Microanalysis of solid surfaces by Secondary Neutral Mass Spectrometry

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Received October 30, 1992

Summary. The application of Secondary Neutral Mass Spectrometry (SNMS) for high resolution microanalysis of solid surfaces is a rapidly evolving field. Significant progress which has recently been made, as the different SNMS techniques are further developed, includes two important aspects. First the outstanding capability of SNMS for depth profiling with high depth resolution, which in the past was essentially restricted to electrically conducting samples, has been extended towards the analysis of insulating materials with dielectric constants approaching unity. Second, great effort has been made to develop a secondary neutral microprobe which allows SNMS surface and in-depth analysis with high lateral resolution. Here two promising approaches exist, which are based on different methods for post-ionization of sputtered neutral particles. The present state-of-the-art of both techniques is shown and a comparison in respect to detection limits and image acquisition times is attempted.

1 Introduction

Since its introduction in 1972 [1], Secondary Neutral Mass Spectrometry (SNMS) has become a widely used tool for quantitative surface and in-depth analysis of solids. In SNMS, the sample under investigation is bombarded with sub-keV or keV primary ions, and the flux of sputtered neutral particles is analyzed by mass spectrometric methods.

Prior to mass analysis, however, sputtered neutrals must be post-ionized; this is generally accomplished either by electron impact [1−6] or by photon absorption in various non-resonant [7, 8] or resonant [9−11] ionization schemes. Due to the decoupling of the sputtering and ionization processes, the neutral-to-ion conversion efficiency is essentially a constant of the apparatus and, hence, chemical matrix effects (as known, for instance, from SIMS) are largely absent in this method. Numerous studies have been published to demonstrate the capabilities and limitations of the different experimental SNMS techniques with respect to quantification, detection limits, depth profile analysis etc. (A brief review of this work can be found in [12]). On the other hand, these data are rapidly altered due to further developments of the experimental techniques. This paper in intended as a short survey of the present state-of-the-art is SNMS technology. A comparison between the different SNMS techniques will be attempted showing the advantages or disadvantages for specific analytical tasks. Special emphasis will be put on recent developments towards laterally resolved SNMS.

2 Experimental techniques

In the following, the different experimental techniques developed for SNMS will be grouped according to the post-ionization method employed, and each method will be described briefly. In order to enable a comparison between the different techniques, Table 1 shows the basic features which may be of immediate interest to the analyst.

2.1 Electron impact ionization

In the initial SNMS setup (i.e. the one for which the acronym SNMS was originally introduced), the sputtered neutrals are ionized by electrons from a hot Maxwellian electron gas [1−3]. The scheme of the setup is sketched in Fig. 1. The sputtered particles traverse a special low pressure rare gas rf-plasma, the electron component of which serves as the ionizing electron gas. In addition, plasma ions can be extracted onto the sample, thus allowing the bombardment of the surface with ions of extremely low kinetic energy (down to the sputtering thresholds) and high current density (∼1 mA/cm²). In connection with the high lateral uniform-

<table>
<thead>
<tr>
<th>Method</th>
<th>Main Application</th>
<th>Detection Limit</th>
<th>Useful Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>e-gas SNMS (quadrupole MS)</td>
<td>Bulk analysis depth profiling</td>
<td>1 ppm</td>
<td>10⁻⁸</td>
</tr>
<tr>
<td>e-gas SNMS (mag. sector MS)</td>
<td>Bulk analysis depth profiling imaging</td>
<td>10 ppb</td>
<td>10⁻⁶</td>
</tr>
<tr>
<td>e-beam SNMS (quadrupole MS)</td>
<td>Bulk analysis (depth profiling)</td>
<td>10 ppm</td>
<td>10⁻⁹</td>
</tr>
<tr>
<td>Laser SNMS (TOF MS)</td>
<td>Static surface analysis imaging</td>
<td>10 ppm</td>
<td>10⁻³</td>
</tr>
</tbody>
</table>
ity of the extracted ion beam, the method is almost ideally suited for quantitative high resolution depth profile analysis of multilayer systems [2]. Examples of such applications will be given in section 4. If the primary ion energy is raised towards the keV region, the technique can also be employed for the analysis of trace elements in the bulk sample. Although the useful yield (i.e. the probability that a sputtered neutral particle of a certain species is detected as an ion) is generally low (see Table 1), detection limits around typically one ppm (atomic) could be routinely reached in the past due to the fact that relatively large sample surface areas can be bombarded with high primary ion current density. Very recently, the useful yield of electron gas SNMS could be improved by two orders of magnitude by replacing the quadrupole mass spectrometer shown in Fig. 1 by a double focusing magnetic sector device [13]. Figure 2 shows a mass spectrum taken from a pure copper sample which was obtained with this setup. It is seen that intensity levels around $10^9$ cps are now achieved with a background of about 10 cps, thus corresponding to a detection limit of 10 ppb (atomic) at a signal-to-noise ratio (S/N) of 1.

A second possibility to use electrons for post-ionization of sputtered neutral particles is sketched in Fig. 3. Here an electron beam is crossed with the neutral beam at some distance above the sample surface. Details of the experimental setup can be found in [5] and [6]. It has been demonstrated that the useful yield and, hence, the detection limits achieved by this method are quite comparable to the values obtained by quadrupole based electron gas SNMS [15]. It should be noted, however, that since in this technique the sample is bombarded with primary ions delivered by an ion gun (rather than those extracted directly from a plasma), the primary ion energies are restricted to the keV regime. This imposes physical limitations regarding the depth resolution (via atomic mixing processes) and useful yield (via tight electronic gating and, hence, acceptance of only a few percent of the bombarding crater area) if the method is to be applied for high resolution depth profile analysis.

### 2.2 Photo-ionization

Apart from electron impact processes, post-ionization of sputtered neutrals can also be performed by means of photon absorption from intense laser fields. For this purpose, a laser beam intersects the plume of sputtered neutral particles emerging from the sample surface. If pulsed lasers are used, the subsequent mass spectrometric analysis of the photo-ions generated this way can be very efficiently carried out by time-of-flight (TOF) methods. Figure 4 depicts the scheme of a corresponding experimental setup which employs a reflection type TOF-spectrometer. The mass resolution $m/\Delta m$ of such a device is largely determined by the temporal width of the laser pulse. If nanosecond lasers are used, typical values of $m/\Delta m$ around 1000 (at $m = 100$ amu) result which increase with increasing mass $m$. It has been recently shown, however, that $m/\Delta m$ can be much higher if picosecond lasers are employed [16].

Photoionisation of sputtered particles can be accomplished by various different ionization schemes. At pre-
Fig. 5. SNMS signals of Ag, Au and Cu atoms sputtered from an Au$_{0.4}$Cu$_{0.6}$ alloy measured by non resonant laser post-ionization versus power density of ionizing laser. The sample was bombarded by Ar$^+$ ions of 5 keV, the laser was operated at a wavelength of 248 nm.

sent, the most widely used technique employs multiphoton absorption which can be done either resonantly [9–11] or non-resonantly [7, 8]. For selected analytical tasks, the resonant ionization scheme has been demonstrated to offer the unique possibility of ultratrace analysis with detection limits down to sub-ppb levels [10, 17, 18]. In the scope of the present paper, however, this technique is disregarded due to the high selectivity of the ionization process involved. Non-resonant multiphoton ionization, on the other hand, allows simultaneous analysis of all elements with the same laser. In combination with a TOF mass spectrometer, all constituents of the sample under investigation can in principle be detected with one single laser shot.

Hence, in connection with a pulsed operation of the primary ion gun (with pulse widths of typically 1 μs), the useful yield of the method can be as high as 10$^{-3}$ [19] if the ionization process can be driven at or close to saturation. This opens the possibility for static surface analysis with SNMS. Due to the low non-resonant ionization cross sections, the laser intensity has to be very high (≥10$^9$ W/cm$^2$) in order to achieve saturation ionization. As an example, Fig. 5 shows the photoion signals measured for Cu, Ag and Au atoms sputtered from a Cu$_{0.4}$Au$_{0.6}$ alloy as a function of the laser power density [20]. The ionizing laser used in this case was an excimer laser operated at λ = 248 nm. It is seen that, while the ionization of Ag and Au is obviously saturated at 5 × 10$^9$ W/cm$^2$, the Cu signal is still found to increase in this region of laser intensity. Other experiments show that intensities of several 10$^{10}$ W/cm$^2$ are needed to saturate the Cu$^+$ signal [21]. It should be noted here that the interpretation of curves like those shown in Fig. 5 is extremely difficult due to the complicated interplay between size variations of the effective ionization volume on one hand and saturation effects on the other hand. Also, it has been demonstrated that, particularly at low laser power densities, the measured atomic ions may be generated to a large extent by resonance enhanced fragmentation processes of sputtered neutral clusters [22].

3 Quantification

The quantification of SNMS data is simple and straightforward [3]. Under steady state sputtering conditions, the composition of the sputtered flux is identical to that of the bulk sample. Hence, the concentration of the different elements X present in the sample is evaluated according to [14]

$$c_x = \frac{I_x/D_0}{\Sigma_{i}I_i/D_i}$$  \hspace{1cm} (1)

Here $I_x$ denotes the intensity recorded for the species X and $D_i$ is a sensitivity factor containing post-ionization efficiency, mass spectrometer transmission etc. Note that the sum in the denominator on the right hand side of Eq. (1) must be performed over all major peaks present in the mass spectrum. Usually, Eq. (1) is applied using relative elemental sensitivity factors (RSF) $D_x^R/D_i^R$ with R being an arbitrarily chosen reference element. Figure 6 shows a compilation of such data which have been determined on a commercial SNMS system from a variety of standard reference materials [14]. It is seen that for most elements the sensitivity factor $D_x^R$ varies less than a factor of 5 with respect to the corresponding value for Fe. In the same work, the transferability of the RSF between different samples was investigated systematically. If the same element was detected in different chemical environments, the RSF was found to be reproducible within an average standard deviation of 30% [14].

The problem of quantification becomes more severe in situations where steady state sputtering conditions cannot be established. This is, for instance, the case during surface analysis of (sub-)monolayer coverages or if sharp concentration gradients are encountered during SNMS depth profiling (see section 4). Preferential sputtering effects may then play a significant role and no general relation between element concentrations and measured SNMS signals can be presumed.

4 Depth profile analysis

A prominent task frequently encountered in routine analysis involves the determination of the concentration of sample constituents as a function of depth below the surface. In SNMS this can be achieved by taking advantage of the fact that the sample surface is eroded by the primary ions and, hence, by recording SNMS intensities vs. time of bombardment. If high depth resolution without lateral resolution is required, electron gun SNMS would in most cases be the method of choice. The reason is twofold; relatively large sample areas can be bombarded with an extremely uniform ion beam and, hence, large amounts of material (which, due to the low useful yield, are needed to achieve reasonable detection limits) can be sputtered by removal of less than one monolayer from the sample surface (see Table 1). The use of low beam bombarding energies also keeps small the distortion of the measured depth profile by ion induced atomic mixing etc. As a consequence, high depth resolution of the order of only ten Å can be achieved and maintained over a relatively large sputtered depth [23]. For a most recent example, the reader is referred to the work of Weißbrodt et al. [24].

A main advantage of SNMS depth profiling is that the acquired profiles contain in principle all the information necessary to convert the measured data into true concentration depth profiles.

First, the measured intensities can be converted into element concentrations by means of Eq. (1). Note, however,
that the assumption underlying the quantification scheme outlined in section 3 may not be valid for all regions of a measured depth profile. In particular, when profiling across sharp interfaces with steep concentration gradients, steady state sputtering conditions cannot be established and the quantification scheme breaks down. A crude estimate which is included as an appendix to this manuscript suggests that the concentrations evaluated according to Eq. (1) should be reliable as long as

$$\frac{dI_i(t)}{dt} \leq \frac{I_i(t)}{\Delta t}.$$  

Here $\Delta t$ denotes the time needed to remove a depth interval $\delta$ which is equivalent to the thickness of the altered surface layer formed by preferential sputtering. Assuming $\delta \approx 1$ nm and inserting a typical removal rate of 1 nm/s for electron gas SNMS yields $\Delta t \approx 1$ s.

Second, a quantitative determination of the eroded depth as a function of sputter time is needed in order to obtain true concentration depth profiles. Therefore the time dependence of the total sample sputter yield $Y_{\text{tot}}$ has to be known; this in turn can be evaluated from the measured data by

$$Y_{\text{tot}}(t) \sim \sum_i I_i(t)/D_i^\delta,$$

provided all major elements $i$ present in the mass spectrum are recorded. Details of this procedure have been published in [25] and [26], which also include a systematic investigation of the accuracy of the resulting depth scale calibration scheme.

Figure 7 shows a concentration depth profile evaluated from an electron gas SNMS intensity-time measurement as described above [27]. The sample under investigation was a multilayer structure consisting of several Si$_{1-x}$Ge$_x$ layers with varying values of $x$ separated by thin layers of pure silicon. The numbers written below the lower and above the upper traces in Fig. 7 denote the individual layer thicknesses in Å as determined by SNMS and transmission electron microscopy (TEM) cross section measurements, respectively. The Ge concentration present in the different Si$_{1-x}$Ge$_x$ sublayers, as determined by SNMS, was found to agree within several percent with corresponding values obtained by Rutherford Backscattering Spectroscopy (RBS). Hence the example shown in Fig. 7 demonstrates that, at least for this particular case, the stoichiometry as well as the individual layer thicknesses can be evaluated from an SNMS depth profile to within an accuracy of approximately 10%.

In the past, large problems were encountered if electron gas SNMS was used for depth profile analysis of electrically insulating samples. Due to the low bombarding energies and the large primary ion current densities employed, charging of the surface often severely hampered or even prevented the analysis of such materials. Very recently, an ion extraction mode was developed in which a rectangularly shaped high frequency voltage rather than a constant dc potential is applied to the sample. Hence, the charge accumulated on the surface during the negative half wave (due to the bombardment with positively charged ions) is balanced by the electron current extracted during the positive half wave. Figure 8 shows an intensity time profile which was acquired in this manner from a Ag-Cu metallization layer deposited onto a glass substrate [28]. No electrical connection was made between the metallization layer and the target electrode below the glass substrate. It is seen that even in this worst case, where the dielectric constant of the bulk sample approaches unity, the sample is eroded very uniformly and, hence, the depth resolution of the method, determined from the measured 90%–10% interface width, can be kept at approximately 10 nm.
5 Imaging

To date, laterally resolved SNMS can only be accomplished in the so called microprobe mode, i.e. a finely focused primary ion beam is raster scanned across the investigated surface and the total current of secondary neutral particles is detected as a function of the ion beam position. To achieve sub-micron resolution, small spot liquid metal ion sources must be used delivering primary ion currents of typically 1 nA or below [29]. It is easily seen that at these low bombarding currents the useful yield of the SNMS technique employed must be higher than $10^{-6}$ in order to keep the detection limit at or below one atomic percent.

As seen from Table 1, only the laser post-ionization technique and the electron gas technique, in combination with a magnetic sector mass spectrometer, fulfill this condition. In the following, the prospects of both methods towards imaging SNMS will be discussed separately. Special emphasis will be put on the interplay between achievable detection limits and image acquisition times.

5.1 Laser SNMS

Due to its high useful yield, laser post-ionization seems to be the most promising method for laterally resolved SNMS. Figure 9 shows images which were acquired from a test sample consisting of a Ni grid pressed into a polycrystalline silver substrate (width of Ni bars: 20 μm; distance between bars: 300 μm) [30]. The ion gun used in this case provided a 6 nA, 25 keV Ga⁺ ion beam with a probe size of approximately 1 μm. The apparent lateral resolution observed in Fig. 9 (between 5 and 10 μm) is due to the fact that the experimental setup was not optimized in respect to vibrational damping. All images shown in the figure have been recorded simultaneously with one single laser shot on each pixel. It is seen that under these conditions the $^{64}$Ni isotope which has a natural abundance of 1.0 at% can clearly be detected. To further investigate the detection sensitivity, a line scan of the $^{64}$Ni signal across several Ni bars (as indicated in Fig. 9) is displayed in Fig. 10 which shows a signal-to-noise ratio of around 6. This corresponds to a detection limit of 1 at% at a primary ion current of 1 nA and one laser shot per pixel. By extrapolation according to typical performance data (ion current vs. beam size) of the employed liquid metal ion source [29], detection limits can be estimated for different probe sizes on one hand and different numbers of acquired laser shots per pixel (over which the measured signal is averaged) on the other hand. The results are displayed in Table 2. It is seen that, even at sub-micron lateral resolution, detection limits in the range clearly below one at% should be achievable. This finding is consistent with the results of Becker's group [31] who managed to acquire an image of the $^{61}$Ni isotope from a TEM nickel grid using a Ga⁺ ion source with a beam current of 0.2 nA and a probe size of 0.2 μm.

The results displayed in Fig. 9 also illustrate the field of view achievable by the imaging method employed. For non-resonant laser post-ionization, this is a critical point since one usually works with a finely focused laser beam to achieve the high laser power densities necessary for efficient post-ionization. In Fig. 9, the size of the rastered area was 1 mm by 1 mm. It is seen that useful images can be acquired even over such large surface areas. Obviously, however, the measured signal decreases with increasing distance of the spot analyzed on the sample surface from the optical axis of the TOF mass spectrometer. This is due to a lateral variation of the corresponding sensitivity factor $D^0$. If we assume that the $D^0$ values for all elements present in the sample exhibit
Table 2. Primary ion current $I_p$ and resulting SNMS detection limit vs. diameter $d$ (FWHM) of the primary ion beam. The relation between beam current and beam size was taken from typical performance data of a standard liquid metal Ga⁺ ion gun [29]. The data given in columns 3 and 4 were extrapolated from those evaluated in the text by assuming the SNMS detection limit to be inversely proportional to the primary beam current times the square root of the number of acquired laser shots.

<table>
<thead>
<tr>
<th>$d$</th>
<th>$I_p$</th>
<th>Detection limit</th>
<th>Laser SNMS</th>
<th>e-gas SNMS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 shot</td>
<td>50 shots</td>
</tr>
<tr>
<td>0.1 μm</td>
<td>0.2 nA</td>
<td>0.2 at%</td>
<td>0.7 at%</td>
<td>5 at%</td>
</tr>
<tr>
<td>1 μm</td>
<td>5 nA</td>
<td>0.2 at%</td>
<td>280 ppm</td>
<td>0.2 at%</td>
</tr>
<tr>
<td>10 μm</td>
<td>50 nA</td>
<td>100 ppm</td>
<td>28 ppm</td>
<td>200 ppm</td>
</tr>
</tbody>
</table>

![Fig. 11. SNMS mass spectrum of a partly oxidized Ta sample measured by electron gas SNMS combined with a double focusing magnetic sector mass spectrometer [13]. The sample was bombarded by Ga⁺ ions of 20 keV with a total current of 3 nA.](image)

essentially the same lateral variation, this effect may be corrected for to first order by applying Eq. (1) to each pixel separately. This, in turn, can be carried out very efficiently if TOF mass spectrometry is used, since in this case the whole mass spectrum is recorded simultaneously on each pixel. It should be noted, however, that the validity of the underlying assumption has not yet been demonstrated. Note also that the quantification scheme of Eq. (1) may only be applied under steady state sputtering conditions. Hence the sample must be pre-bombarded prior to the image acquisition.

A further important point which is of considerable interest to the analyst concerns the time $t_{aq}$ needed to acquire an SNMS image. In general, $t_{aq}$ consists of two contributions. First, the measurement time $t_m = z/v$ is determined by the number $z$ of laser shots accumulated per pixel and by the laser repetition rate $v$. Second, some time is needed for the transfer of the measured data to the host computer controlling the experiment. In principle the TOF method allows a complete mass spectrum to be recorded on each pixel and to be stored in the computer. In practice, however, this would make very inefficient use of the available memory, since most of the stored data would correspond to blank parts of the mass spectrum. Hence, after transferring the acquired time-of-flight spectrum to the computer, one would like to reduce the data in real time and store only the integrated intensities of selected mass peaks. (It should be noted, however, that the number of masses, i.e. the number of images acquired simultaneously, is not limited in this mode of data acquisition.) The total time needed for transfer and reduction of the measured data will certainly depend on the electronic equipment used. For our transient digitizer (LeCroy 9450) and a 386-based PC we estimate this time to be about 0.3 s per pixel, which is consistent with the data given in [31]. Hence the total acquisition time is given as

$$t_{aq} \approx (z/v + 0.3 \text{ s})/\text{pixel}.$$  

It is immediately seen that in this mode of operation the minimum time required to generate an image of $(128 \times 128)$ pixels amounts to 82 min. The optimum number of $z$ would be given if both contributions to $t_{aq}$ were equal, i.e. $z_{opt} \approx 0.3 \text{ s} \cdot v$. With a typical excimer laser repetition rate of 100 Hz, this yields $z \approx 30$ shots/pixel. Then, the acquisition time needed for an image of $(128 \times 128)$ pixels would be around 160 min.

Obviously, in the acquisition mode described so far it would be of no advantage to significantly reduce $z$ below $z_{opt}$. This is different if another image acquisition mode is employed involving hardware integration of selected mass peaks by independent gated integrators, each of which is tuned to the desired mass by setting the gate delay to the appropriate flight time. This method was chosen to acquire the images shown in Fig. 9. The advantage is that in this case only integrated peak intensities are transferred and hence the time needed for data handling becomes negligible. As a consequence, images can efficiently be taken with only one single laser shot per pixel and the total acquisition time is reduced to 164 s for an image of $(128 \times 128)$ pixels. The data presented in Table 2 show that even this fast acquisition mode provides detection limits below 1 at% at a lateral resolution around 1 μm. Very recent results employing a picosecond laser suggest that the useful yield of laser SNMS can be further improved by at least one order of magnitude [16]. This would decrease the detection limits given in Table 2 accordingly and, hence, fast laser SNMS imaging at sub-micron resolution with detection limits significantly below 1 at% seems feasible in the near future.

5.2 Electron gas SNMS

The recent combination of electron gas SNMS with a double focusing magnetic sector mass spectrometer opens the door for imaging applications of this technique. Figure 11 shows the interesting region of a mass spectrum which was measured with this setup from a partly oxidized Ta foil [13]. The sample was bombarded with a beam of 20 keV Ga⁺ ions at a total current of 3 nA and a probe size of approximately 1 μm. It is seen that in this case the detection sensitivity is about $10^3$ cps per nA of primary ion current. Regarding the background noise level of approximately 10 cps, this corresponds to a detection limit of 1 at%, provided the counting time spent on each pixel is sufficient (0.1 s) to count at least one ion of a minor sample constituent abundant with this concentration. If it can be extrapolated to different probe sizes, detection limit as calculated for 0.1 s counting time per pixel are also given in Table 2. All remarks made in section 5 concerning the quantification of SNMS images naturally also apply to electron gas SNMS imaging.
The image acquisition time for electron gas SNMS is dominated by the counting time, since in this case the contribution of the data handling time is negligible. This yields 
\[ t_{\text{acq}} = 0.1 \text{ s/pixel}, \]
which amounts to 27 min for the acquisition of an image consisting of (128 x 128) pixels. Although this is slightly faster than laser SNMS imaging in the “full” acquisition mode (where the whole mass spectrum is recorded for each pixel), it should be noted that this time is needed for the acquisition of only one image of a single preselected mass. If compared to the fast imaging mode of laser SNMS (which still allows simultaneous acquisition of a limited number of images within only 164 s), imaging by electron gas SNMS is apparently much slower than by laser SNMS.

6 Conclusions

The basic experimental approaches to the spectrometry of sputtered neutral particles have been briefly outlined. The main application fields, as well as recent technological developments of the different techniques, have been described. In particular, it is shown that the capabilities of SNMS towards the composition-microanalysis of solids and solid surfaces could recently be extended in two ways. First, high resolution depth profile analysis of non-conducting samples by electron gas SNMS could be made possible by the development of a special high frequency ion extraction scheme. Second, laterally resolved SNMS analysis of solid surfaces with submicron resolution, reasonable image acquisition times and detection limits significantly below one atomic percent has become feasible by i) the use of lasers for post-ionization of sputtered particles and ii) a combination of the electron gas SNMS method with a double focusing magnetic sector mass spectrometer. The prospects for both methods towards imaging SNMS were discussed. It is seen that at comparable detection limits the laser post-ionization method allows much faster image acquisition than the electron gas technique. It is also demonstrated that SNMS methods now span the complete range from static surface analysis (laser SNMS) on one end to ultratrace bulk analysis (new electron gas SNMS) with detection limits down to the 10 ppb level on the other end.

Acknowledgement. The author thanks W. Berthold, W. Bieck and M. Strack for performing the measurements presented in Figs. 9 and 10, 2, 8 and 11, respectively.

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Appendix

A preferential sputtering correction to the quantification of SNMS depth profiles

Assume that in a surface layer of thickness δ the composition of the sample is modified by preferential effects, while at depths larger than δ the original concentration depth profile is preserved. Let the surface concentration \( C_A(t) \) of an element A be defined as the average concentration of A within this altered layer at a sputter time t, whereas \( C_A(t) \) denotes the concentration of A immediately below the altered layer, i.e. at a depth δ from the actual surface. Typically, δ is of the order of only a few atomic layers [32]. This means that in the present treatment long range modifications of the original concentration depth profile due to effects like atomic mixing, radiation enhanced diffusion etc. are neglected.
Then, a simple balance of the particle fluxes into and out of the altered layer yields \cite{32, 33}

\[ \delta \cdot n \cdot \frac{d c_A}{dt} = -j_p \cdot Y_A(t) + j_p \cdot c_A(t) \cdot Y_{tot}(t) \]  

(A1)

where \( n \) denotes the number density of particles in the sample and \( j_p \) is the primary ion current density. The partial sputter yield \( Y_A(t) \), defined as the average number of particles A sputtered per primary ion impact, is related to the total sputter yield \( Y_{tot}(t) \) at any time \( t \) by

\[ Y_{tot}(t) = \sum_i Y_i(t), \]  

(A2)

the sum being performed over all major species abundant in the sputtered flux. If, in addition, it is assumed \cite{34}

\[ Y_A(t) = c_A(t) \cdot Y_A^s \]  

(A3)

with \( Y_A^s \) being a constant independent of the surface composition, the SNMS signal measured for A is obtained as

\[ I_A(t) = I_p \cdot D_A^0 \cdot Y_A(t) = I_A^s \cdot c_A(t). \]  

(A4)

Here, \( D_A^0 \) is the SNMS sensitivity factor described in the text of chapter 3 and \( I_p \) denotes the primary ion current. Note that the assumption (A3) will not be generally valid and has to be examined for every particular interface under consideration. For a binary system (A – B), this can be done by plotting \( I_A(t) \) vs. \( I_B(t) \). According to (A2) and (A3), this should give a straight line, in which case \( I_A^s \) and \( I_B^s \) are determined by the intersects with the \( I_A^s \) and \( I_B^s \)-axis, respectively. Combining (A1) – (A4), the bulk concentration of a species A at a given time \( t \) can be evaluated as

\[ \frac{(A_p \cdot D_A^0 \cdot n) \cdot \delta \cdot \frac{d}{dt} \left( \frac{I_A(t)}{I_A^s} \right) + I_A(t)}{\sum_i I_i(t) \cdot \frac{D_i^0}{D_A^0}} \]  

(A5)

where \( A_p = I_p/j_p \) denotes the target surface area irradiated by the primary ion beam. Note that (A5) approaches the quantification for steady state sputtering [Eq. (1) in chapter 3] if

\[ (A_p \cdot D_A^0 \cdot n) \cdot \delta \cdot \frac{d}{dt} \left( \frac{I_A(t)}{I_A^s} \right) \ll I_A(t) \]  

(A6)

Hence (A6) represents a quantitative criterion for the assumption of steady state sputtering conditions during profiling across an interface. The parameter \((A_p \cdot D_A^0 \cdot n)\) can in principle be evaluated from a known depth interval \( \Delta z_0 \) eroded during a time interval \( \Delta t_0 \) by

\[ \Delta z_0 = \int_{\Delta t_0} \dot{z}(t) dt \]

\[ = \int_{\Delta t_0} \frac{Y_{tot}(t) \cdot j_p}{n} dt = \frac{1}{n \cdot D_A^0 \cdot A_p} \sum_i \int_{\Delta t_0} I_i(t) \frac{D_i^0}{D_A^0} dt. \]

\( \Delta z_0 \) and \( \Delta t_0 \), in turn, may be determined from a mechanical stylus profile subsequent to the SNMS depth profile analysis. Hence,

\[ (A_p \cdot D_A^0 \cdot n) = \frac{1}{\Delta z_0} \sum_i \int_{\Delta t_0} I_i(t) dt \cdot \frac{D_i^0}{D_A^0}. \]

(A7)

For a semiquantitative evaluation of (A6), the definition of \( I_A^s \) is inserted into the left hand side of (A6). This yields

\[ \delta \cdot \frac{n}{j_p \cdot Y_A^s} \frac{d I_A(t)}{dt} \ll I_A(t). \]

Here, the term \( n/j_p Y_A^s \) corresponds to a (hypothetical) sample erosion rate for \( c_A^s = 1 \). For a crude estimate, this is replaced by the average erosion rate of the sample given by \( \dot{z} = \Delta z_0/\Delta t_0 \). Then the steady state criterion (A6) becomes

\[ \frac{d I_A(t)}{dt} \ll \frac{1}{\dot{z} \cdot \delta} \cdot I_A(t), \]

(A8)

where \( \dot{z} \cdot \delta \) denotes the time needed to remove a surface layer of a thickness equivalent to that of the altered layer.