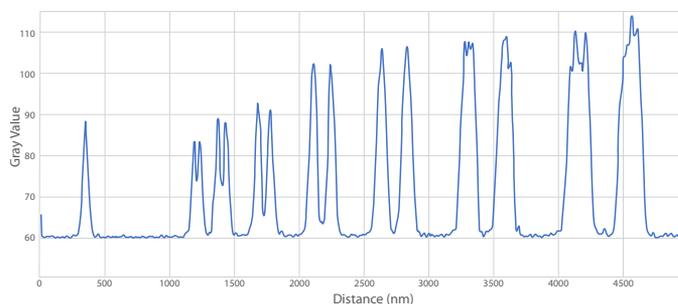

Figure 5. Al TOF signal vertically integrated showing W8 (38 nm) and P8–P2 (left to right) all clearly resolved.

Depth profiling

During the milling process, whenever a new surface is revealed, a depth profile can be made of an elemental distribution in the z-direction of the sample. If we use the same BAM L200 sample, but now with the layers parallel to the ion beam, the different layers will appear when milling deeper in the sample. Depth resolution is strongly driven by the sample ion scattering process (elemental composition of the sample) and by the applied ion energy. In general, it should be taken into account that the milling process induces a forward scattering of the atoms into the material. In a layered structure, therefore, some mixing will occur during the milling process.
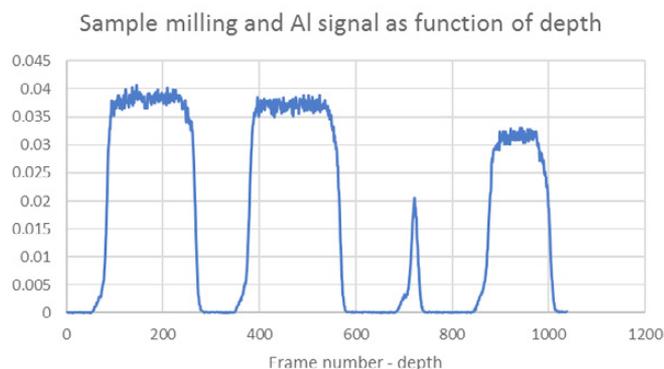

Figure 6. Depth profile milling through layers W3 (left) and W6 (right) of the BAM L200. The small peak refers to layer W5 (19.5 nm width).

Figure 8. Cross-section of a lithium battery cathode.
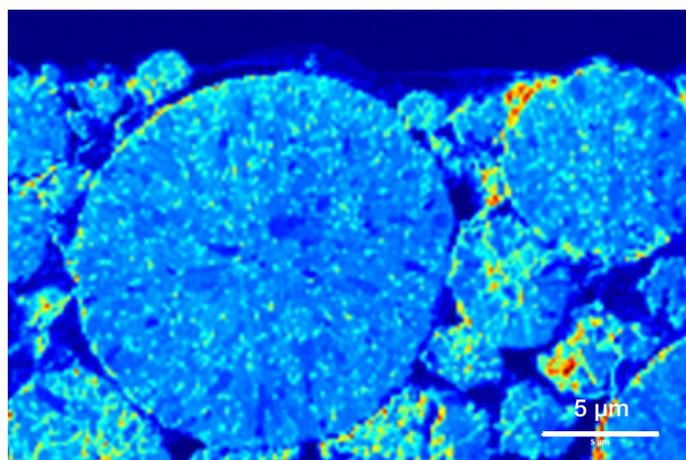
Figure 9. SIMS Map showing the Li distribution over the cross-section.

The TOF software allows users to create data from the spectral set and to obtain a profile in the z-direction of the sample.

The various layers have a very well-defined and sharp transition. It should be noted that W5 is still very visible, while the layer has a thickness of only 19.5 nm. The slope of a peak can be used to derive a depth resolution. To this extent, peak W3 (293 nm) has been magnified (Fig. 7) and used to determine the leading slope 20–80% levels. The distance between these points can be considered the depth resolution, which is 14 nm in this case.

It should be noted that the ion beam energy was set to 5 kV for this measurement, to reduce the forward scattering of substrate atoms.
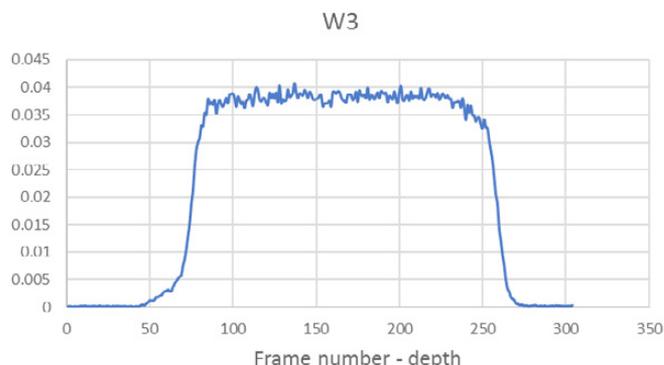

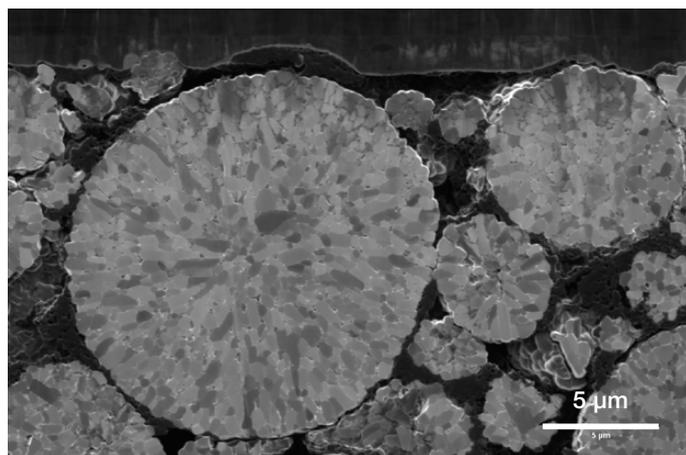Figure 7. Magnification of the first depth profile peak W3 (193 nm).

An application example

One interesting capability of SIMS is the measurement of lithium (Li), an element frequently used in battery research, in a sample. Small particles of Li have been revealed by ion beam cross-section milling, as shown in Figures 8 & 9.

Another example is a Li-based ceramic. This sample requires a serious reduction of charging; if not, the Li signal would drop by two orders of magnitude. The absence of charging is critical for SIMS, as the signal can be reduced to zero.
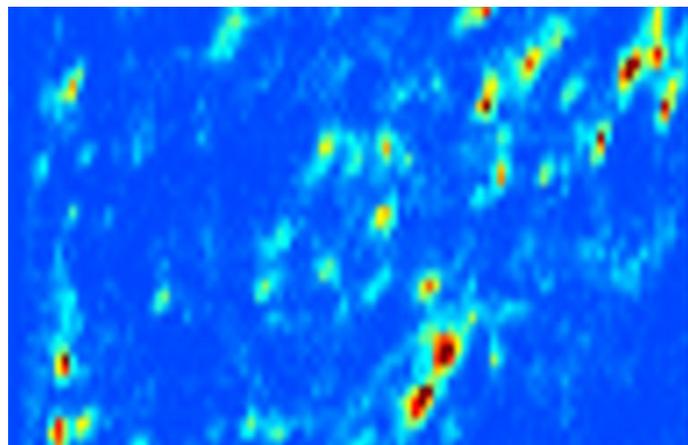

Figure 10. Li map of a ceramic. HFW = 25 um.

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Comparison of EDX and SIMS			
	EDX	SIMS	Remarks
Detectable elements	B and higher	H and higher	New EDX LiK at 52 eV[1]
Signal	Element specific	m/q specific	See notes [2 & 3]
Isotope separation	No	Yes	
Surface technique	No	Yes	EDX penetration depth
Detection limit	0.1%	0.001% (10 ppm)	
Quantitative	Yes, normalized	No, rough estimate	Matrix dependent
Destructive	No	Yes	Even static SIMS
Lateral resolution	200-500 nm typical	50 nm	Depends on kV and Z
Depth resolution	200-500 nm typical	20 nm	Depends on kV and Z
Chemical information	Very limited	Limited	Molecular bonds
Sensitivity to charging	Very low (< 1k V)	Very high (< 10 V)	

Notes:

1. Detection of LiKa with EDX is still very difficult due to the in situ oxidation of Li.
2. SIMS can resolve EDX line overlaps such as: MoL / SKa, BaL / TiKa, WM / SiKa and TiL / NKa.
3. Low-weight molecular fractions (e.g. $(CH_3)+$) can be generated but strongly depend on ion type and sample. Large molecular fractions, such as from biological materials, are not created by Ga or Xe focused ion beams.

Find out more at **thermofisher.com/tof-sims**

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