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Christopher H. Becker

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A NEW SURFACE ANALYTICAL TECHNIQUE WITH ION AND LASER BEAMS

Christopher H. Becker
Chemical Physics Laboratory,
SRI International, 333 Ravenswood Avenue, Menlo Park, CA 94025

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Abstract

This paper reviews recent results and developments, while presenting some new information, regarding the development of a novel surface analytical technique that uses nonresonant multiphoton ionization (MPI) of neutral atoms and molecules sputtered by an ion beam, or desorbed by an electron or second laser beam or by thermal means. In this method, called surface analysis by laser ionization (SALI), the nonresonant MPI, or "laser ionization," is coupled with state-of-the-art time-of-flight mass spectrometry to provide extremely sensitive, general, and readily quantifiable surface analysis. A discussion also describes the favorable prospects for implementation of SALI with submicron dimension liquid metal ion beams for microanalysis, including situations with electron beam sensitive samples.

Introduction

This paper reviews the progress made by the surface analysis by laser ionization (SALI) technique and presents, in addition, new and previously unpublished results of the technique. A basic description of the method is given along with examples of analyses of various types of samples, showing the method's capabilities as well as versatility. A discussion is given of the anticipated improvements in the technique for a second generation instrument which is currently under construction. A discussion is also presented regarding the use of SALI for submicron chemical analysis, which predicts that we should expect to see numerous microanalysis applications of SALI in the next several years.

The SALI approach to surface analysis, developed at SRI International [3], is a mass spectrometric method, applied to material surfaces while under high vacuum. It is extremely sensitive, and chemically general. The surfaces studied have included semiconductors, metals, adsorbed and precipitated molecules, and insulators. Reactant or residual gases also can be detected.

The method can be considered as a three-step process. The surface of interest is first irradiated by a pulse or continuous probe beam of ions, electrons, or photons to cause sputtering or desorption. We have frequently used inert gas sputtering (Ar$^+$ at a few keV) to avoid chemical modification of the surface. Second, the material released due to the probe beam (the vast majority of which typically is neutral in charge) is intersected and ionized by a high intensity pulsed and focused ultraviolet laser beam (the ionizing beam) passing close to, but above and parallel to the surface. The type of ionization performed principally is nonresonant multiphoton ionization.

Typically, for best results, the focused laser intensity should lie in the range of $10^5$ to $10^{12}$ W/cm$^2$. Third, these photolons, being created in a region of electric field, are accelerated, then focused, and allowed to drift in a field-free region for time-of-flight (TOF) mass analysis before detection by a microchannel plate particle multiplier assembly. Figure 1 shows a schematic diagram of the instrument.
Signal detection can be performed in analog or pulse counting fashion, although the signal levels usually are sufficiently high with an ion beam current > 0.1 µA, so that analog detection is the practical choice; indeed, signal attenuation also is frequently required in order to maintain a linear response by the detection electronics. In the type of TOF mass spectrometer used in this section, the reflecting design [13]. The reflector compensates for the kinetic energy permitting good mass resolution. Importantly, we find it also is frequently required in order to maintain a beam current > 0.1 µA, so that analog detection or pulse counting fashion, although the signal.

An important aspect of the present approach is the separation of the desorption step from the ionization step. The separation permits (i) detection of the larger desorbed neutral fraction, (ii) greater control and flexibility in the choices of the types and intensities of the probe and ionizing beams, allowing (with an efficient ionization) a relatively gentle, low fluence, surface irradiation to minimize surface damage and permitting a quantifiable ionization step, and (iii) the avoidance of large matrix effects where the ionization probabilities of atoms and molecules vary greatly as a function of the chemical environment. This is in contrast to the related technique of secondary ion mass spectrometry (SIMS) [9,10,19] where the sputtering process is also responsible for ionization. Generally, one expects the usually much larger desorbing neutral fraction will be more representative of the surface than the smaller ionized fraction because the neutral component is less sensitive to surface properties and surface contaminants.

The "useful yield" is defined as the number of particles detected per particle removed from the surface. SIMS, as implemented in its most efficient instrumental form, may have useful yields exceeding 10⁻² [16,20] in favorable cases. The secondary ion yields can vary by orders of magnitude however for different elements, or a given element in a different chemical matrix. For positive ion formation by atoms of low ionization potential or using cesium (for negative ion formation by atoms of higher ionization potential or electron affinity) to keep the variation in secondary ion yield to within about a factor of 10⁴, but clearly not for all species simultaneously. Interfaces and surfaces remain difficult to analyze with SIMS because of this problem, though there has been much success for bulk materials with standards for calibration. SALI has a demonstrated useful yield of 10⁻⁴ though a value of 10⁻³ is soon anticipated with second generation implantation; this value however is much more chemically uniform, without requiring surface modification such as the addition of oxygen or cesium.

The SALI method should be compared and contrasted with another emerging laser-based approach, the post-ionization of sputtered neutral material, i.e., selective resonant ionization. In the resonant approach, first reported for surface analysis by Winograd et al., [21] and now being investigated in several laboratories [11,14], dye laser radiation is tuned to a specific transition of a desired atom (or small molecule, if the spectroscopy is well characterized) to excite that atom to an intermediate excited state that is then ionized by a subsequent photon. The goal is generally to achieve highly selective, extremely sensitive detection of the specific element (or isotope) being examined. A mass spectrometer is generally employed between the ionization zone and the detector both for isotope analysis, and for increased selectivity and background suppression. This approach is particularly useful in the presence of isobaric interferences.

Our approach is quite distinct. We use an untuned laser of much higher power in an attempt to achieve efficient (even saturated) ionization for all the neutrals within the focused laser zone; we attempt to minimize selectivity in the ionization step and to thereby generate ions that are characteristic of the composition of the surface being probed. Time-of-flight mass spectrometry is used as an efficient method to disperse and collect all of the ions generated from each laser pulse.

Examples of Earlier Analyses

Previous publications have shown numerous examples of surface and material analyses: analysis of parts-per-million (ppm) impurity elements in an NBS copper matrix by sputtering, for all elements simultaneously, while consuming about 12 of a monolayer over mm dimensions (or 10⁻³ mono-layer sensitivity) [3,4,22]; observation of thermal desorption of ppm bulk impurities segregating to the surface at very low desorption fluxes (densities corresponding to < 10⁻¹³ abar) [4]; direct comparison between SALI and SIMS for a contaminated GaAs crystal as well as a comparison between laser desorbed ions and neutrals—showing the naturally much more quantitative nature of SALI [5]; detection of = 10⁻¹ mole of a uranium compound using ion beam sputtering and laser desorption (the latter a two laser experiment) [6]; measurements by depth profiling of the stoichiometry of amodic oxides grown on HgCdTe [17]; observations of very low-level thermal desorption of components from HgCdTe, starting at room temperature [8]; analysis of an NBS oxide glass, with comparisons to SIMS [8]; depth profile studies of the near surface regions of stainless steel samples with different chemical treatments for high corrosion resistance [2]; relative sensitivities by MPI for numerous elements as a function of laser intensity [7] and other laser power dependences of MPI for various elements [3,6,7].

At the present we are unaware of other laboratories using nonresonant MPI for surface analysis. However, we have been told that other laboratories are setting-up similar instruments, and published results can be expected shortly.

Following in this section are a few of the examples just referred to that have been published
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Fig. 1. Schematic of the SALI (Surface Analysis by Laser Ionization) Instrument. Shown are three alternative probe beams (upper left), the ionizing laser beam (hv, lower left) and the path of the photons, focused to compensate for transverse velocities, and deflected slightly into the reflecting TOF analyzer leading to a chevron microchannel plate detector (Ch).

(or are in press). In the next section we present some more examples of SALI work not previously published.

An example of a segment from a SALI spectrum taken of an NBS copper Cl252 standard reference mass spectrum is shown in Figure 2 [4]. The room-temperature sample (99.89% Cu) was first sputter cleaned by a continuous Ar⁺ beam at 27 keV which was later pulsed as the probe beam. The ion beam had an area of ~0.01 cm², a dc current of about 1 µA, and for this pulsed SALI experiment, a pulse width of a few microseconds. KrF excimer laser radiation at 248 nm (passing ~1 mm above the sample) was used with a focused intensity of about 2 x 10⁹ W/cm².

In the mass range displayed in Figure 2, the elements whose bulk atomic composition values were certified by NBS include Ag (with a concentration of 51 ppm at isotopic mass 107), Sb (9 ppm at mass 123), 197Au (11 ppm), 205Bi (6 ppm), and Pb (4 ppm at mass 206). Other features are labeled on the figure. Contaminants include Pt, deposited on the Cu during an earlier analysis of an adjacent Pt sample, and Ta and W from the Ar⁺ ion source. The measured ratios of the certified trace elements to Cu are correct within a factor of about 3, showing (a) that the method can be semiquantitative for the raw data before corrections for ionization efficiencies by comparison with a standard, and (b) that saturation of the ionization can be obtained. Corrections for ionization efficiencies will depend on the laser beam characteristics (power, pulse width, spatial distribution). This figure strongly suggests saturation can be obtained because of the quite uniform nature of the detection of the various species for a nonlinear process where the cross sections would be expected to differ more dramatically, and because the intensity of the signal is only consistent with near completion of ionization given the system throughput.

A SALI TOF mass spectrum for GaAs under steady-state sputtering showed good stoichiometry of the raw data for 248 nm radiation at a power density of approximately 10⁹ W/cm² [5]. Following those measurements, experiments were conducted using an infrared laser beam instead of an Ar⁺ beam. During those experiments the GaAs surface underwent substantial heating and a plasma was (unintentionally) initiated at the surface, which resulted in surface contamination from sputtering of the TOF ion extractor plate (stainless steel covered with remnants of previous samples). This contamination allowed, however, a useful many-element comparison of SALI and SIMS. Using a pulsed (static) Ar⁺ beam for submonolayer sampling, typical results are shown in Figure 3. The SALI spectrum of the contaminated surface [Figure 3b] shows by comparison with the steady-state sputtering results that the surface was arsenic rich after the previous laser irradiation. It also shows significant coverages of Cu, Fe, Ni, and other previous sample material from the ion extractor plate. Figure 3a is a SIMS TOF positive ion spectrum using the same pulsed Ar⁺ beam as the primary ion beam, except reducing the pulse width to ~50 ns. Note that the SIMS spectrum is dominated by low ionization potential elements not giving a really representative picture of the true surface composition. In particular, the As is nearly undetectable. Such spectra provide directly the relative neutral-to-ion yields in a sputtering or desorption process when corrected for photoionization efficiencies.

Examples of Recent Analyses

Examples of some recent analyses not previously published or submitted for publication follow. They are intended to show further the diversity of chemical systems that can be addressed by SALI.

Fig. 2. Segment of a time-of-flight mass spectrum taken of an NBS copper Cl252 standard reference material sputtered by a pulsed 2.7-keV Ar⁺ beam and ionized by a KrF excimer laser. The major observed species are indicated, as are various reference mass numbers.
An interesting submonolayer analysis recently studied was that of an etch residue on a silicon wafer from a C2F6 plasma etcher. Special care was taken to detect impurities deposited by the sputtering process from various surfaces in the particular version of the plasma etcher used for this run; such impurities include Al, Cr, Fe, Ni, and Cu. Two standards were used for calibration: an Al-Si powder (88:12 by weight) (325 mesh powder from Alpha Products) pressed on an In foil, and an NBS stainless steel standard C1154 to calibrate Si, Cr, Fe, Ni, and Cu. Metals can be a particularly troublesome impurity for Si processing because of their energy levels at mid-band gap.

Figure 4 shows a spectrum with static sputtering of the etch residue on a Si wafer, and Table 1 gives the data reduction of this figure. The relative calibrated amounts shown in Table 1 for the various elements can be considered only semi-quantitative because of the prevalent fluoride and oxide bonding, whereas the calibrations were performed for the reduced elements. Nevertheless, the relative calibrations provide a valuable approximate estimate of much of the residue composition. The amount of material sputtered to record this spectrum is estimated to be \(3 \times 10^{-6}\) monolayer, though comparable data could probably have been recorded using only \(1/100\) of this amount. The material consumption estimate for this spectrum runs as follows: ion beam dc current of 1 \(\mu\)A, pulse width of 2 \(\mu\)s, area of 0.01 cm\(^2\), sputter yield of 3, and 1 monolayer (L) of \((10^{-9}/\text{cm})/L\) give (6 \(x\) 10\(^{12}\) /s) \((2 \times 10^{-6}\) s) \((3 \times 10^{-2}\) cm\(^{-2}\))/(10\(^{12}\)/cm\(^2\)/L) \(\approx 3 \times 10^{-6}\) L. Because of the large signal-to-noise ratios, and noting that 40 db (x 100) signal attenuation was used, it is thus stated that only \(1/100\) of this material consumption was actually needed.

Calibrations with oxidized elements can be performed, including the relative sensitivity for both (sputtered and photodissociated) atomic and molecular species such as Si, SiF, SiO, C, and CF; however, this is a more extensive task and was not performed for this etch residue. Because of the "weak" laser power and relatively long wavelength UV light used (248 nm, 5.0 eV), negligible atomic O and F signals were observed. This can be dramatically overcome with about two orders of magnitude increase in power density (a practicality with a state-of-the-art laser), especially at 193 nm. The particularly high sensitivity to some elements observed in Table 1 (e.g., for Fe) is due to an accidental resonance and the fact that the laser output using the stable resonator in this instance is not very tightly focused leading to a significantly larger effective ionization volume for easily ionized species. In this, limit of very high UV power densities (say, \(>10^{11}\) W/cm\(^2\)) with good spatial beam quality, the raw data should accurately approach (because of uniform saturation) the density of the sputtered flux.

Another interesting sample examined, also relevant to the semiconductor industry, was that of a boron-phosphor-silicate glass. This glass was independently determined by electron-induced energy dispersive x-ray (EDX) analysis, using standards, to contain 5% elemental P by weight. The elemental B was estimated to be 2% by weight. No standard for comparison was available to us at this time.

Electrostatic charge build-up on insulators has been a concern to surface analysts for many years. Charging may sometimes be overcome by the use of low energy electrons or by the deposition of a conducting overlayer. However, both techniques are not always satisfactory [18]. We found that the use of a fine tungsten mesh with spaces between wires of typically about a hundred \(\mu\)m was a very suitable solution for our broad, fairly low current density (\(10\mu A/cm^2\)) ion beam. Note, however, that because SALI ionizes desorbed neutrals a macroscopic distance above the surface, charging is generally less of a problem as compared with secondary ion mass spectrometry. For high current density liquid metal ion beams, a flood electron beam will probably be required for depth profiling, but the combination of the conductivity of the deposited metal, the use of the electrostatic potential above the surface, and the energy-spread compensating reflector should help make insulator analysis routine. For surface analysis (static or near static mode) it is unlikely a compensating beam will be needed.

The analysis of the B-P-Si glass is shown in Figure 5 and Table 2. Even though the power density of the laser is low \(\approx 1 \times 10^6\) W/cm\(^2\), note that the use of the shorter wavelength 193 nm (at 6.42 eV versus 5.0 eV for 248 nm) gave an atomic O signal comparable to \(10^7\). The sensitivity to P at this power and wavelength is lower than for B or Si which was expected because of the fairly high ionization potential of P. Nonetheless, the semiquantitative nature of these results is encouraging; a newer high power laser will easily improve these results. Higher mass oxide molecules were observed, but the diatomics were by far the most intense.

SALI can be applied to organic analysis as well. Studies have been performed on small to moderate sized organic molecules adsorbed on metal surfaces and even some polymer analysis using ion beam sputtering (C. H. Becker, published results), though it is anticipated that laser desorption followed by laser ionization often may be superior to sputtering followed by laser ionization for such situations. At any rate, presented below are two examples of a rather surprising study of organic compounds from an "inorganic source."

Olivine is the most important mineral of the earth's mantle. It is principally a magnesium silicate crystal, but many impurities are naturally occurring, frequently up to the 100 ppm level. A current topic of great interest is the possibility that there may be great amounts of hydrocarbons, of nonbiological origin, found deep within the earth coming from the primordial carbon present when the earth formed from earlier stellar remains.

Samples of olivine, naturally uplifted from the mantle, were examined by first cleaving away all of the outer surfaces of the single crystal in the laboratory and then rapidly introducing them into the vacuum system for analysis. Very low fluxes of organic compounds were observed to evaporate from these crystals at room temperature...
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Fig. 3. (a) TOF positive SIMS spectrum from a contaminated surface of GaAs using Ar\(^{+}\) static mode bombardment (see the text). (b) SALI spectrum from the same surface with the same Ar\(^{+}\) probe beam as in (a). The ionizing laser wavelength was 248 nm with a power density of approximately 10\(^9\) W/cm\(^2\).

Fig. 4. SALI time-of-flight mass spectrum taken from static (roughly 3 x 10\(^{-6}\) monolayers) sputtering of an etch residue on a silicon wafer after a C\(_2\)F\(_6\) plasma etch. The spectrum is a result of accumulating signal from 100 laser pulses with a 40 dB attenuated signal, and 248 nm radiation at approximately 5 x 10\(^8\) W/cm\(^2\).

Table 1

<table>
<thead>
<tr>
<th>m/e</th>
<th>Assignment</th>
<th>Relative Raw Signal</th>
<th>Relative Calibrated Atomic Signal(^b)</th>
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<tr>
<td>23</td>
<td>Na</td>
<td>1820</td>
<td>60</td>
</tr>
<tr>
<td>27</td>
<td>Al</td>
<td>440</td>
<td>880</td>
</tr>
<tr>
<td>28</td>
<td>Si</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>CF</td>
<td>2670</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>SiO</td>
<td>420</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>SiF</td>
<td>1130</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>Cr</td>
<td>130</td>
<td>100</td>
</tr>
<tr>
<td>56</td>
<td>Fe</td>
<td>100</td>
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<tr>
<td>58</td>
<td>Ni</td>
<td>120</td>
<td>170</td>
</tr>
<tr>
<td>63</td>
<td>Cu</td>
<td>190</td>
<td>160</td>
</tr>
<tr>
<td>65</td>
<td>Cu+Na(_2)F</td>
<td>130</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Derived from the data of Figure 3.

\(^b\)Using NBS stainless steel Cl154 and Si-Al alloy powder as calibrants, see text.
The thermal evolution (or "thermal profile") of each compound was obtained simply by recording mass spectra during heating. An example of the time/temperature behavior for masses 105 and 107 is shown in Figure 7. Unfortunately, the heated sample probe did not have a linear temperature ramp available at the time. All masses are recorded simultaneously by the time-of-flight mass spectrometric technique. It is apparent from just this example that there is a significant variation in the evolution for the different molecules. The exact nature of these evolution or formation rates is not understood. However, it is apparent that molecules such as simple aromatic or linear hydrocarbons, if physisorbed, would undergo desorption at much lower temperatures than those displayed in Figure 7. Hence it seems safe to conclude that these molecules are outwardly diffusing (intact or still being formed, reacting, or pyrolyzing) from within the crystal by way of microscopic cracks or some other structural defects.

A rough estimate of the amount of compounds evaporating from the surface of the sample cleaved olivine crystal during the course of an observation can be given by data such as presented in Figures 6 and 7, given a high ionization probability and making estimates of the system transmission and molecular thermal velocities. Quickly, over a heating observation lasting 20 min., mass 105 had an average peak height of ~10,000 counts (here, 1 analog count = 2 mV) in a spectrum of 200 laser pulses, or 50 counts/pulse. An average ion registers a signal of 10 counts (20 mV, with amplification), so that means an average of 5 ions/pulse. Mass 105 represents roughly 1/20 of the total spectrum, meaning ~100 ions/laser pulse for all masses. With an estimate of 10^2 combined ionization and mass spectrometer transmission for this set-up, then from a focal volume of 3 x 10^-3 cm^3, 100 detected ions/pulse corresponds to 10^4/(3 x 10^-3 cm^3) or 3 x 10^6/cm^3 neutral density (10^-10 torr), total "pressure" right above the surface. Taking a velocity of 2 x 10^4 cm/s, the flux density is roughly (2 x 10^4 cm/s) (3 x 10^10/cm^3) = 6 x 10^4/cm^2 s. With a macroscopic sample surface area of ~42 cm^2, in 20 minutes this adds up to ~ (10^4 molecules/cm^2) (0.2 cm^2) = 2 x 10^5 molecules; for a nominal molecular weight of 100, this is 3 x 10^9 gram.

Prospects for Submicron Chemical Analysis with SALI

Given the high sensitivity demonstrated for SALI it seems reasonable to expect that this method will be amenable to implementation with a finely focused liquid metal ion beam for chemical mapping, as has previously been done with SIMS [12]. Owing to SALI's higher quantitative capabilities and more chemically uniform sensitivity compared to SIMS, this seems desirable. Though such microanalysis has not yet been performed, one can expect this to be a temporary situation. Calculation of a typical expected signal for SALI microanalysis follows.

Using specifications for a commercial high flux liquid metal ion source such as 300 pA in a 200 nm spot diameter, and pulsing the ion beam...
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with a 1 μs pulse length (which is about optimum for maximizing efficient use of surface material), a sputter coefficient of 5 leads to 10⁶ atoms sputtered per pulse. With a feasible detection efficiency (useful yield) of 10⁻³, 10 photions will be detected per ion beam pulse. If the ionization laser operates at 250 Hz, one can make a picture element (pixel) in ~0.2 second (50 laser and ion beam pulses) resulting in about 500 ions detected and removing ~1 monolayer depth. The chemical map is built-up by accumulating the TOF mass spectrum for a given spatial location, storing in temporary computer memory the TOF mass spectral data, moving the ion beam to the next position, and analyzing the spectrum and storing it in permanent memory while data for the next pixel is being recorded, and so on. This should permit a scan of 10⁵ pixels in about half an hour with simultaneous detection for each pixel of all masses at concentrations ~1% or greater. This is a worthwhile goal.

There are obvious trade-offs possible for parameters such as data acquisition time, sensitivity level, number of pixels, spatial resolution, and ion beam current.

Future Improvements

Future Improvements

A second generation SALI apparatus is currently under construction. The main improvements anticipated are: (1) a new duoplasmatron ion gun and the addition of a liquid metal ion gun, (2) better ultrahigh vacuum conditions including a UHV sample introduction system, (3) a new ionizing laser with much higher power densities and greater repetition rate, (4) improved time-of-flight mass spectrometer transmission, and (5) a variable focus and flux electron flood gun. These improvements should often act cooperatively in achieving significantly improved capabilities for surface analysis, pushing the technique toward its theoretical limits.

Conclusions

Representative examples have been presented showing a wide range of surface and material analyses showing the versatility of the surface analysis by laser ionization technique. Both bulk analyses and static surface analyses have been performed; semiquantitative raw data can be made quantitative with the use of standards which are not necessarily close to the composition of the unknown; the method has been applied to metals, semiconductors, insulators, and organic systems. With minor improvements, it is expected that the SALI method can successfully be applied to sensitive and general quantitative submicron chemical mapping.

Acknowledgments

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C. H. Becker

Instruments Corporation, and Intel Corporation is gratefully acknowledged.

References


Discussion with Reviewers

R. Levi-Setti: What extraction voltage was used for the collection of the post-ionized ions? Are these accelerated further, prior to injection into the TOF-MS?

Author: For this particular set-up, the photoions were extracted with a field strength of 2 keV/cm, to a drift energy of 1.3 keV. They were not further accelerated.

R. Levi-Setti: Is there evidence of doubly ionized species among post-ionized atoms and if so, how does the doubly ionized fraction depend on the laser power density?

Author: Doubly ionized species have been observed at our working laser beam conditions. The behavior with laser power is a function of the
species. The most readily formed doubly charged ions are from the open shell group 3-7 transition metals. Many doubly charged elements of high second ionization potential have not yet been observed. Further discussion and example can be found in References 3 and 7.

R. Levi-Setti: Is there any difference in the isotopic ratios measured by conventional SIMS vs. nonresonant multiphoton ionization? 

Author: We have not yet observed any difference.

R.W. Linton: You indicate that SALI has a demonstrated useful ion yield of $10^{-4}$, although $10^{-3}$ is expected with new instrumentation. Would you briefly discuss the instrumental and fundamental factors limiting useful yields?

Author: The useful yield of a mass spectrometer system can be separated as the product of three factors: (1) the amount of material that can be placed within the ionizing region at the time of ionization, (2) the ionization probability, and (3) the mass spectrometer transmission, including detector response. The first factor can be broken down further into the solid angle fraction subtended and the fraction of the particles' velocity distribution that will fall within the ionization volume at the time of (pulsed) ionization. By working close to the sample ($< 1$ mm) with a laser beam cross sectional area of a few tenths of a mm and extracting over about a 5 mm length of the laser beam ionization volume, a solid angle efficiency of about 10% can be obtained. For an ion beam pulse of about 1 microsecond length and a velocity distribution common to sputtered atom emission, about 5% of the particles with useful emission angles will fall within the ionization volume. This gives a combined efficiency of 0.5% for factor (1). The ionization (2) usually can be saturated (very high probability) within the focal volume. The mass spectrometer efficiency (3), including a 50% figure for the microchannel-plate particle detector, should be about 20-30% for the new system, and a factor of 10 lower for the older system. This includes the extraction and focusing lens systems as well as the time-of-flight mass spectrometer itself. (Note that the three factors are coupled through the ionization volume to be used.) Combining these factors gives the two values of $10^{-3}$ and $10^{-4}$.

R.W. Linton: Can you make any generalizations about the relative importance of polyatomic ions in the SIMS vs. SALI experiment? The ratios of $Ga^{2+}, GaAs^{+},$ or $As^{+}$ to $Ga^{2+}$ in Figure 3a vs. Figure 3b would serve as a simple example.

P. Williams: In many instances, detection limits in SIMS are imposed by mass spectral interferences due to cluster species, or to instrument memory effects, rather than the ionization efficiency. Would you comment on the limitations on your technique imposed by mass spectral interferences arising from sputtered clusters?

Author: It is not really clear just from an examination of Figure 3 whether the ratio of molecular to atomic photoions is as large as for secondary ions. (Figure 3 does show $Ga_2^{+}/Ga$ to be larger for SIMS, with simply low SIMS detection efficiency for the high ionization potential $As_3$.) However, from experience with many different inorganic samples, I can say that in general there are significantly fewer molecular photoions relative to atomic ions for SALI than for SIMS. This is especially true for triatomic and larger species. The primary reason for this is the process of photodissociation. In instances where a molecular interference is especially troublesome, one has the option of increasing the laser intensity to a maximum and/or changing the laser wavelength in order to maximize photodissociation. Furthermore, in instances where doubly charged photoions can be readily created, one can alternatively monitor the doubly charged species to alleviate interferences; this would always be unambiguous for odd values of atomic masses giving half-integer m/e peaks, even for modest mass resolution.

P. Williams: Is it really possible to achieve uniform (saturation) ionization of both low and high ionization potential species given that (a) the sputtered plume must always be larger than the laser focus, and (b) the power density, even if constant across the focus, varies longitudinally, i.e., through the focus? It would appear that there will always be a larger ionization volume for species which can be ionized with a smaller number of photons.
Author: It is possible to achieve uniform ionization within the intense focal region of the laser beam by saturation. Those species which lie outside the laser beam at the time it is pulsed clearly will not be ionized. The pulsed laser ionization acts as a density detector, not as a flux detector, and this has implications relating velocity (as well as angular) distributions and quantitation, without the use of standards; this is discussed elsewhere, e.g., in Ref. 7. The quality of the spatial extent of the laser beam in the transverse direction (its cross-section) actually is of more importance than the length of the extraction volume. Even with saturation near the center of the beam, more easily ionized species will have somewhat larger effective ionization volumes because the outer region of the laser beam will be more effective. This is a reason for having good focusability, so that there is rapid fall-off of the intensity away from the center section of the beam (such as for a Gaussian) so that there is minimal variation in effective volumes. Otherwise, some calibrant is needed for good quantitation. The larger the number of photons required for ionization, the higher the power density required for saturation; for some species, e.g., atomic O, F, and Ne, very high power densities are needed, such as $10^7$ W/cm$^2$ at these UV wavelengths for ns pulses.

P. Williams: In your spectra there appears to be a continuum background signal, decreasing from low to high mass. How does this arise, and what limit does it place on your detection capability?

Author: First, all of the spectra shown were collected in analog mode with a 100 MHz transient digitizer; the baseline for such a device, unlike pulse counting, is rather arbitrary, and this is one reason data frequently are displayed in arbitrary units. This is also why frequently the baseline is not shown at zero, though it could have been so plotted; doing so indeed would be arbitrary. The spectrum in Fig. 2 is sloping from what I believe to be a scattering process, tailing off in time after an intense mass peak, in this case atomic Cu (off scale), but also visible to a lesser extent for Cu$_2$. It is suggested that this is due to scattering from the high transmission grids of the ion reflector. We plan to investigate this with a gridless reflector. The limitation in detection for a case like Fig. 2 then depends how close the mass is, on the higher mass side, to an intense peak. Ppm level signals are clearly seen in Fig. 2. I am not certain what is causing the sloping baseline in Fig. 3a. Most TOF SIMS spectra taken on the machine do not show this; it might have been electronic in nature. Part of the baseline noise that also should be noted is electronic noise, in this case mostly from the transient digitizer bit uncertainty with averaging many cycles. Clearly pulse counting is advantageous in this respect for very low level concentration determination. There seems to be a slight sloping baseline in the low mass region of Fig. 3b, again of unknown origin, but not considered representative. The data of Fig. 3 is now actually quite old. Figures 4, 5, and 6 do not show this sloping baseline, and they are considered representative for spectra displaying fairly high concentration signals. It is expected that signal levels in the ppb range will be routinely detected with new instrumentation.

P. Williams: An advantage of your approach which you miss is that the high ionization efficiency eases the problems of discriminating against background gas signals and secondary ion signals, both of which are considerably higher than the post-ionized signals with e.g., electron impact ionization. In general, it would be nice to see some comparison with the other sputtered neutral analysis schemes as well as with SIMS. You state, 'The SALI method should be compared and contrasted' with the resonant ionization approach. What are the relative merits of the two approaches? The resonant technique has the advantage of great selectivity, but then has problems with quantification -- because the signal depends on sputter yield and ionization efficiency, for quantitative analysis one needs to monitor the sputtered flux of a major element (tedious with a tuned laser) and also to estimate ionization efficiency (i.e., fraction of the sputtered plume intercepted by the laser). The SARISA people even try to calculate their sputtered silicon flux, which must be one of the worst approaches yet to quantitative analysis. In contrast, SALI gives all the necessary signals and is a far more promising tool for general analytical use.

Author: I agree.