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LIMITS OF QUANTITATIVE MICROANALYSIS USING SECONDARY ION MASS SPECTROMETRY

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Abstract

The limitations on secondary ion microanalytical performance imposed by ionization probabilities, mass spectrometer transmission, requirements for standards and sputtering artifacts have been investigated. The sensitivity of a modern magnetic mass spectrometer for sputtered B+ from oxidized Si is ~10^{-10} ions detected/atom sputtered. For this sensitivity, it is shown that ion microscopy of a part-per-million impurity is limited in lateral resolution to ~1 µm. For a 1% impurity, lateral resolution of ~30 nm is achievable. Depth profile analysis at the ppm level requires sample areas ~10 µm². Isotope abundance determinations in volumes ~1 µm³ require the concentration of the least-abundant isotope to be >1%.

Key Words: Secondary ion mass spectrometry, detection limits, quantitative accuracy, depth resolution, lateral resolution, ion microanalysis

Introduction

The unique feature of secondary ion microanalysis (SIMS) is that it combines microscopy with chemical specificity. The technique thereby allows quantitative chemical analysis, in contrast to the more qualitative nature of non-chemical imaging techniques (optical microscopy, scanning electron microscopy). Performance limits quoted for the technique usually include lateral (x-y) resolution better than 1 µm, depth (z) resolution better than 10 nm, and detection limits in the ppm to ppb range. The prospects for a three-dimensional chemical microscopy are often discussed. SIMS also allows quantitative analysis with an accuracy better than 10% and precision of a few percent. However, each of these attainable limits is to a large extent exclusive of the others. With the increasing availability of sub-micron beam sizes, it is of interest to examine the interrelated performance limits of SIMS microanalysis. McHugh, Levi-Setti and Fox and Slodzian have discussed the interrelationship between sample volume and detection limits earlier. The relationship between these factors and the other performance features listed above has not been comprehensively addressed.

The useful yield

The ultimate limiting factor in secondary ion microanalysis is the amplitude of the secondary ion signal detectable from a given microvolume. This signal is determined by the ionization probability, $y_i$, of the sputtered atoms (molecules) and the transmission $T$ of the secondary ion optics and mass spectrometer. Both parameters vary over a wide range; $y_i$ is a sensitive function of the ionization potential or electron affinity of the sputtered species, and of the chemistry of the sputtered surface, while $T$ depends critically on instrumental design. The optimum SIMS performance limits quoted above are typically obtained for easily-ionized species, sputtered from oxygenated or cesiated surfaces (for positive or negative ions, respectively), analysed with the highest transmission secondary ion mass spectrometer, and with performance sacrificed in all degrees of...
freedom but the one to be optimized. Because $y$ and $T$ are difficult to measure independently (each requires knowledge of the other), they are usually combined into a quantity termed the "useful yield", i.e., the ratio of the number of mass-analysed ions detected to the number of atoms of that species sputtered$^{16}$. This quantity is measurable, most simply using ion-implanted samples where the number of atoms sputtered from a given analysed area is given accurately by the implant dose. Table 1 shows useful yield data for high transmission SIMS instruments based on quadrupole (Atomika) and magnetic (Cameca) secondary ion analysers. The data from the author's laboratory was obtained with gas-phase oxygen flooding of the sample in addition to the primary oxygen ion beam, to assure complete saturation of the surface with oxygen.

Table 1

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Useful yield for $B^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cameca IMS3f$^h$</td>
<td>$6 \times 10^{-3}$</td>
</tr>
<tr>
<td>Atomika a-DIDA</td>
<td>$3 \times 10^{-4}$</td>
</tr>
<tr>
<td>Cameca IMS3f (this work)</td>
<td>$2 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

The data in Table 1 should be representative of magnetic and quadrupole secondary ion analysers optimized for good transmission. Notice in particular that without oxygen enhancement (or cesium enhancement for negative ions) useful yields drop precipitously by three orders of magnitude for boron in silicon for example$^{25}$. Such a sacrifice of signal is unacceptable in any of the sample-limited analytical situations described below.

Limits of lateral resolution in depth profiles

The importance of the useful yield in microanalysis is displayed in a sample calculation. Consider a requirement to obtain a depth profile of implanted boron in a single transistor, some 3 x 3 microns in size, on an integrated circuit chip, to determine a junction depth. Each data point will involve integration of the $B^+$ signal over a selected sputtered depth interval. For adequate depth resolution, the interval should be no greater than 10 nm. For adequate precision in determining the junction depth, the minimum acceptable signal from a 10 nm depth interval should be no less than 100 counts (10% standard deviation). Given an instrument with a useful yield for boron of $1\%$, $10^4$ boron atoms must be sputtered from the analytical microvolume in order that 100 ions be detected. $10^5$ boron atoms in a $3 \times 3$ micron x 10 nm microvolume is a concentration of $1 \times 10^{17}$ B/cm$^3$ (about 2 ppm), so that this represents a detection limit for quantitative microanalysis in this area for this particular instrument and species.

Depth resolution in sputtering analysis can in principle be excellent -- recent studies show that at least 80% of sputtered atoms come from the outermost atomic layer$^5$. However, if erosion proceeds beyond the first layer, depth resolution is limited by the effects of ion beam mixing$^{22}$. Roughly speaking, ion beam mixing homogenizes surface and subsurface material over a depth on the order of the primary ion range, $R_p$. Definitions of depth resolution vary depending on the analytical situation. For a delta-function feature broadened into a Gaussian, the resolution can be defined as twice the standard deviation of the Gaussian; an equivalent measure for a broadened step function is the distance over which the signal varies from 16% to 84% of...
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maximum. Alternatively, two features can be said to be chemically resolved if the one contributes less than, say, 10% to the signal from the other; the resolution then depends on the relative intensity of the signals from the two features. Ion-beam mixing tails decay exponentially, with a characteristic length on the order of the primary ion range (i.e., the signal decays by a factor of 10 over a distance \( \sim 2.303rR \)), where \( r \) is a factor, typically between 0.5 and 2, introduced to correct for preferential sputtering effects; two dilute features differing in concentration by a factor, \( K \), will be chemically resolved if separated by a distance \( 2.303rR \log_{10} K \).

At low primary ion impact energies -- 1 - 3 keV -- ion ranges are shallow and depth resolution limits are some few nanometers. However, the necessity for high primary energies (10-50 keV) to achieve acceptable beam brightness in sub-micron probes means that primary ion ranges will be large, and depth resolution in sub-micron systems will be significantly worse -- some tens of nanometers -- than in systems optimized for depth profile studies.

The importance of high depth resolution should not be underestimated. In optimized samples -- thin films homogeneous in the x-y plane -- ion microanalysis offers a one-dimensional chemical microscopy with resolution comparable to the analytical electron microscope and part-per-million detection limits. Figure 2 shows a depth profile through an epitaxial metal multilayer film prepared by molecular beam epitaxy with individual layer thicknesses of 4.3 nm. The layers are almost resolved -- depth resolution as defined above is \( \sim 5 \) nm. Note that for laterally homogeneous thin films such performance is not incompatible with sub-ppm detection limits, because large areas can be sampled.

The prospects for a three-dimensional chemical microscopy are again limited by the useful yield. Figures 3 and 4 indicate the relationships between analysed area, or beam diameter, and sampled depth for analyte concentrations of 1 ppm and 1%. It is clear that localization in the x-y plane to within present

![Fig. 2. Depth profile through a Ta-Nb epitaxial multilayer on a sapphire substrate. The Ta and Nb layer thicknesses are 4.3 nm. Primary beam: O₂ at 5.5 keV impact, ~ 30° to sample normal. Oxygen gas jet on. The Nb profile (complementary to the Ta profile) is deleted for clarity.](image1)

![Fig. 3. Relationship between analysed area and sampled depth for 1 ppm detection limit (minimum signal 100 counts). Also for isotope ratio determination (single determination, 10⁶ counts) for 1% abundant isotope. It is assumed that the major isotope level is \( \geq 1\% \).](image2)

beam capabilities -- \( \sim 100 \) nm -- is only possible within comparable sputtered depths at rather high concentrations, and for high secondary ion transmission and yield (again retaining the requirement that the minimum useful signal is 100 counts). Of course, the limits relax for higher concentrations, but, in the concentration regime above 1%, Auger electron spectroscopy is capable of analysis with 100 nm resolution, and can also give semi-quantitative (30-50%) analysis without standards.

A final, and most serious, limitation on depth resolution is the development of sputter-induced roughening. Initially flat sputtered surfaces behave as though metastable under ion bombardment, and if differences in erosion rate exist for any reason -- different grain orientation in polycrystalline surfaces, chemical inhomogeneities (including contamination), or simply the presence of crystal imperfections -- the surface rapidly develops microfeatures.
comparable in scale to the eroded depth. Unfortunately, the most interesting samples for imaging are exactly those most prone to roughen chemically inhomogeneous materials, grain boundaries, etc. Thus, three-dimensional microscopy, e.g. of a plant or animal cell with dimensions of several microns, or of a fine-grained polycrystalline material, does not seem feasible with nm depth resolution unless the roughening problem can be overcome. Two-dimensional microscopy (x-y imaging), on the other hand, should not suffer from the same limitation, given that the eroded depth is no greater than the lateral resolution desired.

Limits of quantitative analysis

It is well-known that ion yields in SIMS are highly variable, and not yet quantitatively explicable by sputtered ion emission models. Thus standards are required for quantitative analysis. Because ion yields vary sensitively with the chemical composition of the sputtered substrate, standards should either have the same major element composition as the analytical sample, or bracket this closely. The difficulties of solid-state chemistry severely inhibit conventional sample preparation; the difficulty is exacerbated when the substrate composition is not independently known as will frequently be the case in sub-micron areas. By far the most powerful standards technique for SIMS is the use of ion implantation. Comparison of the mean count rate over the depth profile of an implanted analytical species with the mean concentration over that depth, calculated from the implanted dose, calibrates the signal strength directly in concentration units. It is essential that the implant concentration be low enough (typically 1% or lower) to ensure that the signal is linear with concentration. Impurity levels above a few percent become comparable with the major element levels and can themselves influence ion yields. The assumption that the signal is linear with concentration then becomes invalid, and the simple linear averaging of the integral signal is not possible. A major source of ion yield variations arises from variations in the amount of surface oxygen or cesium. Such variations can arise under oxygen or cesium in bombardment if the impurity level in question is high enough to influence the sputtering yield. Alternatively, if oxygenation is accomplished by adsorption of oxygen from the gas phase, an impurity-induced change in sticking coefficient can lead to changes in ion yields.

Analysis using implant standards is particularly simple when the implanted profile is superimposed on the analyte level in the analytical sample, as the analyte concentration can be directly determined from the linear concentration scale thereby established. Major element levels (> 1%) can similarly be determined if the element in question has a minor isotope which can be implanted as a standard. The accuracy of such analyses has been shown by comparison with Rutherford backscattering techniques to be ~ 10%.

The use of implant standards in microvolume analysis imposes relatively minor restrictions. The main requirement is that the implant profile be contained in a single-phase region over an in-depth extent sufficient to contain > 90% of the profile (again for 10% precision) and that > 90% of the profile lie deeper than 10-20 nm, because ion yields can vary in the near-surface region as the implanted primary beam level increases. This means that the implant peak should lie at a depth of 50-100 nm, and that the single-phase region should extend in-depth roughly three times as far. On the other hand, depth resolution requirements are loosened; one needs only enough resolution to distinguish the implant region from the intrinsic background. It seems safe to say that the implant standard technique will allow quantitative "bulk" analysis of ppm levels in single-phase regions with lateral dimensions of a few microns, and depths of a few hundred nanometers. At the 1% level, Figure 4 indicates that quantitative analysis (with optimum useful yield) should in principle be possible in areas with lateral dimensions as small as 10 nm (but depths ~ 100-200 nm). Clearly, such analyses would proceed in a rastered beam mode with electronic aperturing used to restrict the signal to the desired region. It seems probable, however, that lateral transport of sample material during the erosion of some hundreds of nanometers would cause some degradation of lateral resolution, so that a realistic limit for both lateral and depth resolution in quantitative analysis might be ~ 100 nm.
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![Graph showing relationship between analysed area and depth for isotope ratio determination](image)

**Fig. 5.** Relationship between analysed area and depth for isotope ratio determination (single determination -- 10⁶ counts) for 50% abundant isotope. It is assumed that the major isotope level is \( > 1\% \). Also for qualitative imaging of 1 ppm component (minimum signal 1 count/pixel).

Isotope ratio determination

The capability for isotope ratio determination in microvolume regions of complex samples is an important attribute of SIMS, as the difficulties of microchemical manipulation may largely be avoided. Often the isotopes in question are present in high abundance -- 1% or higher, promising high signal levels. Countering this advantage is the fact that significantly higher precision is generally necessary for isotope ratio determination. Although a few isotopic anomalies may be so large as to be measurable with 1% precision, in general precision on the order of 0.1% is a minimum requirement. Counting statistics then demand at least 10⁶ ions in the minor isotope channel. From Figures 5 and 3 the analysed volumes necessary to comply with these restrictions can be determined for two cases -- minimum minor isotope levels (product of abundance and elemental concentration) of 50% (the maximum possible) and 1%. Since depth resolution is generally not a requirement, it seems possible in principle with the highest useful yield to determine isotope ratios with \( \approx 0.1\% \) precision in microvolumes on the order of 1 \( \mu \text{m}^3 \) for 1% abundant isotopes.

Improvements

The restrictions imposed on the discussion in the earlier sections of this paper have been quite strict -- they are those in practical use for dopant analysis in semiconductors, where 10% precision or better is demanded, together with 10 nm depth resolution, albeit with unlimited analytical area, for trace impurities. It is undoubtedly true that many important problems exist to be solved where these restrictions do not apply -- where qualitative imaging rather than quantitative microanalysis is sufficient, for example. This section examines performance possibilities with these relaxed restrictions and the possibility of improvement in the physical restriction -- the useful yield.

Qualitative imaging

Images frequently can solve problems with yes/no answers -- "is element X present in a given region in high concentration or not?" In such instances a signal strength of 1 count/pixel may be sufficient; the information in a single pixel may have a large uncertainty, but the overall image shows clearly that the element in question is, or is not, in a specified location. Figure 5 shows microanalytical limits for this relaxed criterion. Assuming that localization is optimum when the sampled depth is no greater than the beam diameter, it is clear that qualitative imaging is possible at the ppm concentration level with a resolution of ~100 nm.

Stable isotope tracer studies

Requirements for isotope ratio determination may occasionally be relaxed, if, for example, isotopic anomalies of several tens of percent were discovered. But in general the restrictions outlined in the previous section will apply. However, stable isotope tracer studies can involve qualitative localization, if the tracer levels are sufficiently high. In such instances, limits of resolution can approach those indicated in Fig. 4 -- 20-50 nm for comparable beam diameter and sampled depth.

Improvements in ionization probability

Although ionization probabilities are not known with great accuracy, it is not unreasonable to ascribe the 2% useful yield value in Table 1 to a combination of 20% probability for ionization and 10% transmission. Recent developments in multiphoton resonant ionization (MPRI) seem to indicate that sputtered neutrals can be ionized with 100% efficiency. It is tempting to consider whether this approach can eliminate the loss in the sputtered ion formation process. The outlook does not seem promising, for several reasons. First, ionization probabilities for sputtered species seem to be significantly greater than 10% for lower ionization potential species; for example, Kimock et al. estimate that some 25% of the sputtered atomic flux from oxidised indium is In^+, 25% is neutral excited and, only 50% is ground-state In^+. Similarly, studies by Grischowsky et al. indicate that > 90% of the flux of sputtered ground-state Ba atoms from barium metal disappears on oxygenation, again presumably into excited and ionized channels. Bernheim and Slodzian estimate that yields of Cu^- and Au^- from fully cesiated Cu and Au surfaces are ~50% and 100% respectively. Thus at best minor improvements seem possible by sampling the sputtered (ground-state) neutral with the MPRI technique, at least in instances where the sample chemistry can be manipulated by oxygenation or...
Mass spectrometer entrance aperture (and its limits extensively demagnifies the secondary beam crossover at the areas. By selecting a transfer lens which transmits the analysed area on the sample to ~25 microns, useful yields have not been determined positive and negative ion yields $B_1$, and the high yields found for $t$-$i:s^+$ under $c$s$+$ bombardment, other examples of the latter approach are the matrix element as for instance SiN$^-$ for N in silicon or GaN$^-$ for N in GaAs$^{21}$, in or combination with the primary beam species, e.g. CN$^-$ which can be formed in high yield if the primary ion is a carbon-containing species. In this case molecular species can be used to advantage, either formed by combination with the matrix element as for instance SIM$^-$ for N in silicon or GaN$^-$ for N in GaAs$^{21}$, or in combination with the primary beam species, e.g. CN$^-$ which can be formed in high yield if the primary ion is a carbon-containing species. Other examples of the latter approach are high yields found for $M$-$i^+$ under $C$s$^+$ bombardment, for species (M = Zn,Cd) which have low atomic positive and negative ion yields$^{16}$, and the high MD$^+$ yields observed from oxygenated surfaces of, e.g. $U^{13}$. Useful yields have not been determined for such species, so that absolute sensitivities cannot be estimated here. Nevertheless in many instances it appears possible to manipulate the chemistry of the analytical process to great advantage to optimize ion yields and detection limits.

Improvements in secondary ion mass spectrometer transmission

Slodzian has analysed this problem extensively$^{17}$ and points out that higher transmission is indeed possible from limited areas. By selecting a transfer lens which demagnifies the secondary beam crossover at the mass spectrometer entrance aperture (and limits the analysed area on the sample to ~25 microns) the useful yield is improved by about a factor of 3 over that listed in Table 1 for the Cameca IMS 3F. If indeed the useful yield of Table 1 corresponds to a transmission of 10%, then transmission from micron and sub-micron regions can be as high as 30% (useful yield ~6% for boron in silicon). The performance limits quoted earlier can then be appropriately modified. It is clear, however, as has repeatedly been stressed$^{17,12}$ that ion microanalysis can only achieve its full potential when the secondary ion optics are as carefully optimized for the task as is the primary optical system. Compromising the secondary ion collection efficiency in order to achieve optimally small working distances for the primary ion objective lens can sacrifice all possibilities for useful microanalysis, even if the primary beam is exceptionally small and bright. It seems clear that increased attention should be paid to the suggestion of Liebl$^{11}$ that primary beam focussing and secondary beam collection be considered as an integral problem.

Elimination of roughening

It is clear from Fig. 5 that the capability to erode materials without inducing gross roughening would make possible qualitative three-dimensional microscopy with ~10 nm resolution for constituents at the 0.1% to 1% level. Sputtering with reactive species or saturation of the surface with oxygen during sputtering can reduce roughening$^2$, but in general does not eliminate it$^{24}$. In sample thinning for electron microscopy rotation of the sample in a sputtering ion beam directed at a large angle to the surface normal is felt to give smoother erosion. Clearly, such rotation is incompatible with simultaneous high resolution imaging of the surface; however, sputtering with rotation in an auxiliary (large area) ion beam could be combined with intermittent sampling in the microfocussed beam. In fact, such a technique could also be combined with scanning electron microscopy, so that three-dimensional imaging should be possible here also, although without the chemical specificity of SIMS.

Conclusions

This article has reviewed some of the practical limitations placed on secondary ion microanalysis by the destructive nature of the sputtering process and the inefficiency of ionization and collection of the sputtered signal. It should be clear that the performance limits of the technique -- lateral resolution, depth resolution, trace level detection -- cannot all be achieved simultaneously, ultimately because small microvolumes do not contain sufficient atoms to form a statistically significant signal. Sacrifice of any part of the signal, by foregoing chemical enhancement of ionization probabilities or inadequately designing secondary ion optics, should be strenuously avoided. In the limit, if detection limits degrade to those routinely attainable by Auger spectroscopy, the advantages of the SIMS technique become the relatively minor ones of isotope and hydrogen sensitivity. In contrast it
now appears that the limitations on performance can be significantly less severe than had been assumed in the design studies of Levi-Setti and Fox*: ionization probabilities in the range 10-100% can be achieved, rather than 1%, and mass spectrometer transmission from small areas may exceed 10%. Thus the prospects for SIMS microanalysis, when both instrumental and analytical parameters have been optimized, appear bright.

Acknowledgements

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References

Discussion with Reviewers

R. W. Linton: In addition to ion yield and transmission, a limitation to sensitivity in direct-imaging ion microscopes (e.g., Cameca IMS 3f) is the conventional microchannel plate array detector. What is the magnitude of improvement that you estimate may be gained by the use of newer channel plate technologies such as higher gain dual stage devices, direct anode encoders, etc.?

Author: The calculations presented in the paper assume 100% efficiency in the detector -- the calculated useful yield values for the Cameca instrument were for ion currents measured using an electrometer, and the calculations do not include losses in image conversion. Clearly, losses in image convertors degrade performance, and useful work is now proceeding to alleviate these problems. Ideally one needs quantum efficiency of one for the ion-to-electron conversion step, and a uniform gain thereafter. Thus when coupled with noise levels low enough to use anode encoders which allow spatially-resolved pulse counting these appear to be preferable to analog systems which introduce a noise level associated with the statistical straggle in gain in different channels of a microchannel plate, apart from any noise and non-linearity of the analog detector (vidicon or CCD array) itself.

R. W. Linton: In addition to advances in primary sources and secondary optics, many possibilities exist to use modern image enhancement or restoration algorithms to improve sensitivity and/or spatial resolution (Kowalski, Anal. Chem. 55 (1983) 557). Would you comment on the general role of image processing techniques for improved quantitative SIMS microanalysis?

Author: I have no direct experience in this area; there appear to have been no significant SIMS analytical problems solved with such techniques to date. The problem seems to be that resolution enhancement is only the first of a suite of problems. By definition, resolution enhancement is required at the boundary between two phases; by definition, matrix effects are changing (non-linearly) in that region. Thus, without information about the ion yield effects, standard techniques to enhance spatial resolution may not greatly help the quantitative chemical analysis problem, although they may certainly enhance image quality.

R. W. Linton: What is your overall view of the relative merits of ion microscope vs. microprobe approaches to high spatial resolution in the next generation of SIMS instruments?

Author: The limit of resolution in the ion microscope is ~0.5 µm; in fact, the ion microprobe approach begins to excel below ~5 µm because lateral resolution in the microscope mode is increasingly achieved at the expense of sensitivity. Given the ability to deliver a micron or sub-micron probe to a sample in a high electrical field (for efficient secondary ion extraction) the microprobe approach must be preferred in sample-limited situations (e.g., depth profiles in limited areas). However, where the resolution and sensitivity of the ion microscope are adequate, this approach is strongly to be preferred on the grounds of speed (parallel rather than serial imaging).

S. J. B. Reed: Please comment on possible practical limitations in the use of ion implantation for quantifying trace element analysis with particular reference to: (a) range of choice of implanted elements, (b) purity of implanted species, (c) uniformity of dose and accuracy of dose monitoring.

Author: Dose accuracy and uniformity in commercial implanters are generally good (i.e., uniformity of 3-5% across a 6" (15.3 cm) dia. silicon wafer, accuracy generally better than 10%). However, problems can arise, and not be detected; one needs to calibrate the personnel as well as the implanter. Where possible, we try to have our implant doses separately measured by Rutherford backscattering spectrometry. The range of implanted species is also limited in commercial systems; the number of research implanters capable of dealing with exotic elements or isotopes, (and odd sample geometries) is small. Purity is an issue that needs to be watched -- as noted in reference 21, implanters are low resolution mass spectrometers and interferences should be suspected wherever they are possible. On the other hand, one can check for impurities using SIMS.

R. Gijbels: Could the author comment on the instrumental characteristics required for arriving at a 0.1% precision (counting system dead time, artifacts due to changing count rate when switching from one isotope to another, especially effects in the electron multiplier)?

Author: I'm not aware of artifacts due to changing count rates, other than the problem of count losses in the major isotope signal but for signals so different that the higher one is best be calibrated in the material of interest.

R. Gijbels: Could you comment on magnetic and quadrupole instrument transmission and on the electron multiplier detection efficiency as a function of mass and chemical nature of the ionic species?

Author: Transmission in magnetic instruments should be independent of mass; quadrupole instruments may discriminate to some extent against higher masses, depending on the tuning of the quadrupole. Both types of instrument will exhibit some chemical discrimination, because different species, particularly atomic and molecular species, can have different initial energy distributions. In addition, electron multipliers will discriminate to a small extent (even in pulse-counting mode) because at typical impact energies of 3-4 keV,
there is a 10-20% species-variable probability that an impact will not generate a secondary electron. However, the sensitivity calibration necessitated by the massive chemical discrimination in the sputtered ion ejection process simultaneously calibrates these other factors, so that they are not analytically significant.

Reviewer IV: Can you comment on the role of initial sample roughness on resolution?

Author: The consideration of resolution limitation due to the initial sample roughness is somewhat meaningless; either one finds a microarea which is initially flat, or one does not attempt a depth profile which is expected to have any quantitative significance.

G. Blaise: Regarding the first sentence in your section on "Limits of Depth Resolution", it is known for a long time, from experiments or simulations, that the major part of sputtered atoms come from the outermost atomic layer. See for example Harrison et al., 1973, Rad. Effects, 17, 167. Authors mentioned in text ref. 5 seem completely to ignore the work done on this problem. Furthermore, the estimation of 80% is not really an independent measure of the fraction of atoms sputtered from the top layer because, as they say, "it is based on the plausible assumption that most of the atoms sputtered from a surface originated in the top monolayer".

Author: Harrison's simulations are model-dependent, in particular on the potential function used for the ion-surface interaction. They cannot be considered evidence for escape depths. The experiments of Dumke et al. (text ref. 5) are the first direct measure of the sputtered fraction from the outermost monolayer, a segregated monolayer in liquid metal alloy which is constantly renewed by diffusion. They are of great significance.