Laser Postionization Secondary Neutral Mass Spectrometry for Analysis on the Nanometer-Scale

Igor V. Veryovkin, Wallis F. Calaway, C. Emil Tripa, and Michael J. Pellin

Materials Science Division, Argonne National Laboratory,
9700 S. Cass Ave., Argonne, IL 60439, USA, verigo@anl.gov

Abstract

The potential of Laser Postionization Secondary Neutral Mass Spectrometry (LPI SNMS) applied to materials characterization on the nanometer scale is discussed. Optimal analytical approaches and required instrumental capabilities are outlined, and the current state-of-the-art in ion sputtering based analytical techniques is summarized. A new generation of analytical instruments specifically optimized for LPI SNMS has been developed at Argonne National Laboratory (ANL). Key design features of these time-of-flight (TOF) mass spectrometers (MS) making them capable of quantitative MS analysis at the nanometer scale are highlighted. Finally, the analytical capabilities of these instruments, which have been experimentally verified or are anticipated after near-future upgrades, are reported.

Keywords: *laser postionization, mass spectrometry, SNMS, SIMS, useful yield*.

1 Introduction

Few analytical techniques posses the sensitivity and discrimination required when the sample volume for analysis is restricted to nanometers. The need for high sensitivity arises from the small number of atoms present, while discrimination is desirable to detect trace constituents. Presently laboratory-scale instruments for surface composition analysis on the nanoscale are based on one of the following methods: scanning Auger electron spectroscopy (AES), scanning electron microscopy and transmission electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDS and TEM-EDS, respectively), and secondary ion mass spectrometry (SIMS). The difficulty for nanometer-scale analysis arises because these techniques must be used in combination in order to ameliorate their specific strengths and weaknesses. In this work, only MS techniques, i.e., SIMS and LPI SNMS (also known as laser-SNMS), as applied to nanometer-scale analyses will be discussed. The goal is to clarify what can be accomplished on the nanoscale using these methods today and in the near future.

2 Current State-of-the-Art in Ion Sputtering Based Methods

SIMS is a very well established ion sputtering based analytical technique with two major variants, dynamic and static. Both variants have been used effectively in the analyses of ultra-fine features with submicron and nanometer dimensions. The distinction between the two methods reflects the fact that all ion probe analysis methods are destructive, since sample material is sputtered away during the analysis. In dynamic SIMS which is typically performed with quadrupole or magnetic sector mass analyzers, a continuous flux of primary ions on the sample surface alters its composition due to ion mixing, ion implantation and preferential sputtering. In static SIMS, the ion dose is limited so that <1% of the surface is damaged during analysis making these effects negligible. TOF-SIMS is often used for static SIMS, since secondary ions of all masses can be measured simultaneously.

Dynamic quadrupole SIMS pioneered nanometer-scale analysis more than two decades ago, when Levi-Setti and co-workers [1] demonstrated 20 nm lateral resolution measurements using a Ga^+ liquid metal ion gun (LMIG). This relatively cost-efficient approach combines a focused ion beam (FIB) with a quadrupole MS (FIB-SIMS). Quadrupole FIB-SIMS has been used effectively to investigate composition at the nanoscale and has to date the best lateral resolution in the SIMS world. Stevie and coworkers [2] have demonstrated elemental imaging of semiconductor materials with 10-15 nm resolution with FIB-SIMS. Unfortunately this method has relatively low sensitivity and dynamic range. For SIMS analyses that need lower detection limits, magnetic sector mass analyzers, which can have a higher transmission than a quadrupole instrument, must be used. For example, implementing a magnetic sector mass analyzer has improved secondary ion detection on the Levi-Setti instrument [3]. The magnetic sector in a Mattauch-Herzog configuration has been used to produce the most sensitive SIMS instrument, the CAMECA NanoSIMS 50.[4] This instrument is capable of 50 nm lateral resolution with a Cs^+ ion beam while maintaining a mass resolution >4000 and a *useful yield* approaching and in special cases exceeding 1%.

A key figure of merit which quantifies the analytical capabilities of SIMS and LPI SNMS instruments is *useful yield*, defined as *the ratio between the total number of ions detected and the total number of atoms consumed by the analysis during sputtering*. A 1% useful yield, as is the case for the NanoSIMS, means that one out of every one hundred sputtered atoms is detected. For S in sulfide samples, the NanoSIMS has demonstrated a remarkable useful yield of 18%! This is due to the exceptionally high formation probability of S^- under Cs^+ bombardment [4].

It is well known that for different primary ions, the ionization probabilities for sputtered atoms of the same element can vary by two to three orders of magnitude [2, 5].

In order to achieve the highest possible useful yields in SIMS, primary ion beams of elements that can enhance the ionization probability must be used. Unfortunately, these *reactive* ions are not the best choices for forming the smallest ion beam spots that determine lateral resolution of the analysis. In the NanoSIMS, the O^- beam that enhances positive secondary ion yields can be focused to ~100 nm only, while the Cs^+ beam that enhances negative secondary ion yields goes down to 50 nm. This size is about a decade larger than what can be achieved in LMIG with Ga^+ and other *non-reactive* ion beams (5-10 nm). The benefit of using reactive ion beams in SIMS is two to three decades improvement in ion yields, which translates into a correspondingly improved useful yield and sensitivity.

It is important to understand the limitations of SIMS when analyses of ultra-fine features are needed [2, 5]. Because ion yields are very small fractions of the sputtered flux (typically of order of 10^{-3}), many atoms must be sputtered from the surface in order to produce detectable quantities of secondary ions. Therefore, detection limits are constrained because the total number of such ions produced from a sample with nanometer dimensions is insufficient! These issues have been discussed in details by Stevie et al in Ref.[2], who pointed out that this kind of a sample (nanoparticle, nanostructure etc.) might be totally sputtered away before the identification of its composition was complete. This problem is exacerbated in dynamic SIMS since quadrupole and magnetic sector instruments require time to scan a mass range. The primary ion beam creates secondary ions of all masses continually, but only one or a few masses are detected at any one time. These undesirable losses of sample material reduce the *useful yield*, to a value which can be called *effective useful yield* [6]. Using peak switching in quadrupole instruments and parallel multi-element (or multi-isotope) detection in magnetic sectors can improve the latter problem, but this imposes limitations on the analytical mass range. For example, while NanoSIMS 50 can analyze secondary ions with masses up to 400 a.m.u. [5], in multi-collection mode it can handle masses up to ~30 a.m.u. (upgraded to ~60 a.m.u. in the 50L modification). True multi-element detection over a wide mass range in a single measurement is only possible in TOF instruments.

In TOF-SIMS instruments, all secondary ions of one polarity can be detected quasi-simultaneously, within a few hundred microseconds. Such instruments manufactured by ION-TOF and Ulvac-PHI can match in many cases the mass and depth resolutions (>10000 and fractions of nanometers, respectively) of dynamic SIMS instruments. The lateral resolution of LMIG-equipped TOF-SIMS machines approaches that of the NanoSIMS (<100 nm). However, TOF-SIMS cannot fully benefit from installation of a FIB as the mass resolution and the beam spot size are in this case interdependent [7]. This interdependency arises from the need to bunch the primary ion pulses to lengths <1 ns for good mass resolution. The bunching increases the energy spread in the beam to 3-5 % of the nominal energy, which leads to high chromatic aberrations in the LMIG ion optics and limits the minimal spot size at high mass resolution to several micrometers. In order to maintain ion beam spots between 50 and 100 nm, primary ion pulse lengths in TOF-SIMS should increase to 100-300 ns, which results in a mass resolutions of <2000 [7].

TOF-SIMS can achieve good mass and lateral resolutions with very high depth resolution, comparable to that of a quadrupole dynamic SIMS instrument that is optimized for depth profiling (such as the CAMECA SIMS 4550). This became possible with the development of the *dual-beam analysis mode* [6]. This method combines two ion beams with different energies, one for sputtering and one for analysis. Used in combination, one beam can be independently optimized to achieve the best depth resolution by minimizing the energy of the sputter ion beam, while the second beam can be optimized for lateral resolution by minimizing the ion beam spot size. Using low energy *reactive* ion beams for sputtering (e.g., Cs^+, O_2^+ etc. at a few hundred eV) causes implantation of these species in a shallow near-surface layer. This enhances ionization probabilities for surface atoms sputtered by the analysis ion beam to the extent that TOF-SIMS is approaching magnetic sector SIMS in terms of useful yield. An analysis beam from a LMIG can have sufficient high energies (25-30 keV) to achieve ultra-small beam spots. Since the analysis is performed in *static* mode, where the surface damaged due to the analysis is kept to <1%, undesirable effects induced by the analyzing beam (such as ion mixing) can be neglected, and the sample surface composition as well as the depth resolution are controlled predominantly by the characteristics of the low energy sputtering ion beam [6]. Such a dual beam capability makes TOF-SIMS suitable for three-dimensional analysis of ultra-fine features [8]. However, similarly to dynamic SIMS, total sample consumption during a dual beam TOF-SIMS analysis is limited by ion yield. An *effective useful yield* [6] in this case can be a factor of ~100 lower because of the 1% requirement imposed by the static SIMS mode.

To summarize, the SIMS method has evolved both in instrumentation and analytical procedures over the past 20 years. Presently the physical limits imposed by the ion formation process have been essentially reached. The main physical limitation of SIMS is the *low probability of secondary ion formation*. For the quantification accuracy, the sensitivity of the ion formation process to the surface composition is also limiting, since the ion yield can vary by orders of magnitude for different elements sputtered from the same matrix as well as for the same element sputtered from different matrices [9]. For compositions varying on the nanoscale, standards are difficult to produce and use effectively.

Further improvements in ion sputtering based mass spectrometry for the nanoscale are possible if the dominant neutral fraction of the sputtered flux is converted into ions. This is accomplished in LPI SNMS by photoionization of sputtered neutrals using pulsed laser light before mass analysis. Among LPI techniques, single photon ionization

(SPI) and resonantly-enhanced multiphoton ionization (REMPI) can produce ion yields that are both much higher and more consistent for most species compared to secondary ion yields with reactive primary ion beams. In principle, these advantages allow accurate quantitative analysis on the nanometer-scale.

For more than two decades, efforts at ANL focused on the development of LPI SNMS methodology and instrumentation, as well as the application of LPI SNMS to ultra-trace analysis and ultra-small sample characterization. The SARISA (Surface Analysis by Resonant Ionization of Sputtered Atoms) instrument [10] was developed at ANL in the mid 1980's to explore the limits of trace analysis with LPI SNMS. This machine has a demonstrated high useful yield of ~3-4% for a wide range of elements and was used in trace analysis studies as well in basic studies of ion-surface interactions. In the mid 1990's, another advanced LPI SNMS instrument was developed at ANL. The CHARISMA (Chicago-Argonne Resonant Ionization Spectrometer for Mass Analysis) instrument was optimized for analysis of ultra fine features [11]. Many successful trace elemental and isotopic analyses of single micron sized micrometeorites and presolar grains have been conducted with this machine [12]. CHARISMA resembles a reflectron-type TOF-SIMS with two ion guns, one LMIG and the other operating with noble gas plasma. The useful yield of this instrument for analyses with a LMIG varies from ~0.5 to 1.5% for many elements, at a mass resolution of >1000. Alternatively, CHARISMA can perform laser postionization of neutral species ejected from micron-sized features due to laser desorption by a microfocused laser beam using an in-vacuum high resolution Schwarzshild microscope. This microscope is also used for in-situ sample imaging. Most analyses with SARISA and CHARISMA were performed using REMPI, which allows both high photoionization efficiency and high selectivity. REMPI is single element selective, greatly reducing isobaric mass interferences. The only other ionized species present in such measurements are secondary ions suppressed by many decades using the instrument electronics. In many respects, CHARISMA operated with REMPI is very similar in analytical capabilities to NanoSIMS operated with multiple collectors. Both instruments simultaneously detect several isotopes and are capable of probing submicron features. The capability of CHARISMA to perform dual beam analysis combining 1-2 keV Ar^+ with 25 keV Ga^+ or Au^+ ions should give it some advantage in depth resolution over NanoSIMS, but at the expense of useful yield (as discussed above for TOF-SIMS).

The experience of operating SARISA and CHARISMA has resulted in many improvements in analytical capabilities. These ideas formed the basis for development of a new generation of LPI SNMS instruments at ANL.

3 SARISA: LPI SNMS Instrument for Mass Spectrometry on the Nanoscale

The new instrument inherited its name from the previous SARISA instrument which was decommissioned in 2001. Although new SARISA [13] instrument was specifically developed to analyze the elemental and isotopic composition of solar wind samples returned to Earth by the Genesis spacecraft, it has a broad range of analytical capabilities that allow it to be applied to nanometer-scale analyses. The new SARISA was specifically designed to minimize sample consumption during LPI SNMS analyses . In 2005, construction of the new SARISA was completed and analyses of Genesis samples began.

Ion optics of the new SARISA instrument was designed and optimized using advanced three-dimensional computer modeling. This optics efficiently extracts photoions from a large volume (~30 mm^3) and delivers them to an ion detector through a TOF reflectron-type mass analyzer. The overall transmission of photoions is ~95%. This results in an experimentally demonstrated useful yield for the new SARISA instrument that exceeds 20% [13]. Moreover, the useful yield of SARISA (Fig.1) is presently limited by the efficiency of the pair of microchannel plates (MCP) used as a photoion detector. This efficiency is determined by the MCP open area ratio (~50%). Thus, successfully implementing a more efficient detector, such as electron multiplier optimized for TOF applications, would double the useful yield of SARISA. This is a near-term goal for our research effort. The extremely high useful yield of SARISA permits analyses of samples containing very small numbers of atoms of interest, as is the case on the nanometer scale.

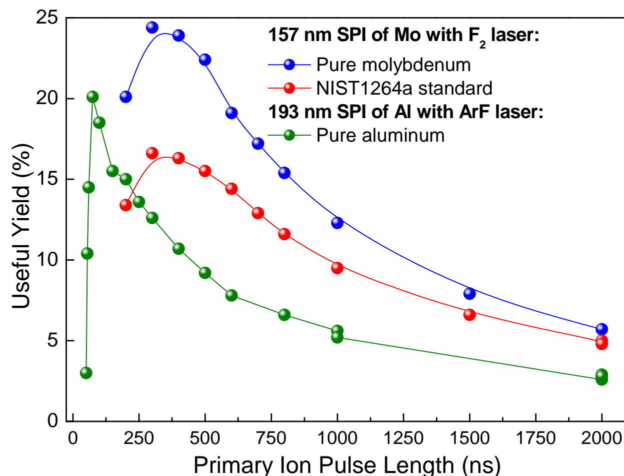

Figure 1. Measured useful yield of the new

To better understand the importance of high useful yield, consider a 50 nm spherical Si particle doped with a rare earth element such an erbium. Atomic concentrations of erbium that can be measured if 100 atomic ions are counted (10% statistics) as the entire nanoparticle is consumed (3.3×10^6 Si atoms) are calculated as a function of useful yield and shown in Table I. To detect a 76 ppm concentration with a magnetic sector SIMS, the particle would need to be 170 nm in diameter. An 0.3 at.% detection limit with the future 40% efficient LPI SNMS could be achieved in a ~15 nm particle. Clearly, improving the useful yield is crucial for improving analytical capabilities on the nanometer scale.

Table I. Detection Limit versus Useful Yield

Instrument	Useful Yield	10σ Detection Limit
SARISA (improved detector)	40%	0.000076
SARISA (present)	20%	0.000153
Magnetic Sector SIMS	1%	0.003
Quadrupole SIMS	0.1%	0.03

Similar to CHARISMA, the conversion of sample material into neutral gas phase atoms and molecules can be performed in the new SARISA with ion sputtering or with laser desorption. In addition, electron stimulated desorption of neutral species can be performed in SARISA also. These ion, laser and electron microprobes are meant to be used as analysis beams in the dual beam mode in combination with low energy ion sputtering for sample material removal. Analysis beams in SARISA have presently the following minimal spot sizes: ion beam = 2 µm with an Atomika WF421 plasma ion gun, electron beam = 100 nm with a VG LEG1000 electron gun and laser beam = 0.5 µm focused by an in-vacuum Schwarzshild microscope with three-fold improved resolution compared to CHARISMA. The ion and electron analysis beams are pointed at a 60° angle from target normal. Low energy sputtering in SARISA is accomplished by a dedicated ion gun, which partly uses the same ion optics as the TOF MS. This permits *normal incidence angle* low energy ion sputtering whose impact energy can be controlled by the target potential from 2000 eV down to the sputtering threshold. Since for normal incidence ion bombardment there is a negligible amount of induced surface roughness, one atomic layer resolution is feasible for dual beam depth profiling in SARISA. The diameter of the low energy beam can be maintained at ~200 µm for impact energies down to 100 eV with >1 µA total current. An important benefit of dual beam depth profiling with LPI SNMS compared to TOF-SIMS is that SARISA does not need *reactive* ions to enhance secondary ion formation and therefore can use inert gases such as Ar^+ or Xe^+ that do not alter surface chemical composition. Moreover, analysis guns in SARISA do not need ion pulse bunching because its mass resolution (up to 2000) is defined by the size of the laser postionization volume rather than by the primary ion pulse length. This is why it is possible to use the FIB as the analysis gun in SARISA and to maintain the finest spot size of the ion probe <50 nm.

Also, extremely important to nanometer-scale analyses is precise sample positioning. Installed in the vacuum chamber of the new SARISA is a sample manipulation stage containing three axes of translation plus rotation. It is unique in that all axes can maintain better than 50 nm closed loop precision for travel of up to 50 mm.

SARISA can operate with both SPI and REMPI. Each method has certain advantages, and the availability of both widens the range of analytical applications. Using SPI with 7.9 eV photons allows simultaneous photoionization and detection of most elements (similar to SIMS). REMPI can be performed using a set of tunable solid-state lasers that allow selective detection of one or two elements of interest.

4 Conclusion

Quantitative trace analysis in *atom-limited samples* is a serious challenge. As analytical techniques such as SIMS and SNMS are extended to the nanometer scale, *high useful yield is paramount* (Fig 2). The new LPI SNMS instrument developed at ANL has an experimentally demonstrated useful yield of 20% and thus can maintain the sensitivity as well as the spatial and depth resolutions needed for three-dimensional MS analysis of nanometer scale features.

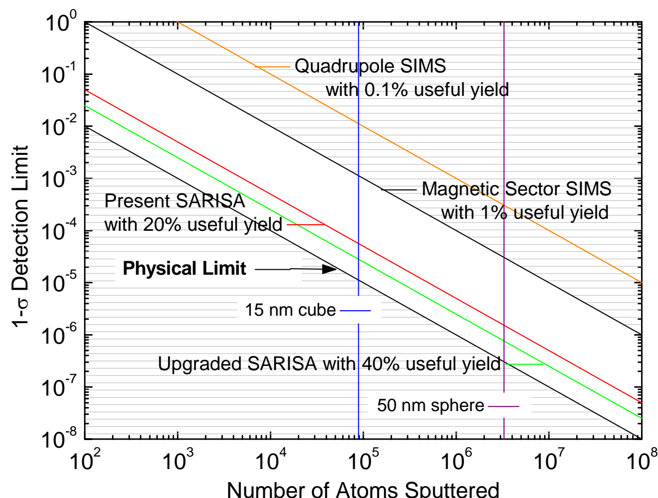

Figure 2. Detection limits of SARISA compared to SIMS.

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