

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

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ABSTRACT

The SARISA laser post-ionization secondary neutral mass spectrometer (LPI SNMS) at Argonne National Lab has recently been upgraded with new tools and probes enabling nanometer-scale analytical capabilities. While tests of the lateral resolution for two fine focused probes (ion and electron) are still in progress, the initial tests of the dual-beam sputter depth profiling capability of SARISA have been completed and demonstrated sub-nanometer depth resolution.

Keywords: imaging mass spectrometry, depth profiling SIMS, SNMS, SEM

1 INTRODUCTION

The booming field of synthesis of novel functional materials by nanostructuring underscores the need for analytical techniques capable of accurate three-dimensional characterization of the materials structures and chemical compositions with nanometer-scale resolutions. The grand challenge in measuring this kind of samples is that they are atom-limited. Analytical methods probing these samples by beams of charged particles, such as electrons and ions, appear to be in many cases the methods-of-choice because of their remarkable lateral and (sometimes) depth resolution, as well as sensitivity and discrimination. However, these techniques often alter or destroy the samples. Therefore, they must efficiently measure each atom removed from the sample in order to accomplish concentration and structure determinations before the samples are consumed.

With this paper, we are following up on our Nanotech 2006 presentation [1], which described the development of an advanced analytical instrument for quantitative three-dimensional mass spectrometric (MS) analyses at the nanometer scale, SARISA, and discussed the potential of the LPI SNMS technique to further advance the state-of-the-art of analytical MS instrumentation. Determination of the elemental concentrations of minor and trace elements in solid samples is now routinely accomplished, with either high lateral or depth resolutions, by directing fine focused energetic ion beams onto sample surfaces followed by evaluation of the sputtered ions using efficient Secondary

Ion Mass Spectrometers (SIMS) with magnetic sector, quadrupole, or time-of-flight (TOF) mass analyzers [2]. Combining the imaging MS capability of these instruments with depth profiling produces stacks of two-dimensional (2D) compositional maps of sample surfaces so that three-dimensional (3D) sample characterization can be accomplished by SIMS [3, 4].

Approaches to 3D imaging analysis by SIMS have greatly matured over more than two decades [5, 6] and by now become a procedure available from a control software menu of an instrument. However, it has been difficult to perform such analyses on real nanometer scale, when dimensions of the volumetric analytical pixel (*voxel*) fall below 10 nm. As we discussed in great detail in Ref.[1], the main limitation in this case is the useful yield of an analytical MS instrument, because voxels in this size range can contain only a few thousand atoms of interest, which makes detection of each atom removed a high priority. In order to improve its detection efficiency, the SIMS technique has to use approaches that enhance ionization probability of sputtered atoms. These require *reactive* primary ion beams such as O_2^+ and Cs^+ , in order to improve detection of positive and negative secondary ions, respectively [2]. For such primary ion species, it is very difficult to produce ion sources bright enough to deliver sufficient ion currents into probe spots smaller than 100 nm. This naturally limits the lateral resolution of the “efficient” SIMS by a benchmark of about 50 nm demonstrated by the CAMECA NanoSIMS instrument with Cs^+ ion beam [7]. The recent development of the inductively coupled plasma ion sources by Oregon Physics [8] enabled O_2^+ and noble gas ion probes with about the same size. In order to resolve smaller features in compositional mapping by SIMS, liquid metal ion guns (LMIG) must be used. This noticeably deteriorates the useful yield and the ability of a SIMS instrument to detect small concentrations of the element of interest in small features of the sample: there are just too few secondary ions generated by *non-reactive* (typically Ga^+) ion beams. Thus, the effective analytical volume size of Ga^+ LMIG equipped SIMS is not better than that for NanoSIMS operated with Cs^+ beam.

There is one more fundamental difficulty to overcome, if one aims at 3D MS analysis on the nanometer scale: high *lateral resolution* requires relatively high primary ion energies in order to overcome space charge limitations, while high *depth resolution* requires very low primary ion

energy in order to minimize ion mixing processes. The invention of the *dual-beam* sputter depth profiling analysis [9] permitted to resolve this conundrum by using two independently optimized ion sources: one producing probing beam with higher energy - for the best lateral resolution, and the other one producing milling beam with low energy and higher current - for the best depth resolution and, sometimes, for enhancing secondary ion yields. Presently, dual beam approaches are standard in commercially available TOF SIMS instruments.

Unfortunately, despite all its elegance and proven efficiency, the dual beam sputter depth profiling is not free of SIMS-specific drawbacks outlined above. Additionally, serious doubts regarding accuracy of the 3D SIMS analysis arise if one has to characterize surfaces and sharp interfaces in nanolayered materials. Because secondary ion yields in SIMS are enhanced by creating one (or a few) atomic layer(s) enriched (or saturated) with cesium, oxygen or other reactive species, the inevitable alterations of the sample composition become then the major source of uncertainty in 3D reconstruction. For the same reasons, it is extremely difficult for 3D SIMS to produce credible quantitative analytical data.

For more than two decades at Argonne National Lab, we have been exploring an alternative route to accurate quantitative MS analysis of solids, the LPI SNMS [10]. As a natural derivative, very similar to SIMS in its layout, this method permits easy implementation of the best analytical approaches and solutions developed for SIMS, and, at the same time, can stay free of its major drawback, the low and matrix-dependent ionization probability of ion sputtered atomic and molecular species. We have recently demonstrated that the sputter depth profiling with LPI SNMS operated in time-of-flight regime with Resonantly Enhanced Multi-Photon Ionization (REMPI) can achieve the same (or better) levels of sensitivity and depth resolution [11] as the best dynamic SIMS instruments such as CAMECA IMS-6f [2]. The key difference important for the discussion below is that, in contrast to *reactive* O_2^+ [2], we used *non-reactive* Ar^+ primary ions [11], which allowed us to avoid compositional alteration of the sample.

The next logical step for LPI SNMS is the implementation of the dual beam sputter depth profiling in combination with the smallest possible probing ion beam. This should enable quantitative 3D MS analysis on nanometer scale with the best possible lateral and depth resolutions and the lowest possible detection limits, as was discussed in Ref.[1]. To this end, we have developed for SARISA a versatile ion optics solution, which also allows for an efficient secondary electron collection mode enabling Secondary Electron Microscopy (SEM) to be conducted in concert with the more damaging, but element and isotope specific 3D LPI SNMS [12]. In this work, we will report our recent progress towards making such analyses real.

2 DUAL-BEAM SPUTTER DEPTH PROFILING WITH SARISA

Our implementation of the dual beam sputter depth profiling in SARISA is significantly different from the one used in commercial TOF-SIMS instruments [9]. From the beginning, we aimed at the best depth resolution, not limited by the effect of the micro-roughening occurring at non-normal incidence. The conclusion from Ref.[13], that *the combination of ultra-low energy and normal incidence provides constant and high depth resolution throughout the measured depth range*, triggered our decision to combine normally incident ion beam for milling and obliquely incident ion beam for analysis in the dual beam arrangement of SARISA. An important extra benefit of normally incident primary ion milling beam is that the ions can be decelerated to the desired ultra-low impact energy by the target potential, which means their extraction from the source can be done at nominal high voltage thus guaranteeing the highest possible ion current delivered onto the target.

After evaluating a few ion sources coupled to the SARISA low energy primary ion column [12], we have installed a VG EX05 ion gun and optimized the ion optics so that there were no noticeable differences in ion currents and beam spots over a wide range of impact energies. For example, at 5 keV (the nominal ion extraction energy and zero target potential), the FWHM of the milling ion beam spot in SARISA is about 140 μm at $>2 \mu A$ current. At 250 eV impact energy achieved with the target potential of 4750 V, the FWHM of the beam spot is about 170 μm at the same current. These beam benchmarks (9-13 mA/cm² current densities) are comparable to those optimized for high resolution SIMS depth profiling Ionoptika FLIG ion source (~ 25 mA/cm² for O_2^+ ions [14]), with the difference that the total primary ion current in SARISA is more than an order of magnitude higher than that in the FLIG. This means ultra-high resolution depth profiling analyses can be conducted in SARISA noticeably faster than in FLIG-equipped SIMS instruments, and without chemical alteration of the surface and interface compositions.

The initial series of tests of the dual beam sputter depth profiling in the SARISA's unique arrangement has been recently completed. These experiments aimed at comparing the dual beam regime with the conventional approach using the same obliquely incident 5 keV Ar^+ ion beam (60° from normal, generated by the Atomika WF421 ion gun) for time-of-flight mass analysis in both cases, and also for ion milling in the latter case. In the former case, normal incidence low energy Ar^+ ions for ion milling were generated by the VG EX05 gun with 3 kV nominal extraction, and delivered onto the target with 250 eV and 500 eV impact energies. A special test sample was fabricated by Atomic Layer Deposition (ALD), such that 16 alternating 5.5 nm layers of MgO and ZnO (8 of each) were grown on Si single crystal substrate. Due to high concentrations of Mg and Zn, there was no need to use laser

post-ionization, so that the experiments were conducted in the TOF SIMS regime, and their results are summarized in Figure 1.

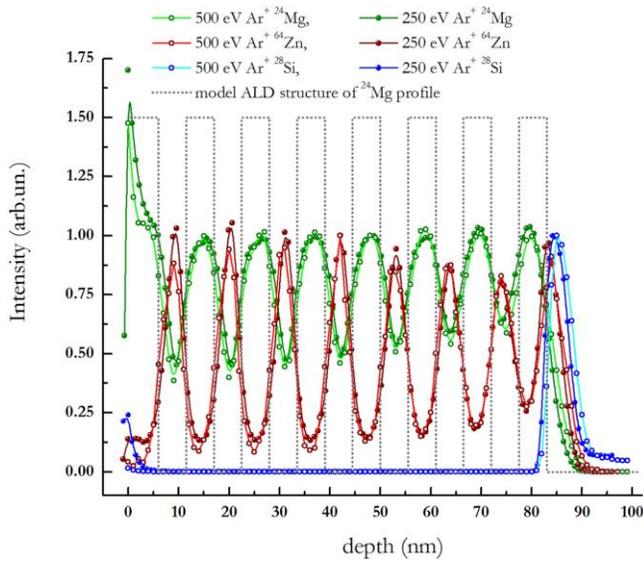


Figure 1: Dual beam depth profiling of a stack of MgO/ZnO nanolayers fabricated by the ALD method.

A higher resolution measurement having shorter ion milling increments per depth unit is shown on Figure 2.

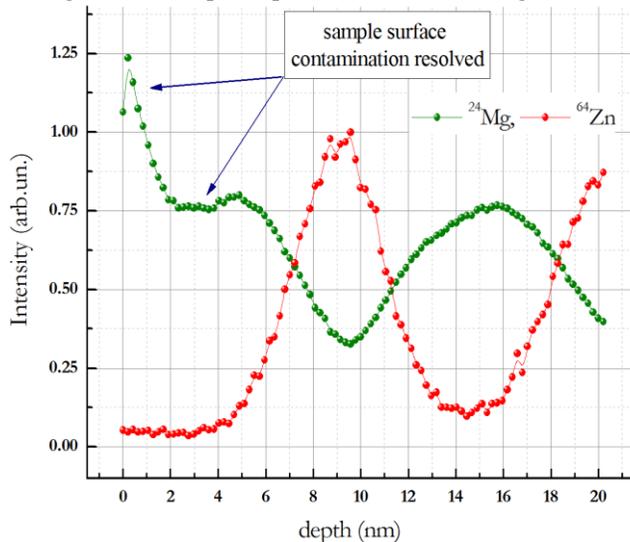


Figure 2: High resolution dual beam depth profiling with 500 eV Ar⁺ ions.

Analysis of these results for the dual beam approach, summarized in Table 1, reveals dynamic ranges within a single ALD layer of about 2 and 10 for ²⁴Mg and ⁶⁴Zn, respectively. It is customary to characterize the depth resolution in SIMS experiments by experimental values of rise-up λ_{up} and decay λ_{decay} lengths. The general definition for rise-up/leading and decay/trailing lengths in sputter depth profiles is an inverse first order coefficient of a linear fit of the leading or trailing tails of an ion implant peak when depth profile is plotted in a semi-logarithmic scale as $\ln(Intensity)$ versus $Depth$ [15]. As one can see from Table

1 for the dual beam experiment, both these values are, on average, about 5 nm for Mg and 2 nm for Zn. For the interface between the substrate and the ALD layers, the dynamic range of dual beam depth profiling approaches four orders of magnitude, and decay lengths for Mg and Zn shrink by about a factor of five. Moreover, the rise-up length λ_{up} determined for Si signal over the span of about three orders of magnitude is 0.38 nm for both 250 eV and 500 eV. Since this value corresponds to the sharp interface between Si substrate and the first ALD layer, it can be considered as a “true” instrumental depth resolution of the SARISA instrument. Other average λ values obtained for the region between the layers are “blurred” by the natural roughness of the ALD layers estimated to be on the order of 2 nm. For comparison, the conventional single beam depth profiling with 5 keV Ar⁺ produced Si λ_{up} of about 1.1 nm, and much larger values of $\lambda_{decay}/\lambda_{up}$.

Beam Energy	5 keV			250 eV		
	²⁴ Mg	⁶⁴ Zn	²⁸ Si	²⁴ Mg	⁶⁴ Zn	²⁸ Si
$\langle\lambda_{up}\rangle$ nm	39.5	14.2	-	4.93	2.2	-
$\langle\lambda_{decay}\rangle$ nm	38.3	21.3	-	4.72	1.98	-
Si interf λ_{decay}	10	7.2	-	0.88	0.75	-
Si λ_{up}	-	-	1.14	-	-	0.38

Table 1: Comparison between the conventional single-beam and the dual-beam depth profiling approaches in SARISA: rise-up and decay lengths for ²⁴Mg and ⁶⁴Zn in different regions of the depth profiles: the two bottom rows correspond to the interface between the Si substrate and the first ALD layer, and the two rows above those correspond to the average values of rise-up and decay lengths calculated for 8 layers.

3 THE NEXT STEP: HIGH LATERAL RESOLUTION ANALYTICAL PROBES

As one can see from test results above, we have demonstrated sub-nanometer depth resolution of the SARISA instrument operated in dual beam regime with ultra-low energy normal incidence Ar⁺ ion milling beam and 5 keV pulsed analysis Ar⁺ beam, with spot size as area ratios of about 2:1. Obviously, the 50-100 μm beam spots delivered by the analysis Atomika WF421 ion gun were not meant for high spatial resolution analysis. Moreover, even with the smallest beam aperture, this gun cannot produce spots smaller than $\sim 2 \mu\text{m}$, and thus it is best to use it in measurements where the best combination of depth resolution and dynamic range is needed.

In order to enable 3D MS analysis in the nanometer range, we have recently installed on SARISA two more fine focus probe guns manufactured by FEI: the Magnum LMIG (Ga⁺) and the 2LE electron gun. These FEI probes are designed to generate 25-30 keV focused ion and electron

beams with spots smaller than 10 nm. Adding the electron gun to SARISA enables SEM sample characterization, which can be overlapped with LPI SNMS measurements. The SEM measurement will soon be incorporated in the dual beam depth profiling protocol to maximize the useful information extracted from small samples of interest. Thus, each 2D LPI SNMS map of the sample composition in the 3D depth profile stack will be accompanied by the matching SEM map. Moreover, an X-ray fluorescence detector is planned to be installed on SARISA in the near future to combine SEM with X-ray microanalysis (SEM/EDX regime). This will permit non-destructive characterization of the elemental composition prior to LPI SNMS analyses.

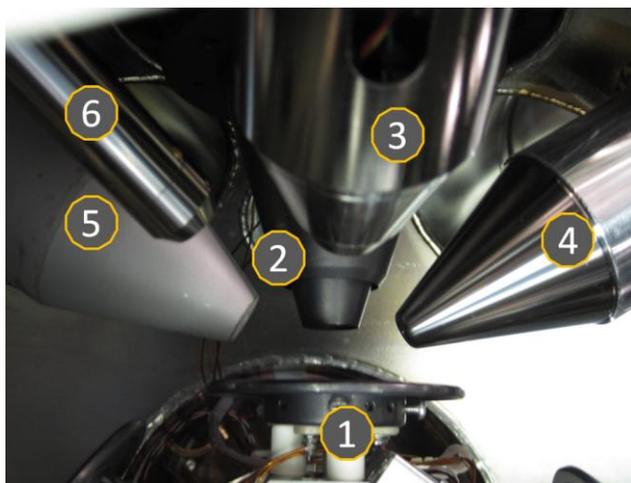


Figure 3: Sample region of the SARISA instrument: (1) target electrode enabling samples up to 25 mm in diameter; (2) “push-pull” ion optics for extraction of photo-ions [12]; (3) Atomika WF 421 ion gun; (4) FEI Magnum ion gun; (5) FEI 2LE electron gun; (6) Kimball Physics EFG-7 electron flood gun.

4 CONCLUSION

As was discussed in detail in our Nanotech 2006 presentation [1], the LPI SNMS technique is uniquely suitable for quantitative MS analyses on the nanometer scale with trace level detection limits. This is because of a high and matrix-independent useful yield of this technique.

In this work, we have demonstrated that *sub-nanometer depth resolution* of such analyses can be achieved with LPI SNMS in dual beam regime by implementing ion milling with normally incident noble gas ions having ultra-low impact energies (<500 eV). This approach to material removal in sputter depth profiling, in combination with pulsed analysis beam of non-reactive ions, assures minimal changes in surface morphology and chemical composition and enables the most accurate and sensitive MS characterization of surfaces and interfaces.

The ongoing effort of incorporating fine focused ion and electron probes into the SARISA’s analytical protocols will soon allow us to test the limits of lateral resolution of

the LPI SNMS analysis. While these probes are capable of delivering ~5 nm analytical pixel sizes, it is unclear what signal-to-noise ratios can be achieved with those: 1 μ s pulse of Ga^+ ions at 1 pA current delivers only ~10 ions onto the target. Obviously, we will have to find optimal combinations of pulse lengths and spot sizes / ion currents, such that the counting statistics does strongly affect our detection limits. Nevertheless, we are confident that once fine focused pulsed Ga^+ ion beam becomes the analytical half of SARISA’s dual beam depth profiling scheme, a quantitative 3D MS analysis with the finest analytical voxels in the nanometer scale will be demonstrated.

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