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FIB-ToF-SIMS - RECENT ADVANCES IN SECONDARY ION MASS SPECTROMETRY FOR ANALYTICAL DUAL BEAM FOCUSSED ION BEAM INSTRUMENTS

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1. ABSTRACT

The global trend in miniaturisation, a search for environmentally friendly energy solutions as well as thin film coatings for industrial and biomedical applications implies a strong need for reliable analytical techniques. The chemical characterisation is of particular interest as mechanical, electrical, thermal and optical properties are determined by material's structure. The state-of-the art time-of-flight secondary ion mass spectrometry (ToF-SIMS) is one of very few methods, which provide insights into material's chemical structure in 3D with nanoscale resolution. Furthermore, compact high-vacuum compatible TOF detectors can be integrated within focussed ion beam scanning electron microscope (FIB-SIMS) instruments, upgrading them into precise and efficient chemical analysis stations.

In this short review, we present recent developments in FIB-ToF-SIMS, which allowed chemical image quality and reliability to be significantly improved. This was achieved by instrumental improvements as well as a novel approach of combining in situ ToF-SIMS with gas injection systems (GIS). The presence of supplementary gases (water vapour or XeF_2) significantly enhanced generation of positive secondary ions, improving spatial resolution. Furthermore, the presence of fluorine showed potential for overcoming the main drawbacks of the ToF-SIMS technique, such as mass interference. The presented method is expected to play an important role in the development of future batteries, micro-devices and systems based on thin films.

2. INTRODUCTION

Dual beam systems combining focussed ion beam (FIB) with scanning electron microscope (SEM) are the most common analytical instruments used in nanotechnology and material science as they enable multilevel and complementary material characterisation as well as complex sample preparation. SEM imaging provides information on a sample surface topography with resolution as high as 0.4 nm [1]. FIB milling is broadly applied for preparation of transmission electron microscopy (TEM) lamellas and tips for atom probe tomography (APT) and X-ray computed nano-tomography (CNT) [2-4]. Furthermore, FIB-SEM instruments equipped with additional detectors can provide information on sample's chemical structure (energy-dispersive X-ray spectrometry (EDS), and wavelength-dispersive X-ray spectrometry (WDS), crystallographic structure by electron backscatter diffraction (EBSD), topography and mechanical properties by atomic force microscopy (AFM), optical information by cathodoluminescence (CL), and vibration modes (Raman spectroscopy).

The development of high vacuum (HV) compatible time-of-flight secondary ion mass spectrometry (ToF-SIMS) detectors [5, 6] opened new possibilities of upgrading FIB-SEM instruments into precise and fast chemical analysis stations at relatively low cost (compared to the dedicated standalone detectors working under ultrahigh vacuum, UHV). In the case of FIB-ToF-SIMS, a continuous (i.e., not pulsed) primary ion beam is used for sputtering and

analysis. During a measurement, a sample surface is bombarded with primary ions, which results in an ejection of secondary species, i.e., atoms, molecules and ions. However, only these species, which carry electric charge can be directed towards a detector, and therefore be detected. A primary ion beam scans a pre-defined area pixel-by-pixel, line-by-line and for each data point, a corresponding mass spectrum is acquired. This means a parallel detections of all ions (assuming sufficiently high ionisation efficiency) within a specified mass range, which is a great advantage over mass quadrupoles (MQ) [7]. Furthermore, since all (light and heavy) generated ions can be detected, ToF-SIMS overcomes limitations of commonly used STEM-EDS, which cannot measure light elements, such as Li, unless electron energy-loss spectroscopy (EELS) is used. The comparison of ToF-SIMS and STEM-EDS techniques is provided in Ref. [8]. The HV-compatible TOF detectors have lateral resolution < 50 nm and depth resolution < 10 nm. The mass resolving power of the most widely used ToF-MS detectors, fibTOF, compact TOF (CTOF) and high resolution TOF (HTOF) (from TOFWERK AG, Switzerland) is 700 - 1,100 Th/Th and 3,000 - 7,000 Th/Th, respectively. The detector sensitivity is in the order of ppm. It is worth mentioning that the operation of HV-compatible ToF add-ons, such as HTOF and CTO,F which are discussed in this review, is quite different from the operation of dedicated stand-alone detectors, such as TOF.SIMS5 from IONTOF. The comparison of the two techniques is discussed in Ref. [9].

ToF-SIMS is a powerful chemical analysis technique with many advantages such as afore-mentioned parallel detection of all ionised species (both, ionised atoms and molecules), recognition of isotopes, and capability of representing a sample's 3D chemical structure with nanoscale resolution. Furthermore, in contrast to STEM-EDS or APT, which required time-consuming and challenging milling of lamellae and tips (and consequently, additional instrumentation), no specific sample preparation is needed prior to a TOF-SIMS experiment. The only requirement is that a sample surface is conductive and flat [10]. The size of a scan area can be adjusted over several orders of magnitude (usually between several micrometres and hundreds of micrometres) providing insight into local and global sample composition. However, ToF-SIMS have also several drawbacks. The most important issue is quantification, which in general, is not possible unless dedicated standards are provided (this is not a case for materials with unknown composition). The problem with quantifying ToF-SIMS data results from a strong dependency of ionisation efficiency on the sample's chemical state (so-called matrix effect) [11-14], which can cause signal variations by several orders of magnitude [15]. Furthermore, the ToF-SIMS principle is based on measuring time-of-flight of generated ions, which is determined by its mass-to-charge ratio (m/q). This implies that different ions (for example different element isotopes or complex ionised molecules) can arrive to a detector at the same time. Such mass interference can lead to data misinterpretation, if detector's mass resolution is not sufficiently high. Although there are various methods of recognising mass interference (such as comparison of the measured isotope abundance to the natural element's isotope abundance), it is still problematic in the case of mono-isotopic elements, such as Be, Na, F, Al, P etc. Furthermore, ionisation efficiency of some elements under certain chemical conditions are insufficient to represent their distribution in 3D (despite the detection in a mass spectrum).

Finally, ToF-SIMS is a destructive method. In conjunction with the fact, that during a single measurement, only either positive or negative ions can be detected, this means that a complete information on a sample structure might not be directly accessible from the same volume (as some elements ionise preferentially with a positive charge and the others dominantly generate negative ions). Although to overcome this issue, complex ions (such as metal oxide ions) are usually used to represent element's distribution in a sample, this approach not always is completely representative [16].

Some of the described limitations of the TOF-SIMS technique are even more decisive in the case of the TOF add-ons to FIB-SEM instruments as 1) they usually operate under HV (in contrast to the dedicated instruments operating under UHV),and 2) the ion optics is adjusted to fit to an existing FIB/SEM instrument, usually equipped with other detectors, and therefore, is not optimal (whilst dedicated instruments have ion optics designed to maximise the collection of generated ions). Therefore, various technological solutions have been recently developed to improve the performance of FIB-ToF-SIMS. This includes both, instrumentation upgrades as well as using additional homemade and commercial equipment (Fig. 1).

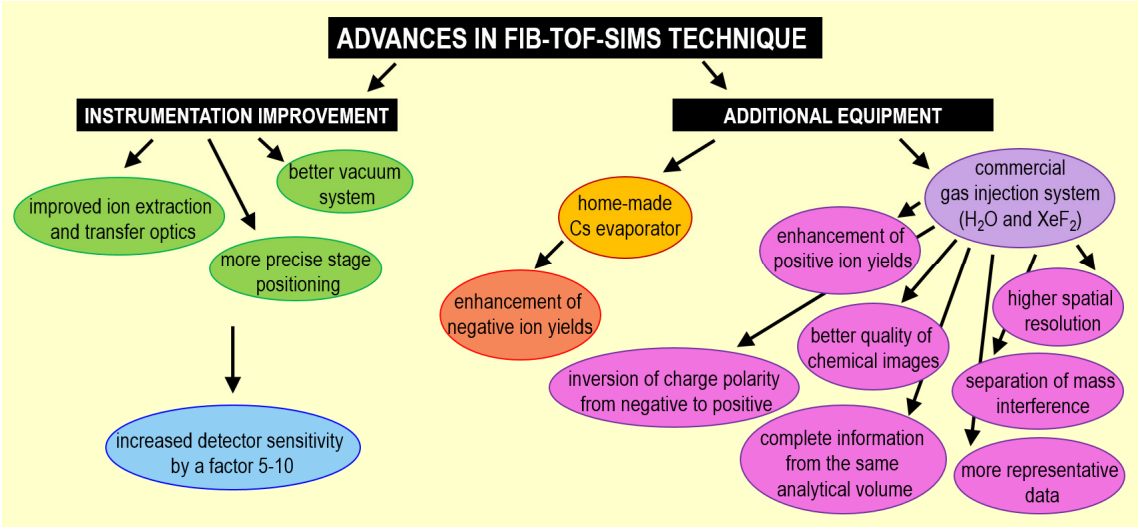

Figure 1. Diagram of the recent advances in FIB-TOF-SIMS technique.

3. *INSTRUMENTATION IMPROVEMENTS*

One of the major advances in HV-compatible TOF detector technology were improvements of the ion extraction and transfer optics, more precise sample stage positioning and better vacuum system, which resulted in an increase of detector's sensitivity by a factor of 5 - 10.

To the best of our knowledge only two experiments were conducted on the same samples using a dedicated UHV TOF.SIMS5 instrument, a HV-compatible CTOF detector and STEM-EDS. Although these studies were dedicated to demonstrating the potential of the ToF-SIMS technique to chemically image the 3D distribution of Al nanoparticles in an inorganic matrix, they also show directly the effect of instrumentation upgrades onto the quality of chemical images obtained with CTOF. In the case of the previous generation of CTOF detectors, Al signal distribution, associated to the Al nano-particles immersed in ZrCuAg bulk metallic glass (BMG) matrix, was observed but was not as distinct as in the case of measurements conducted with TOF.SIMS5 (Fig. 2) [17]. However, during the next stage of the studies conducted under optimised dedicated experimental parameters and using the newest CTOF prototype, Al nano-particles buried under 50 nm thick Cu thin film were well-assessed (Fig. 3) [8]. Furthermore, the use of Ga^+ primary ion beam at very low current of 4 pA allowed significantly reducing the beam spot size, and therefore most likely obtaining more accurate nano-particle size and shape compared to the results obtained with the Bi-cluster beam. Remarkably, before the afore-mentioned CTOF advances, the use of such low currents was not practical due to too low count rates. In conjunction with the lowest reported Ga^+-beam spot size of 2.5 nm at 1 pA [18], this can potentially further lead the higher lateral resolution of ToF-SIMS add-ons.

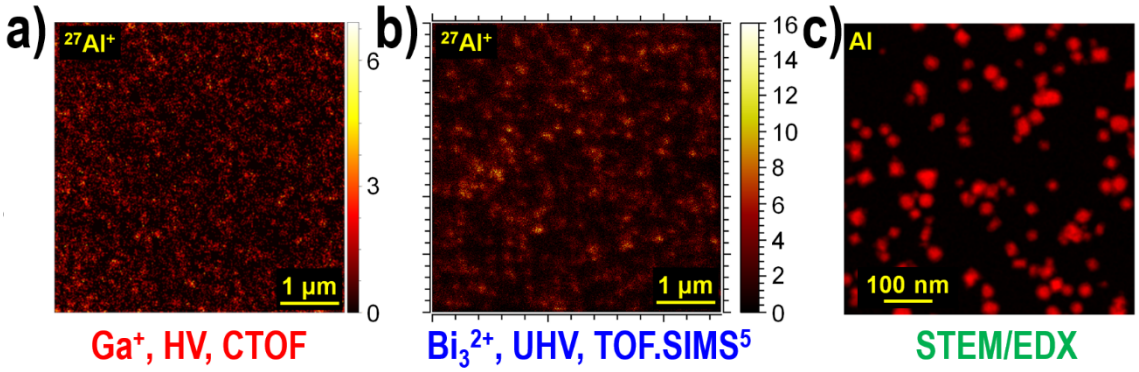

Figure 2. Chemical imaging of Al nano-particles immersed in ZrCuAg BMG. A) The $^{27}Al^+$ secondary ion signal distribution obtained with CTOF under HV and using Ga^+ primary ion beam, and b) obtained with TOF.SIMS5 under UHV and using Bi_3^{2+} analysis beam. c) Data obtained with STEM-EDS. Note different scales. (Adapted with permission from [17]. Copyright © 2019 American Chemical Society).

4. *UPGRADING HV-COMPATIBLE TOF DETECTORS WITH ADDITIONAL EQUIPMENT*

As mentioned, ToF-SIMS sensitivity is very high (in the order of ppm - ppb, depending on a detector), allowing trace elements to be detected in a specimen (i.e., to observe a corresponding peak in a mass spectrum). However, in some cases, low ionisation efficiency of elements or their low ionisation efficiency under specific conditions (such as an unfavourable matrix) prevents assessing their distribution in 3D. Therefore, supplementary methods have to be

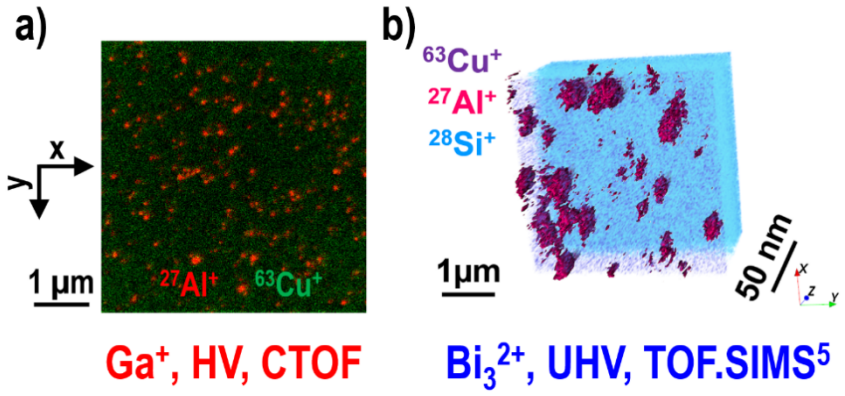

Figure 3. Chemical images of Al nanoparticles buried under a 50 nm thick Cu thin film. a) The data obtained with HV CTOF and using Ga^+ primary ion beam, and b) with UHV TOF.SIMS5 and using Bi_3^{2+} analysis beam. (Adapted with permission from [8]. Copyright © 2020 American Chemical Society).

provided to increase secondary ion yields. In the case of dedicated dual-beam instruments, which use one beam for sputtering and the other for analysis, this is usually performed by using oxygen or caesium primary beams for sputtering to enhance generation of positive or negative ions, respectively. This solution cannot be employed in the case of FIB-ToF-SIMS as only a single beam (usually Ga) is used for both, sputtering and analysis. Therefore, another approaches, based on delivering supplementary gases to a sample surface, have been recently developed (Fig 4). A lab prototype of Cs-evaporator, using commercial alkali metal dispensers containing a stable Cs-salt, enabled enhancement of negative secondary ion signals by a factor of 260 in the case of Au. Furthermore, a stable Cs^+ signal flux was obtained for approximately 1.5 h, which is longer than a typical duration of a ToF-SIMS depth profiling measurement [19]. This proved the applicability of the designed prototype for real chemical analysis. The significant positive ion enhancement was achieved by combining FIB-ToF-SIMS with a commercial in situ gas injection system (GIS), delivering H_2O and XeF_2 [20].

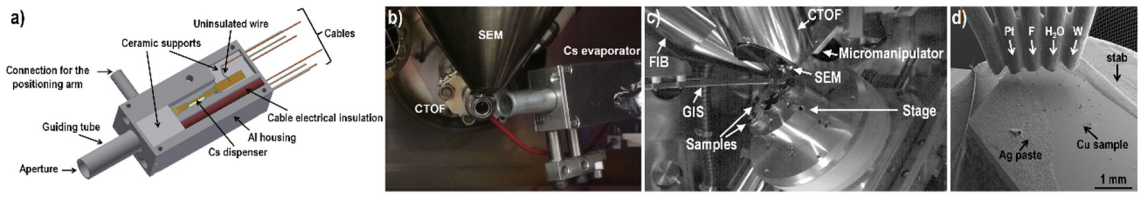

Figure 4. Systems delivering supplementary gases to a sample surface during FIB-ToF-SIMS measurements: a) a diagram of a homemade Cs evaporator, and b) its location in a FIB-SEM instrument; c) an optical image of FIB-SEM chamber equipped with a CTOF detector and a commercial gas injection system, GIS, and d) an SEM image of 5-line GIS nozzle. Reprinted from [3]. (Copyright © 2019, with permission from Elsevier). Adapted with permission from [19]. (Copyright © 2019, American Chemical Society).

5. *ADVANTAGES OF GAS-ASSISTED FIB-TOF-SIMS*

The systematic studies conducted on pure metals [20], two-element alloys [12, 14], multilayer systems [13, 21], Li solid-state batteries [22], and commercial alloys [23], demonstrated impressive potential of fluorine gas-assistance for enhancing the generation of positive secondary ions by up to 2 - 3 orders of magnitude. This allowed the quality of the measured depth profiles as well as chemical images to be significantly improved (Fig. 5). Remarkably, the higher lateral resolution and depth resolution were achieved during single FIB-ToF-SIMS measurements. This is a great progress when compared with measurements conducted under standard vacuum conditions (i.e., without any supplementary gases), during which the highest lateral resolution is obtained at the highest primary ion beam energy (usually 30 keV) and the highest depth resolution requires using low primary ion beam energies (usually ≤ 5 keV).

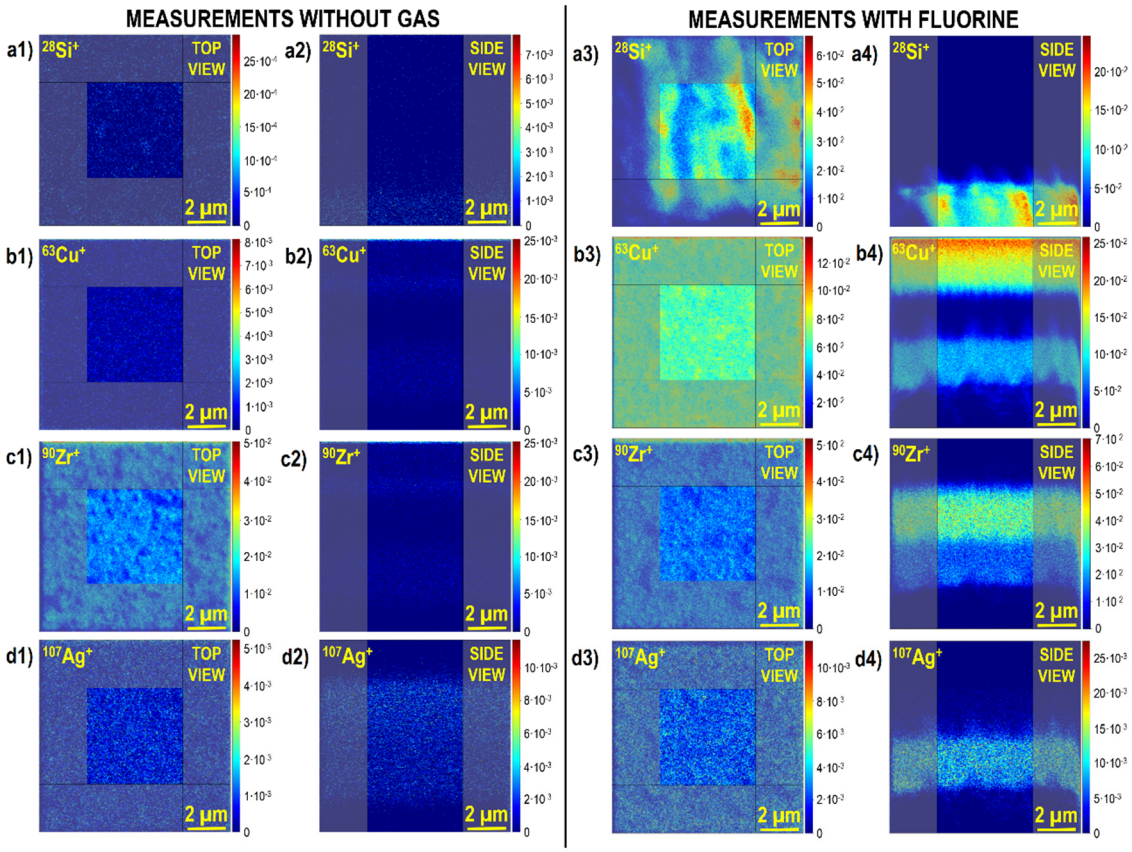

Figure 5 Chemical images of Cu/Zr/ZrCuAg@Si multilayer obtained a1 to d1 & a2 to d2) without, and a3 to d3 & a4 to d4) with fluorine gas. a1 to d1 & a3 to d3) Signal distribution in the lateral plane (i.e., x-y), and a2 to d2 & a4 to d4) signal distribution in the depth plane (x-z). The co-injection of XeF_2 during FIB-ToF-SIMS measurements significantly improves the generation of positive secondary ions, resulting in higher lateral resolution and depth resolution as well as better quality of chemical images. Reprinted with permission from [20]. (Copyright © 2019 American Chemical Society).

Furthermore, it was observed that the simultaneous delivery of fluorine to a sample surface during Ga^+ primary ion beam bombardment has potential for separating mass interference [21], which is one of the main drawbacks of the ToF-SIMS technique making the correct data interpretation difficult or even impossible. Figure 6 shows depth profiles measured for a Cu/Zr/ZrCuAg@Si multilayer. In the case of data acquired under standard vacuum condition, a strong mass interference at m/q = 107, resulting from the contribution of $^{107}Ag^+$- and $^{91}Zr^{16}O^+$-ions is observed. In conjunction with low and noisy secondary ion signals (resulting from low count rates), this prevents assessing the location of interfaces between subsequent thin films, and, therefore, the obtained data is not conclusive. However, during fluorine gas-assisted FIB-ToF-SIMS all secondary ion signals were significantly enhanced and the mass interference between $^{107}Ag^+$- and $^{91}Zr^{16}O^+$-ions was separated providing accurate signal distributions with respect to the sample composition. Further studies, dedicated to understanding the mechanism of fluorine gas-induced separation of mass interference during FIB-ToF-SIMS [13], showed the contribution of both the characteristic response of an element to the presence of fluorine (i.e., the changes of secondary ion yields are different for different materials) as well as fluorine induced modifications of metal oxides and metal hydrides formation to this phenomenon.

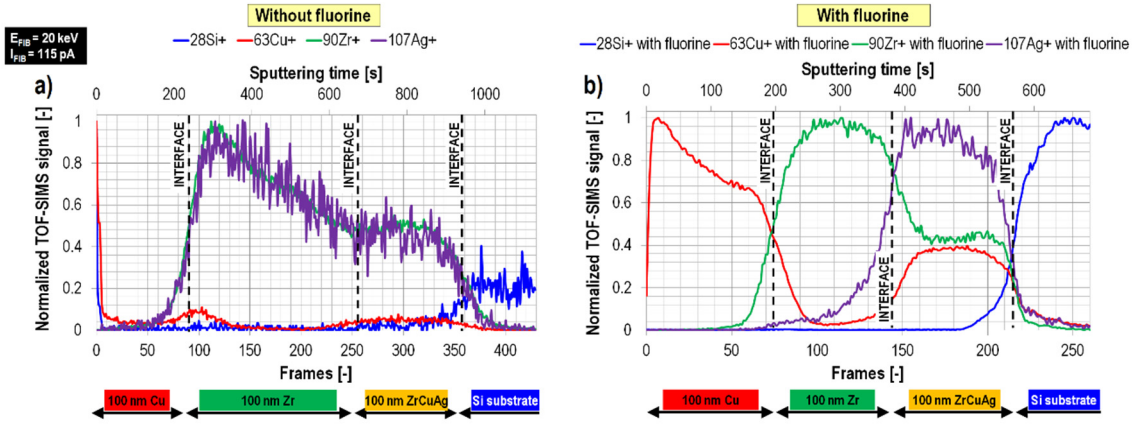

Figure 6. The depth profiles of main sample isotopes present in a Cu/Zr/ZrCuAg@Si multilayer, which were measured a) without, b) with fluorine gas. In the latter case, the separation of mass interference at m/q = 107 was induced, providing representative secondary ion signal distributions with respect to the sample composition. Reprinted with permission from [19]. (Copyright © 2019 American Chemical Society).

Finally, the most recent studies show that fluorine can invert the polarity of generated secondary ions from negative to positive. This is a remarkable finding, especially in the view of different polarization of main elements forming, for example, batteries. Under standard vacuum conditions, either positively ionising elements or negatively ionising elements can be measured from a given analytical volume. Although the chemical information on both types of elements can be indirectly obtained by using complex ions (such as metal oxides), this approach is not always completely representative [16]. As presented in Fig. 7, in the case of gold the negative

ions are dominantly generated during Ga^+ primary ion beam bombardment when no supplementary gas is provided. However, co-injection of XeF_2 modifies the chemical state in the way that $^{197}Au^+$-ions are efficiently produced. Furthermore, the generation of $^{197}Au^+$-ions is almost 2 orders of magnitude higher compared to the generation of $^{197}Au^-$ without any gas [22]. So far, similar results were also obtained for Si and Pt. Furthermore, the detailed analysis of the previous studies dedicated to the ionisation process of elements under O^- and Cs^+ primary ion beam bombardment [24] suggests that other elements, such as C, S, As, Se, Ag, Sb, Te, Ir, and Bi can behave similarly.

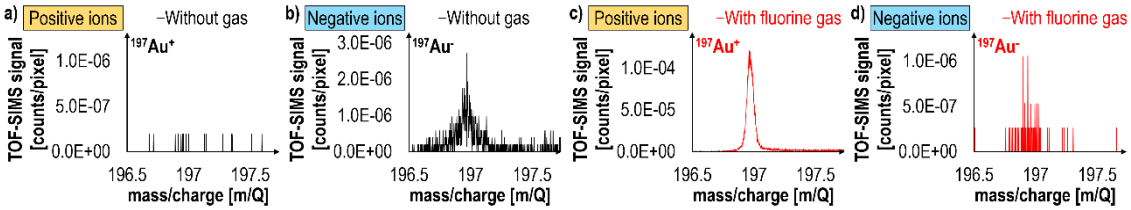

Figure 7. Mass spectrum range corresponding to Au signal measured with FIB-ToF-SIMS. a & b) Under standard vacuum conditions (without any gas) Au ionises dominantly with a negative charge. c & d) However, the delivery of fluorine gas to a sample surface results in inversion of charge polarity from negative to positive. Reprinted (adapted) with permission from [22]. (Copyright © 2021 American Chemical Society).

6. CONCLUSION

In this short review, the most recent advances in the FIB-ToF-SIMS technique are discussed. The extensive efforts dedicated to the development of gas-assisted FIB-ToF-SIMS measurements under HV conditions enabled significantly enhancing the generation of secondary ions, leading to increased lateral resolution and depth resolution. Consequently, this allowed the quality of depth profiles and chemical maps to be significantly improved. Remarkably, for the first time fluorine-induced separation of mass interference and fluorine-induced inversion of charge polarity from negative to positive were reported. These finding open new opportunities for obtaining more accurate and complete information on material's chemical structure. However, further studies are needed to explore potential limitations and drawbacks of this method.

The potential of gas-assisted FIB-ToF-SIMS was demonstrated on various thin films [14, 20], multilayers [9, 13, 21], novel batteries [22, 25, 26], and alloys [14, 23].

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