Multi-Modal Characterization with Secondary Ion Mass Spectrometry on ZEISS ORION NanoFab
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In recent years, ZEISS ORION NanoFab has been recognized for its outstanding capabilities in high-resolution imaging and nanofabrication. Based on the Gas Field Ion Source (GFIS) technology, it is capable of generating both helium and neon ion beams with very small spot sizes and high brightness, enabling high-resolution imaging and fabrication of structures with less than 10 nm feature size. While the secondary electrons released from the specimen provide unique contrast and a very high surface sensitivity, ORION NanoFab’s analytical microscopy capabilities remain limited.

Secondary Ion Mass Spectrometry (SIMS) is a powerful technique for analyzing surfaces due to its high sensitivity, high dynamic range, excellent mass resolution, and ability to differentiate between isotopes. The combination of Helium/Neon microscopy and SIMS offers the prospect of both obtaining SIMS information limited only by the size of the probe-sample interaction and directly correlating SIMS images with high-resolution secondary electron images of the same sample area \textit{in situ}.\[^1\]

**Introduction**

ZEISS ORION NanoFab is a third generation ion beam microscope based on gas field ion source (GFIS) technology that offers a selection of helium, neon, and gallium beams in a single instrument. It is similar to a traditional FIB-SEM (focused ion beam scanning electron microscope) such as instruments from the ZEISS Crossbeam Family [2], but instead of using electrons ORION NanoFab utilizes a high brightness helium or neon beam to characterize or modify a sample [3]. Since helium and neon are relatively light ion species, they can be used to create structures much smaller than other technologies, such as gallium. Examples include plasmonic devices with sub-10 nm gap sizes [4], coaxial optical resonators [5], fabrication of solid-state nano-pores for biomolecule detection [6], or semiconductor applications such as failure and circuit analysis [7].

The helium beam in particular offers several major advantages over conventional scanning electron microscopy: the very small wavelength of the helium ion beam generated from a mono-atomic tip results in an extremely small probe size (<0.5 nm) and high spatial resolution [8]. Secondly, the electrons detected for imaging (secondary electrons) are emitted much closer to the impact point than in an SEM leading to extremely high surface sensitivity with high contrast [9]. And thirdly, insulating samples can be observed directly without the need for conductive coating by using an electron flood gun for charge compensation [10].

![Figure 1](image.png) **Figure 1** Single sheet of graphene supported by gallium nitride (GaN) pillars. Image from M.Latzel, M. Heilmann, G. Sarau, S. H. Christiansen, Max Planck Institute for the Science of Light, Erlangen, Germany.
Figure 1 shows an example of a graphene thin sheet suspended on top of GaN pillars imaged with a 30 kV helium ion beam. The image exhibits abundant surface details, such as holes, ruptures, multilayer folds and ridges, all of which would be very challenging to observe with an SEM.

**Secondary Ion Mass Spectrometry (SIMS)**

SIMS is a very versatile analysis technique that provides a powerful combination of capabilities for molecular detection and trace element determination, imaging and microanalysis, and shallow depth profiling. It is capable of detecting impurity elements at parts per million (ppm) concentrations and even parts per billion (ppb) under favorable conditions. It also offers very high dynamic range and the ability to differentiate between isotopes. In addition, state-of-the-art commercial instruments can achieve high lateral resolutions down to 50 nm.

**Time-of-flight instruments** determine the mass of the secondary ions by measuring their flight time between a given origin and the detector. They offer an unlimited mass range and can achieve very high mass resolution; however, a pulsed primary beam (or pulsed ion extraction) is required, which can limit the sensitivity.

**Quadrupole mass spectrometers** use oscillating electric fields applied to an arrangement of metal rods to filter out secondary ions. The quadrupole is tuned to a specific mass-to-charge ratio and thus only allows a certain ion to reach the detector at any given time. This allows them to analyze a specific ion for an extended period of time, but they have relatively low mass resolution and transmission and cannot detect several secondary ion species in parallel.

**Magnetic sector mass spectrometers** utilize a magnetic field to separate secondary ions by their mass-to-charge ratio according to the Lorentz force law. Most modern instruments of this type combine an electrostatic analyzer with the magnetic filter into a double-focusing magnetic sector instrument, allowing them to focus the ion beams both in direction and velocity. These systems can achieve higher sensitivities than time-of-flight instruments and can operate in continuous mode, however, they have a limited mass range and can only detect a few different ion species at the same time (depending on the design and number of detectors used).

Traditional SIMS instruments are typically equipped with a surface ionization Cs⁺ ion source and a plasma source delivering an O₂⁺ and/or O⁻ primary ion beam, but other ion species such as Ga⁺, Au⁺, and Bi⁺ or even ion clusters like C₆₀⁺ are also used. The choice of primary ion species impacts instrument parameters such as sensitivity, effective yield, and lateral and depth resolution amongst others and must be carefully considered.

In microprobe mode a specimen is sputtered by raster-scanning a finely focused primary ion beam over the analyzed area and mass-filtered secondary ion images are acquired pixel by pixel. SIMS lateral resolution in microprobe mode is limited by [1]:

1. The probe size or brightness of the primary ion beam
2. The physical dimensions of the collision cascade

![Graphical representation of the ion interaction process. The primary ion beam sputters particles from the target material, some of which are positively or negatively ionized. These secondary ions are collected and mass separated to obtain chemical information about the sample.]
3. Efficiency and transmission and detection. If a meaningful secondary ion signal has to be detected from a very small volume and thus from a very small number of sputtered ions, the sensitivity of the instrument must be sufficiently high.

These factors have to be taken into account when designing an instrument that aims to further improve the capabilities of SIMS imaging, especially when trying to achieve the highest lateral resolution possible.

SIMS Applications

Due to the large variation in ionization probabilities among different materials (matrix effect), SIMS is generally considered to be a qualitative technique, although a quantitative analysis is possible with the use of standards. SIMS is commonly used to acquire mass spectra, whereby sputtered ions are detected and the count rate is plotted as a function of mass. Figure 3 shows an example of a mass spectrum acquired from a copper-aluminum alloy in positive mode and atoms that charge positively during ionization are detected ($^{23}$Na$^+$, $^{27}$Al$^+$, $^{39}$K$^+$, $^{40}$Ca$^+$, $^{63}$Cu$^+$).

![Figure 3 SIMS mass spectrum of a CuAl alloy sample showing 23Na, 27Al, 39K, 40Ca, and 63Cu peaks. The data was acquired in positive mode.](image)

Depth profiling is very similar, but in this case the secondary ion signals are plotted as a function of time, which is then converted into a depth by either using known or calculated sputter rates. SIMS depth profiling has been used for more than 30 years by the semiconductor industry, in display technology, optoelectronic and memory applications, and solar cells and energy storage devices.

Imaging SIMS is used for spatially-resolved elemental analysis. In microprobe mode, the primary ion beam is scanned across the specimen pixel by pixel, similar to an SEM, but instead of detecting secondary electrons, a mass spectrum is obtained from each pixel. This information is then used to reconstruct a mass-filtered two-dimensional secondary ion image. A high lateral resolution is desirable, but is typically limited by the effects described previously. Imaging SIMS can also be combined with depth-profiling to generate 3D data sets. A second mode in imaging SIMS is the microscope mode, details of which can be found elsewhere.

2D and 3D elemental imaging by SIMS provides important information about sample composition in many applications. Examples include metallurgy where it is used to determine diffusion, ageing, oxidation, or corrosion mechanisms, geology, oil & gas exploration, or astronomy. In life sciences it is a powerful technique to track certain isotopic markers such as $^{15}$N or $^{13}$C for research in metabolism, pharmacological studies, or nano-toxicology. Imaging SIMS also becomes increasingly popular in areas like solar cell research, energy storage devices, or battery research and development due to its ability to detect even very light elements such as hydrogen or lithium.

SIMS with ZEISS ORION NanoFab

The SIMS detector integrated into ORION NanoFab was designed and manufactured by Advanced Instrumentation for Ion Nano-Analytics (AINA), MRT Department, at the Luxembourg Institute of Science and Technology (LIST) under the supervision of Dr. Tom Wirtz. It is a double-focusing magnetic sector spectrometer attached to the chamber (Figure 4). The magnetic sector type was chosen after a careful consideration of several design criteria: The system is compact and compatible with mounting on ORION NanoFab, the extraction optics are removable, do not degrade the probe size of the ion beam, and do not interfere with standard operation of the instrument (i.e. ion imaging and milling). Furthermore, it allows operation in both negative and positive mode in order to detect both anions such as O$^-$, or Cl$^-$, and cations like Na$^+$, Ti$^+$, B$^+$, etc. The instrument features a very high extraction efficiency and overall transmission, with acquisition times as fast as a few minutes.

Although the instrument is capable of SIMS acquisition with both helium and neon beams, typically neon is chosen due to the much higher sputter yields compared to helium. Furthermore, a study has shown that sputter yields with...
a neon primary ion beam are very comparable to those obtained with oxygen, at least for certain samples such as silicon [1]. Since ORION NanoFab is able to maintain a small probe size (<10 nm) even with relatively high beam currents of up to 10 pA, the acquisition time is very similar to that of traditional SIMS instrument, which typically have to use much lower probe currents to achieve ultimate resolution.

A schematic of ORION NanoFab-SIMS is shown in Figure 5. The extraction optics are mechanically actuated and can be retracted if SIMS operation is not being performed. With the SIMS optics extracted, ORION NanoFab can be used for high-resolution imaging and nanofabrication with almost no loss of performance. The extraction unit was developed by Dowsett et al. [15] and designed to maintain a small probe size while simultaneously optimizing the extraction efficiency and overall transmission (> 40%). Ions are extracted at 240 V, post-accelerated to 3.5 keV and guided into the spectrometer, which contains five ion detectors: one total ion current (TIC) detector and four continuous channel electron multiplier detectors for mass-filtered imaging (one fixed and three moveable). Ions with a mass-to-charge ratio of up to 400 can be detected with a mass resolution M/ΔM of about 400. The detectors can be positioned such that the difference between minimum and maximum observable mass is about 100 amu.

The instrument also allows for the acquisition of SIMS images with very large fields of view of up to 200 µm, which is several times larger than what traditional SIMS system can achieve. The count rate has been measured to be greater than 1000 counts per second per pA of Neon of $^{115}$In$^{+}$ from an indium phosphate (InP) wafer.

As mentioned earlier, the lateral resolution during SIMS imaging mainly depends on the brightness of the primary ion beam and the size of the collision cascade. Compared to other popular ion source technologies, ORION NanoFab’s Gas Field Ion Source (GFIS) is able to produce an ion beam with smallest probe size and highest brightness [1].

### Table 1: Comparison of typical ion sources.

<table>
<thead>
<tr>
<th>Species</th>
<th>Surface ion source</th>
<th>Hyperion plasma source</th>
<th>Liquid metal ion</th>
<th>Gas field ion source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Probe Size</td>
<td>50 nm</td>
<td>50 nm</td>
<td>&lt;10 nm</td>
<td>&lt;2 nm (Ne)</td>
</tr>
<tr>
<td>Brightness</td>
<td>$10^7$ A cm$^{-2}$ sr$^{-1}$</td>
<td>$10^4$ A cm$^{-2}$ sr$^{-1}$</td>
<td>$10^8$ A cm$^{-2}$ sr$^{-1}$</td>
<td>$10^9$ A cm$^{-2}$ sr$^{-1}$</td>
</tr>
</tbody>
</table>

As mentioned earlier, the lateral resolution during SIMS imaging mainly depends on the brightness of the primary ion beam and the size of the collision cascade. Compared to other popular ion source technologies, ORION NanoFab’s Gas Field Ion Source (GFIS) is able to produce an extremely sharp neon ion beam with the smallest probe size of less than 1.9 nm and highest brightness of about $10^9$ A cm$^{-2}$ sr$^{-1}$ (Table 1). Simulations show that the diameter of the collision cascade under 30 keV neon bombardment is about 10 nm, which represents the minimal resolution that can be achieved in SIMS imaging.
Performance

Figure 6 shows a SIMS image of a tungsten carbide sample, which has been cemented into a composite by using cobalt as a binder metal.

![Figure 6](image)

Cemented carbides are very hard and abrasion resistant composites commonly used for machining through other hard materials such as stainless steel, in the mining industry, or for making surgical instruments.

The images were acquired with neon as the primary ion species and the SIMS spectrometer operating in positive mode. The $^{69}$Co map shows cobalt grains with different sizes and very sharp edges, which are useful to determine the lateral resolution of the instrument. In this case the 25-75% edge criterion was used by acquiring a line scan across a sharp edge and plotting the intensity as a function of distance revealing a lateral resolution of about 15 nm. This is three to four times better than what commercial state-of-the-art instruments can achieve. The experiment was repeated with other samples (such as copper grid on aluminum substrate and tin balls on carbon), consistently yielding resolution values between 10 nm and 18 nm.

Another test sample used was a certified reference material, the so-called BAM L200, from the German Institute of Materials Research and Testing (Bundesanstalt für Materialforschung und –prüfung, BAM). The BAM L200 is a nano-scale stripe pattern for testing of lateral resolution and calibration of length scale. It is a GaAs substrate with well-defined layers of InGaAs and AlGaAs.

Figure 7 shows the total ion count signal (a) acquired with a 25 keV neon primary ion beam and a probe current of 9.5 pA with the system operating in positive mode. The contrast between the GaAs substrate and the aluminum lines is very strong and allows for a very accurate characterization of the instrument. Figure 7b is a mass-filtered composite image with the aluminum signal displayed in red and gallium in green. Figure 7c shows a line profile of the corresponding SIMS image, which was acquired by taking a higher magnification scan of the lower part of image 7b. The schematic below the image was taken from the BAM L200 description and aligned to the SIMS signal. The different lines are clearly resolved and the resolution is high enough to even show the layers with a pitch of only 17.5 nm as separate structures.
This experiment again confirms a lateral resolution of less than 20 nm.

The experiments confirm that ORION NanoFab SIMS currently has the highest lateral resolution during SIMS imaging. Other commercially available instruments can achieve about 100 nm and even down to 50 nm by using specific primary ion species and under favorable conditions. In contrast, ORION NanoFab routinely obtains SIMS images with better than 20 nm resolution, large fields of view, high sensitivity, and unprecedented ease-of-use. In addition, the SIMS detector can be retracted and thus does not interfere with ORION NanoFab’s high resolution imaging and precise sub-10 nm nanofabrication capabilities.

Application Examples

Perovskite Solar Cells

Solar cells made out of a perovskite structured compounds are being actively researched as they can achieve very high efficiencies with very low production costs. However, the perovskite self-organization upon crystallization and the final elemental distribution, which are paramount for device optimization, are still not well understood [17].

In a recent publication, Gratia et al. studied the iodine (\(^{127}\)I) and bromine (\(^{79}\)Br) distribution in a perovskite compound deposited on a mesoporous TiO\(_2\) scaffold by using ORION NanoFab SIMS with a neon primary beam energy of 25 keV and a probe current of 2.2 pA [17]. The perovskite crystal grains are typically 100-500 nm in size. It was observed that the \(^{79}\)Br content varies from null/very low to high intensity, indicating compositional non-homogeneity at the nanometer scale with several local minima extending to regions of up to 300 nm.

Furthermore, combining both \(^{79}\)Br and \(^{127}\)I signals into one image reveals a clear correlation between bromine and iodine intensity: regions with low \(^{79}\)Br content correspond to areas with high \(^{127}\)I intensity and vice versa. Systematic bromine absences extending up to 50-200 nm are clearly visible, showing that part of the mixed perovskite film intrinsically segregates into iodine-rich perovskite nanodomains on a length scale of up to a few hundred nanometers.

Although the authors caution that SIMS is not a quantitative technique per se, they do point out that this is a critical result as this chemical variation has a great impact on the optoelectronic properties of perovskite solar cells [17].

Photocatalytic Multilayer Structure

A TiO\(_2\)/Au/TiO\(_2\) photocatalytic multilayer structure produced by plasma-enhanced chemical vapor deposition was studied with HIM-SIMS and a series of SE and SIMS images were taken [11].

**Figure 8** SE image of the surface of a TiO\(_2\)/Au/TiO\(_2\) photocatalytic multilayer structure. (b) \(^{39}\)K SIMS map. (c) \(^{40}\)Ti SIMS map. (d) Overlay of \(^{39}\)K (green) and \(^{40}\)Ti (blue). Images were acquired with a neon primary ion beam energy of 27 keV and a probe current of 5 pA.

Photocatalysis is the process of accelerating a chemical reaction induced by the absorption of photons in the presence of a catalyst and is used in many different applications, e.g. conversion of water to hydrogen gas, disinfection of water, conversion of carbon dioxide into gaseous hydrocarbons, or decomposition of crude oil. In this example, the multilayers are designed to shift the absorbed UV light to lower (visible) wavelengths, which increases the performance of the device.
High purity films are required in order to achieve a high efficiency, and SIMS can be used to detect and track impurities.

Figures 8b and c show the $^{39}$K and $^{40}$Ti elemental maps respectively, obtained by using a primary neon ion energy of 27 keV and a probe current of 5 pA. The $^{39}$K signal shows trace levels of contamination, whereas the $^{40}$Ti signal gives an overview of the microstructure of the surface. Both signals can be combined into a single image (Figure 8d, $^{40}$Ti in green, $^{39}$K in blue). SIMS imaging gives valuable additional information compared to the SE image in figure 8a, which shows great contrast and surface topography, but cannot distinguish between elements.

**Multi-Modal Imaging**

One of the unique advantages of ORION NanoFab SIMS is its ability to acquire both extremely high-resolution secondary electron (SE) and SIMS images in one instrument. Using the helium beam, a SE image of the specimen with resolution of less than 0.5 nm is obtained, followed by a SIMS analysis of the same region. Both data sets are then overlaid, resulting in an image with high-resolution, high-contrast surface information and a SIMS elemental map. Typically, the SIMS extraction unit is retracted, the image acquired with the helium beam, and the system switched to neon for a subsequent SIMS analysis. This approach guarantees ultimate performance; however, retracting and inserting the extraction unit takes under a minute. Changing the source gas, i.e. from helium to neon or vice versa, is accomplished by simply changing the gas supply and is completely software-controlled. The process takes about only a few minutes.

The SE image can also be acquired with the SIMS extraction system inserted and is thus faster, although this leads to a slightly lower SE signal since the ET (Everhart-Thornley) detector is partially blocked by the extraction optics. In either case, elemental/chemical information with high surface sensitivity is obtained with SIMS, while excellent spatial resolution is provided by overlaying the SIMS imaging with very high-resolution secondary electron images.

Figure 9 shows images acquired from a lithium titanate boron nitride nanoparticle mixture on a silicon substrate. This material was chosen as a test sample to determine the performance of the instrument and to develop the correlative SE-SIMS workflow. The secondary electron image in Figure 9a was acquired with a 25 keV helium beam using a 0.4 pA probe current and clearly shows the structure of individual nanoparticles. The SIMS unit was then switched on and an elemental map was obtained by increasing the helium beam current to 9 pA. A $^{28}$Si (green) and $^7$Li (red) composite image is shown in Figure 9b. Finally, the SE and SIMS images where overlaid and displayed in one single image (Figure 9c). $^{28}$Si is shown in green, $^7$Li in magenta. It is worth noting that this experiment was carried out with helium only, proving that helium ions can be used to acquire SIMS data sets with ORION NanoFab. However, neon ions provide higher sputter yields with almost the same lateral resolution and are thus the preferred ion species.

Another nanoparticle sample containing Ti, In, and Na is shown in Figure 10. The secondary electron image was acquired with the helium beam (a), whereas neon was used for the SIMS analysis. Figure 10b displays a combined $^{40}$Ti (green) and $^{113}$In (red) SIMS map. The $^{23}$Na elemental distribution was also added (10c, blue) and this combined SIMS map was then overlaid onto the SE image (Figure 10d) using an image fusion algorithm developed by LIST.
The workflow is as follows: After helium imaging the system is switched to neon source gas operation. The total ion count (TIC) detector is then used to acquire a secondary ion image of the specimen. A mass spectrum can be recorded by turning on the mass filter, followed by tuning the magnetic field so that the heaviest ion to be detected hits the 4th detector, which is fixed. The other three detectors are then moved mechanically for the other three selected ions. After that, mass-filtered SIMS images are collected.

A screenshot of the SIMS software is shown in Figure 11. The graphical user interface is user-friendly and displays important information such as a schematic overview of the spectrometer with the current beam path, the position of the four detectors including controls to move them, and the output of the four channels.

Summary

ORION NanoFab can be equipped with an optional high-performance secondary ion mass spectrometer (SIMS) developed by the Luxembourg Institute of Science and Technology (LIST) and manufactured exclusively for ZEISS by Luxembourg Ion Optical Nano-Systems [20]. It is a double-focusing magnetic sector with high transmission, isotopic mass resolution, and ultimate spatial resolution. Combined with ORION NanoFab’s high brightness neon ion beam the lateral resolution approaches physical limits and is in practice only limited by the size of the collision cascade. SIMS maps with resolutions of less than 20 nm can routinely be achieved. The compact design of the spectrometer does not affect ORION NanoFab’s standard operation performance: simply retracting the SIMS extraction unit allows acquisition of very high resolution images with excellent surface sensitivity and high contrast, and extremely precise sub-10 nm nanofabrication. A unique and powerful feature of the instrument is its ability to obtain multi-modal, correlative SE-SIMS data sets: A high resolution SE image is acquired by using the helium beam followed by collecting SIMS elemental maps with high sensitivity from exactly the same region.
References:

[12] Luxembourg Institute of Science and Technology: https://www.list.lu/en/research/mrt/advanced-instrumentation-for-ion-nano-analytics/