

## SIMS Imaging Performed on Focused Ion Beam - based Platforms

Jean-Nicolas Audinot<sup>1\*</sup>, Alexander D. Ost<sup>1,2</sup>, Charlotte Stoffels<sup>1,2</sup>, Patrick Philipp<sup>1</sup>, Olivier De Castro<sup>1</sup>, Antje Biesemeier<sup>1</sup>, Quang Hung Hoang<sup>1</sup> and Tom Wirtz<sup>1</sup>

<sup>1</sup> Advanced Instrumentation for Nano-Analytics (AINA), MRT Department, Luxembourg Institute of Science and Technology (LIST), Belvaux, Luxembourg

<sup>2</sup> University of Luxembourg, Esch-sur-Alzette, Luxembourg.

\*Corresponding author : jean-nicolas.audinot@list.lu

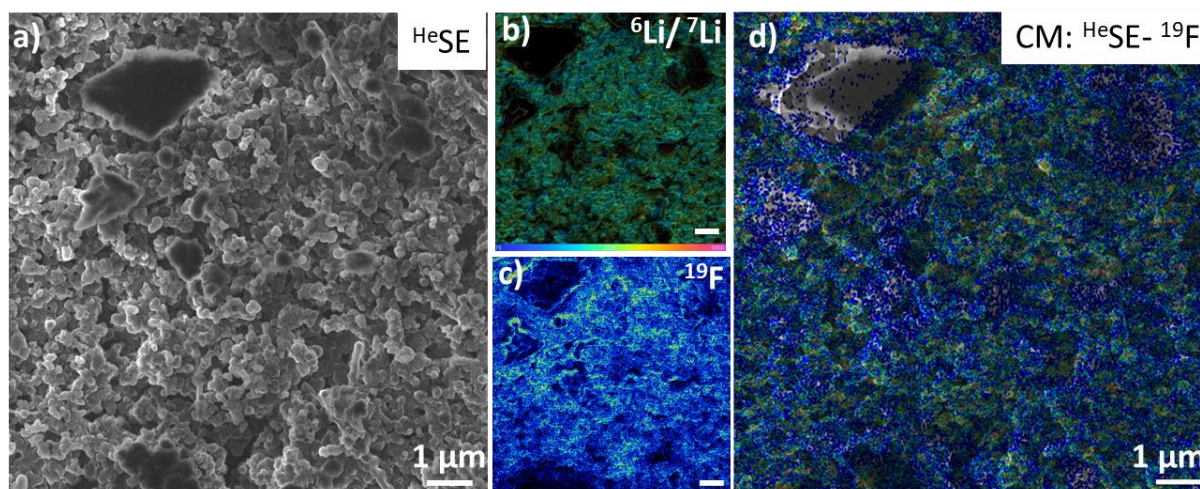
Secondary Ion Mass Spectrometry (SIMS) is a surface analysis technique based on the identification of characteristic secondary ions generated by exposing the sample to a primary ion beam. It is an extremely powerful technique allowing in particular the detection of all the elements of the periodic table and their isotopes, including H and Li, with excellent sensitivity (detection limits down to the ppb) and high dynamic range (a same signal can be followed over several orders of magnitude)[1]. In the 1980s, SIMS has experienced important developments thanks to a strong push of the microelectronics sector [1]. In fact, the technique was, and still is, heavily involved in the semiconductor research and production process as it has unique capabilities in terms of characterization of dopants in wafers used in microchips technology. In parallel, geologists started to recognize this technique as a powerful tool for measuring isotopic variations with extreme precision, in order to reconstruct the chronology of rock mineral and fluids (e.g. magma), to study deep earth chemical cycling (water evaporation) and petrology (carbon degradation). More recently, in cosmochemistry the H isotopic composition of water in both, lunar rocks and soils, was measured with SIMS [1]. Numerous applications in materials science, such as the analysis of thin films (e.g. coatings, car windshields), metallurgy (e.g. nuclear reactors), energy production (e.g. photovoltaic devices), have contributed to the dissemination of this technique to a larger community. From the 2000s onwards, thanks to new instrument developments, essentially based on the possibility of focusing the primary beam very finely, e.g. 50 nm with a caesium surface ionisation source having a brightness of  $10^2 \text{ A cm}^{-2} \text{ sr}^{-1}$ , biology has seen this technique as a tool that allows to trace elements and isotopes at a sub-cellular level [2].

Traditionally, Focused Ion Beam (FIB) Platforms are equipped with an electron beam column (FIB-SEM) to allow in-situ sample preparation (FIB milling), imaging in different electron microscopy (EM) modes (SE, BSE, EBSD, STEM) and chemical analysis (WDS/EDX) [3,4]. However, the electron beam probes for EDX analyses present very large interaction volumes within the sample (several  $\mu\text{m}$ ) and EDX does not allow the detection of light elements (H, Li, ..) and trace elements (<1% in at.). Thus, this technique is not suitable for analyses where both high lateral resolution and high sensitivity surface information is needed. In the recent years, the ion sources integrated in FIB platforms have considerably improved in terms of source brightness, leading to better spatial resolution and current density. For example, the Gas Field Ion Source (GFIS), which emits  $\text{He}^+$  or  $\text{Ne}^+$  ions, has a brightness of  $10^9 \text{ A cm}^{-2} \text{ sr}^{-1}$  and thereby enables a spatial resolution of 0.3 and 2 nm (in SE mode), respectively [5]. Similarly, the Low-Temperature Ion Source (LoTIS) operating with Cs ions and providing a brightness of  $10^7 \text{ A cm}^{-2} \text{ sr}^{-1}$  enables very small probe sizes while keeping high ion currents, which is of high interest for imaging and patterning applications [5,6].

Hence, the prospect to associate a SIMS spectrometer with a FIB platform has emerged in order to combine high spatial resolution imaging with highly sensitive analytical data. To maximize the extraction and detection of the secondary ions emitted from the sample, a compact SIMS system based on a magnetic sector and optimized for state-of-the-art FIB platforms was developed at LIST [5-7]. The SIMS system was designed to optimize first the collection of secondary ions, by positioning an insertable extraction box as close as possible to the analysed sample surface, second the transmission by using a post-acceleration stage coupled to dedicated ion optical systems. Finally, the secondary ions are detected with either a multi-collector system allowing to count simultaneously several isotopes or a continuous focal plane detector allowing the detection of the full mass spectrum for each sputtered voxel. The parallel detection capability is key for fast analysis times (acquisition times as low as 1 s to obtain a full mass spectrum or 2 min to obtain a 512 x 512 pixel SIMS image with highest count rate and excellent dynamic range) and for collecting the full data set during the sputtering of the area of interest.

These FIB-(SEM)-SIMS instruments (named FIB-SIMS) are capable of producing (i) a full mass spectrum with mass resolution  $M/\Delta M = 400-500$  for each single pixel, (ii) very local depth profiles making it possible to follow the chemical composition in real time during nano-patterning in FIB for applications such as end-pointing and (iii) elemental SIMS maps with a lateral resolution down to 12 nm. Furthermore, they open the way for in-situ correlative imaging combining high resolution SE images, EDX data, etc. with elemental and isotopic ratio maps from SIMS. To this end, complete acquisition workflows and multimodal image processing approaches were developed to facilitate the data interpretation [8-10]. With these performances FIB-SIMS microscopes open up new perspectives to meet current and future analytical challenges.

Here we will review the performance of the FIB-SIMS platforms developed at LIST with a focus on new developments, methodologies, correlative microscopy, and high-resolution 3D chemical imaging by presenting applications chosen from various domains. For materials science, we will show the characterization of FinFet devices [5-6], photovoltaic devices (lead halide perovskite [11,12]) and batteries [5-6] (Figure 1). In geology, preliminary work was carried out on chalks, meteorites, soil particles and natural zircon grains [6]. Finally, the investigation of metal nanoparticles and chemical pollutants in life science, e.g. for toxicology studies, will be presented [6-13] [14].



**Figure 1.** FIB-SIMS analysis of an electrode surface isotopically labelled with  $^6\text{Li}$ ; a) SE image obtained with a 25 keV  $\text{He}^+$  beam showing the structure and morphology of the electrode. SIMS images obtained with a 25 keV  $\text{Ne}^+$  beam of b) the  $^6\text{Li} / ^7\text{Li}$  isotopic ratio (color gradient from natural abundance to 100X of the natural abundance) and c) fluorine (coming from the electrolyte). d) SIMS fluorine distribution overlaid with co-registered SE image [10].

#### References :

- [1] L. Sangely et al. in “Sector Field Mass Spectrometry for Elemental and Isotopic Analysis “. Ed. T. Prohaska, J. Irrgeher, A. Zitek, N. Jakubowski (Royal Society of Chemistry, Cambridge) p. 439.
- [2] J. Nuñez et al., *Biointerphases* **13**, (2018) p. 03B301. doi: 10.1116/1.4993628
- [3] M. Sezen in “Modern Electron Microscopy in Physical and Life Sciences”, Ed. Milos Janecek and Robert Kral (IntechOpen Book Series) p. 121.
- [4] Introduction to Focus. Ion Beams Instrumentation. Ed. L. F. Giannuzzi, F. A. Stevie, (Springer, Boston, MA) p 1. doi: 10.1007/B101190.
- [5] T. Wirtz, O. De Castro, J. N. Audinot, and P. Philipp, *Annu. Rev. Anal. Chem.* **12** (2019), p. 523. doi:10.1146/annurev-anchem-061318-115457.
- [6] B. Knuffman, A. V. Steele, and J. J. McClelland, *J. Appl. Phys.* **114**, (2013), p. 044303. doi: 10.1063/1.4816248.
- [7] D. Dowsett and T. Wirtz, *Anal. Chem.* **89** (17), (2017), p. 8957, doi: 10.1021/acs.analchem.7b01481.
- [8] A. D. Ost et al., *Environ. Sci. Technol.* **55**, (2021), p. 9384. doi: 10.1021/acs.est.1c02971.
- [9] F. Vollnhals and T Wirtz, *Anal. Chem.* 2018, **90**, (20), p. 11989. doi: 10.1021/acs.analchem.8b02530.
- [10] F. Vollnhals et al., *Anal. Chem.* **89**, (2017), p. 10702. doi: 10.1021/acs.analchem.8b02530.
- [11] J. Usiobo et al. *J. Phys. Chem. C*, **124**, (42) (2020), p. 23230. doi : 10.1021/acs.jpcc.0c07464.
- [12] Y. Liu et al. *Nat. Mater.* **17** (11), (2018), p. 1013. doi: 10.1038/s41563-018-0152-z.
- [13] Gillois et al. *Sci. Total Environ.* 2020, 754, 142324. doi: 10.1016/j.scitotenv.2020.142324.
- [14] The authors gratefully acknowledge support by the Luxembourg National Research Fund (FNR) under grant no. INTER/DFG/17/11779689, and grant no. INTER/ANR/18/12545362.