Relative elemental sensitivity factors in non-resonant laser-SNMS

M. Wahl, D. Koch, W. Berthold, A. Wucher

Fachbereich Physik, Universität Kaiserslautern, Erwin-Schrödinger-Strasse, D-67663 Kaiserslautern, Germany

Received: 27 February 1995/Accepted: 1 March 1995

Abstract. Using a reflectron time-of-flight mass spectrometer, the ionization process in non-resonant Laser postionization Secondary Neutral Mass Spectrometry (SNMS) has been investigated. In particular, the postionization efficiencies (PIE) achieved by multi photon and single photon absorption have been compared by ionizing ten elements sputtered from a NIST standard reference material by excimer laser radiation of 248 nm, 193 nm and 157 nm. Only in the case of single photon ionization (SPI) the measured laser intensity dependence of the PIE can be understood quantitatively in terms of corresponding theory. From the results, absolute values of the SPI cross sections have been evaluated for atoms of nine elements, which show a total variation over about two orders of magnitude. Furthermore, even in the regime of high laser intensity, where the ionization of all atoms is completely saturated, different elements have been detected with relative sensitivity factors which scatter over about one order of magnitude. This has been attributed to element dependent variations of the effective ionization volume which are caused by the different kinetic energy and angular distributions of different sputtered atoms.

I Introduction

The mass spectrometric analysis of neutral particles released from a solid surface by ion sputtering (SNMS) is now a well established tool for quantitative surface characterization and depth profile analysis of thin films. Postionization of the sputtered neutrals – which is necessary to render them accessible to mass analysis and detection – is generally performed either by electron impact or by photoionization from a pulsed laser beam. It is particularly the latter technique – commonly referred to as “Laser-SNMS” – which we focus on in the present study. Here, postionization is achieved by either resonant (REMPI) or non-resonant (NRMPI) multiphoton absorption. Resonant schemes are sensitive only to specific particles sputtered in specific electronic states. They will therefore be disregarded here, since their high selectivity makes them unsuitable for the day-to-day analysis of general unknown samples. Non-resonant schemes, on the other hand, offer the possibility to non-selectively ionize all ejected particles with the same laser setup. The advantages of such ionization schemes for surface analysis were first pointed out by Becker et al. [1] who introduced this version of Laser-SNMS under the acronym SALI. An important feature of this technique is that photon flux densities achievable with present state-of-the-art UV lasers are in many cases high enough to drive the postionization process close to saturation. Therefore, in spite of the non-resonant character of the ionization mechanism, different elements may be detectable with comparable postionization efficiency.

Probably the most stringent parameter in non-resonant laser postionization is the photon energy hv, which determines the number n of photons necessary to ionize a specific particle. In principle, hv should be as high as possible (corresponding to n being as low as possible) in order to decrease the photon flux density needed for efficient postionization. Therefore, UV excimer lasers have been widely employed which are commonly operated at wavelengths of 248 nm (KrF) or 193 nm (ArF) providing photon energies of 5.0 eV and 6.4 eV, respectively. With these lasers, atoms of most elements are detected by a non-resonant two photon ionization (NR2PI) process which requires fairly high laser power densities to achieve saturation ionization [2]. In addition, NRMPI of sputtered molecular species is often inhibited by photon induced fragmentation. Therefore, it was suggested to use a single photon ionization (SPI) scheme for surface analysis [3,4]. This, of course, requires photon energies in excess of the ionization potential of the investigated species and, hence, laser radiation in the VUV spectral range must in most cases be used. In refs. [3] and [4], radiation at 110 nm (hv = 10 eV) was generated by frequency tripling the third harmonic of a Nd-YAG laser in a gas cell. The resulting pulse energy of the order of 1 μJ was much too low to saturate the ionization process. In the present work, we apply an F2 excimer laser emitting VUV radiation at a wavelength of 157 nm (hv = 7.9 eV) which permits single photon ionization of most elements. The
high pulse energy obtainable with this laser enables us to
investigate the saturation behavior of the SPI process and
determine corresponding ionization cross sections for
a number of different elements. Using a certified standard
reference material of known composition as a test sample,
we evaluate relative elemental sensitivity factors for SPI of
ten elements as a function of the laser power density. The
results are then compared to those obtained by non-resonant
two photon ionization at 248 nm and 193 nm, respectively.

II Experimental

The experimental setup employed in the present work has
been described in great detail elsewhere [5,6]. A thor-
oughly degreased, polished sample consisting of a NIST
standard reference material of certified composition (In-
conel 1245a) was bombarded by a pulsed rare gas ion
beam of 5 keV impinging under 45° with respect to the
surface normal. Neutral particles which are sputtered
from the sample surface are ionized by a pulsed laser
beam directed closely above and parallel to the surface.
During the primary ion pulse, the sample was kept at
a negative potential in order to prevent positively charged
ionic species from leaving the surface and, hence, to
reduce the secondary ion background. The photoions
created during the laser pulse are extracted towards a
reflectron-type time-of-flight mass spectrometer (TOF-
MS) by an electric field which is switched on shortly
(\(\approx 20\) ns) after the laser pulse. The operating conditions
of the mass spectrometer were chosen to provide a mass
resolution of \(m/\Delta m = 1000\) at \(m = 52\) amu.

The ionizing laser employed in the present experi-
ments is a conventional excimer laser (Lambda Physik
model LPX 120i) operated either with KrF, ArF, or F_2.
Under optimized conditions, this laser produced pulses of
about 300 mJ (KrF), 200 mJ (ArF) and 2 mJ (F_2) energy
and about 20 ns duration at wavelengths of 248 nm,
193 nm and 157 nm, respectively. The output beam was
coupled into the ultrahigh vacuum (UHV) chamber hous-
ing the TOF experiment by a CaF_2 window and focused
into the interaction region above the sample surface by
means of a 200 mm focal length of the CaF_2 lens mounted
on a precision xyz-manipulator. The beam line as well as
all optical elements were contained in a flow box which
was flushed with dry nitrogen. This box was particularly
needed to transport the VUV radiation (157 nm) which is
strongly absorbed in air. In order to study the depend-
ence of the photoion signals on the intensity of the ionizing
laser, the laser pulse energy could be reduced in a control-
led fashion by a stack of two variable dielectric atten-
uation filters located in front of the lens, which were tilted
in opposite directions to compensate for the beam walkoff
with increasing tilting angle. The laser intensity was
monitored in situ by a home made photoelectric detector
described elsewhere [7] which was mounted directly
in the UHV chamber. An absolute calibration of this
detector was performed at the highest possible pulse
energy level by a conventional pyroelectric radiation
detector (operated in the flow box outside the vacuum
chamber).

The ionizing laser was fired about 200 ns after the end
of the primary ion pulse. The primary ion pulse length
\(\tau\) was chosen to be long enough (typically 5 \(\mu\)s) to ensure
that a further increase of \(\tau\) did not increase the measured
signals. Hence, particles of all emission velocities are pre-
sent in the ionization volume, and the measured signal
represents the total number density of the corresponding
sputtered neutral particle integrated over its entire veloc-
ity distribution. The laser beam was shaped to a cross
section of 0.7 mm \(\times 1.5\) mm (FWHM) in directions along
and perpendicular to the surface normal, respectively, and
positioned at a distance of 1 mm above the surface. The
exact beam dimensions in the interaction region were
controlled without breaking the vacuum by scanning a
5 \(\mu\)m diameter pinhole mounted to the sample holder
across the profile. Provisions were made to correct for the
different focal lengths of the CaF_2 lens at the different
wavelengths in order to ensure the same beam profile for
all measurements. Due to the geometrical arrangement,
the angular distribution of sputtered particles was sam-
pled over a relatively large solid angle corresponding to
polar emission angles up to 36° with respect to the surface
normal.

III Results and discussion

For each of the three investigated wavelengths of the
ionizing laser, a series of mass spectra were recorded on
the NIST standard reference material 1245a sample with
the laser intensity being varied over several orders of
magnitude. All certified sample constituents which are
given in Table 1 could be unambiguously identified in the
spectra, and the most abundant isotope of the respective
element was selected for further evaluation. Figure 1
shows the integrated signals of the corresponding mass
(or flight time) peaks as a function of the ionizing laser
power density \(P_L\). The absolute calibration of the \(P_L\)-axis
was performed by assuming rectangular spatial and tem-
poral laser beam and pulse profiles (with dimensions
given by the FWHM values of the true profiles) and,
hence, may contain an error of up to roughly a factor of
two. Note, however, that the relative scaling of \(P_L\) is not
affected by this error.

From the figure, it is obvious that qualitatively differ-
ent laser intensity dependences on the measured signals
are found for different photon energies. For a more de-
tailed discussion, it is useful to look at the theoretically
expected laser intensity dependence of the ionization effi-
ciency. In general, the probability for non-resonant multi-
photon ionization of a sputtered neutral species \(X\) should
be given by first order perturbation theory [8] as

\[
x_n^X = \left[1 - \exp(-\sigma_n^X I_0^L \Delta t)\right]
\]

Table 1. Constituents and certified element concentrations in atomic%

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>60</td>
</tr>
<tr>
<td>Cr</td>
<td>25</td>
</tr>
<tr>
<td>Mo</td>
<td>5.3</td>
</tr>
<tr>
<td>Fe</td>
<td>4.8</td>
</tr>
<tr>
<td>Nb</td>
<td>2.2</td>
</tr>
<tr>
<td>Si</td>
<td>0.9</td>
</tr>
<tr>
<td>Al</td>
<td>0.4</td>
</tr>
<tr>
<td>Ti</td>
<td>0.3</td>
</tr>
<tr>
<td>Cu</td>
<td>0.3</td>
</tr>
<tr>
<td>Mn</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Here, $I_t = P_t/h\nu$ is the photon flux density (or “intensity”) of the ionizing radiation, $\sigma_t$ denotes the generalized ionization cross section, $\Delta t$ the laser pulse duration and $n$ the number of absorbed photons needed to overcome the ionization potential of X.

At 248 nm, the photon energy of 5.0 eV is below the ionization potential of all investigated species. Therefore, two photon absorption processes are needed for ionization and all measured signals are expected to show a proportionality to $P_t^n$ in the region of low $P_t$. It is clearly seen from Fig. 1a that none of the measured signals truly obeys this predicted behavior (which has been included as a dotted line for comparison). This finding, which has also been observed by others [2], is presumably caused by a disturbing influence of metal clusters—in particular dimers—created during the sputtering process. Due to the fact that dissociative ionization of these molecules is always a resonance enhanced process, the corresponding cross section may be many orders of magnitude larger than that for NR2PI of atoms and, hence, the number of atomic ions generated by cluster fragmentation may significantly contribute to or even dominate the measured signal. Direct evidence for this influence has been found for sputtered copper atoms [2], where it was found that the true saturation behavior of the NR2PI process at 248 nm was completely masked by cluster fragmentation.

At 193 nm, the photon energy of 6.4 eV is still below the ionization potential of all elements except aluminum. At low laser intensities, we therefore expect a linear $P_t$-dependence of the aluminum signal and quadratic $P_t$-dependences of all other signals. This large difference in saturation behavior is indeed observed in Fig. 1b. At a first glance, it seems that at low laser intensity the predicted quadratic intensity dependence of the NP2PI signals (indicated as a dotted line) is approached more closely than for 248 nm ionization. Also in this case, however, we find significant deviations from the prediction of Eq. (1) which preclude a quantitative determination of generalized two photon ionization cross sections as well as extrapolation of our data to the regime of completely saturated ionization.

Finally, at 157 nm the photon energy of 7.9 eV is high enough to ionize all investigated atoms except silicon by absorption of only one photon. Hence, linear $P_t$-dependences are expected and observed in Fig. 1c for all measured signals (except Si). Apparently, only in the case of molybdenum the maximum available laser intensity is high enough to achieve complete saturation. This finding already indicates that at this particular wavelength the SPI cross section of Mo atoms must be exceptionally large. For the remaining elements, complete saturation is obviously not reached. At our highest achievable laser intensity, however, the signals deviate enough from the linear dependence to permit a meaningful fit of Eq. (1) to the data. Figure 2 shows examples of such fits which were obtained by treating both the ionization cross section and the saturation signals as fitting parameters. It is seen that in this case the measured laser intensity dependence can be quantitatively understood in terms of the theoretical expectation of Eq. (1). This finding clearly distinguishes the single photon ionization from the multiphoton ionization processes discussed above. The very good agreement observed in Fig. 2 is presumably due to the fact that at 157 nm the efficiencies for direct ionization of atoms and fragmentation of clusters are of comparable

![Image](image_url)

**Fig. 1.** SNMS signals (integrated mass peaks) of different elements sputtered from a NIST standard reference material vs. power density of the ionizing laser. The dashed and dotted lines represent the theoretically expected linear and quadratic $P_t$-dependences, respectively.

![Image](image_url)

**Fig. 2.** Fit of theoretically expected laser intensity dependence of single photon ionization [Eq. (1) in the text with $n = 1$] to measured SNMS signals of different elements.
magnitude. Then, due to the relatively small total number of clusters within the sputtered flux [9] the role of cluster fragmentation can be neglected. Figure 3 shows the SPI cross sections obtained from the fits displayed in Fig. 2. For completeness, a corresponding value for silver atoms which has been determined elsewhere [10] is included in the figure. It is seen that for the limited numbers of elements investigated here the cross sections for single photon ionization at 157 nm vary over about two orders of magnitude. In principle, this finding is not surprising, since due to the small difference between photon energy and ionization potential we expect the photoionization efficiency to be still influenced by continuum structure [11]. Obviously, at the particular wavelength of 157 nm the photoionization efficiency of molybdenum atoms is strongly enhanced by an autoionization resonance. The cross sections determined for the remaining elements scatter over about one order of magnitude. We believe this to be representative for the truly non-resonant single photon ionization process. Conclusive evidence in this respect, however, requires tunable UV radiation in order to identify possible resonances, which at present is not at our disposal.

From the signals depicted in Fig. 1, we can evaluate the relative sensitivity of the Laser-SNMS method with respect to different elements. To start the discussion, we begin with a quantitative description of the signal $S_X$ (in counts per laser shot) measured for a species X:

$$S_X = I_p \cdot Y_X \cdot \int_{\Delta \Omega} f_X(\Omega) d\Omega \int_{\Delta v} \frac{f_X(v)}{v} [\Delta r + v \Delta t] d\varepsilon \cdot \alpha_X^p \cdot T_X \; (2)$$

Here, $I_p$ is the primary ion current (during the on-time of the primary pulse), $Y_X$ is the partial sputter yield of X and $T_X$ is the mass spectrometer transmission for the created photoions $X^+$. The quantities $\Delta r$ and $\Delta t$ denote the spatial width (in the direction along the surface normal) and the temporal width of the laser pulse, respectively. The integrals in Eq. (2) depend on the angular and velocity distributions $f_X(\Omega)$ and $f_X(v)$ of sputtered particles X, respectively, and describe the fraction of sputtered species X which interacts with the laser beam. Due to the pulsed nature of the experiment, only particles ejected into a limited solid angle element $\Delta \Omega$ with emission velocities within a limited range $\Delta v$ are accepted for position- and detection. The actual values of $\Delta \Omega$ and $\Delta v$ critically depend on the geometrical arrangement and the timing of the experiment [5]. For the purpose of the present discussion, we combine both integrals to an element dependent geometry factor $G_X$. Then, Eq. (2) is equivalent to the well-known SNMS equation

$$S_X = I_p \cdot Y_X \cdot G_X \cdot T_X \cdot \alpha_X^p$$

which is often reduced to

$$S_X = I_p \cdot Y_{tot} \cdot c_X \cdot G_X \cdot T_X \cdot \alpha_X^p = D_X \cdot c_X$$

(4)

Here, $Y_{tot}$ denotes the total sputter yield and $c_X$ is the bulk concentration of X in the sample. It is important to note that Eq. (4) is only valid under steady state sputtering conditions. This condition, however, is not necessarily fulfilled in a (static) Laser SNMS experiment due to the pulsed nature of the primary ion beam. In the present work, the validity of Eq. (4) was ensured by pre-bombardment the sample to ion doses exceeding $10^{12}$ ions/cm² prior to the analysis. Then, relative sensitivity factors (RSF) can be calculated from measured signals (corrected for isotopic abundance) by

$$D_X = \frac{S_X \cdot c_{ref}}{S_{ref} \cdot c_X}$$

(5)

Figure 4 depicts these factors vs. the laser power density with nickel being chosen as a reference element. The first important observation is that although the absolute signals vary over many orders of magnitude as a function of the laser intensity, the RSF values do not change as dramatically as long as the order of the ionization process is the same between different elements. This is particularly seen in the data taken at 193 nm, where the RSF of all elements except titanium are practically constant over three orders of magnitude in laser intensity. Aluminum, on the other hand, is at this wavelength ionized by a SPI process, which at low laser intensities is far more efficient than the NR2PI process required for all other elements. Therefore, an aluminum RSF of 13400 is found in this region which strongly decreases as the laser intensity is increased. Above $3 \times 10^7$ W/cm², the RSF finally becomes independent of $P_L$ due to saturation of the different ionization processes. Note, however, that even under these conditions aluminum is detected at least 10 times as efficient as all other elements.

At 157 nm, the observed RSF values spread over three orders of magnitude at low laser intensities. Since in this regime the measured signals are directly proportional to the respective ionization cross sections, this variation is in part understood from the data presented in Fig. 3. Interestingly, the range of RSFs measured in [4] on a similar NIST standard reference material with higher energy (118 nm, $h\nu = 10.5$ eV) ionizing radiation is somewhat smaller than the one determined here, thus indicating that at photon energies high above the ionization threshold SPI cross sections may be closer together. As the laser

1 Note that, in contrast to electron impact ionization SNMS, $G_X$ in Eqs. (3) and (4) has the dimension of a time and, hence the sensitivity factor $D_X$ is dimensionless.
The values of $G_X$, on the other hand, are determined by the angular and velocity distribution of the sputtered particles which may significantly differ between different elements. In order to estimate the role of different velocity distributions $f(v)$, we use a common expression [12]

$$f(v) = 4v_B^2 \frac{v^3}{(v^2 + v_B^2)^3}$$

(7)

and note that, as explained in section II, the range of accepted velocities practically extends from zero to infinity. Then, the first term of the velocity integral in Eq. (2) —describing the number density of sputtered particles within the ionization volume— scales with the inverse of the characteristic velocity $v_B$ which is determined by the surface binding energy $E_B$ and the mass of the ejected particle. Typically, $E_B$ is set equal to the sublimation energy, which for the elements studied here varies between 3.0 eV (pure Mn) and 7.5 eV (pure Nb) yielding $v_B$ values between 3.3 and 5.0 km/s. The second term of this integral (which is only important if the photoionization process is saturated [2, 5]) describes the flux of particles into the ionization volume during the laser pulse and is independent of $v_B$. The largest element dependent variation of $G_X$ which is introduced by the velocity dependent integral is therefore less than a factor of two. As a consequence, we must conclude that the large variation observed in Fig. 4 is caused by the solid angle integral in Eq. (2). In part, this may be due to differences between the angular distributions of the sputtered particles, the significance of which has been demonstrated for electron impact SNMS [13]. Due to the relatively large solid angle probed in the present experiments, however, we expect this variation to be small. Instead, we suggest that the large variation of $G_X$ observed in our experiments is caused by an element specific variation of the accepted solid angle $\Delta \Omega$. As a possible explanation, we state that the width of our ionizing laser beam is comparable with or larger than the lateral dimension $d_{\text{TOF}}$ of the sensitive volume accepted by the ion optics of the TOF MS. In this case, the value of $\Delta \Omega$ is primarily determined by $d_{\text{TOF}}$ rather than by the laser beam dimensions, and any element dependence of the acceptance area $A_{\text{TOF}} \sim d_{\text{TOF}}^2$ is directly reflected in the geometry factor. More specifically, photoions created far out of the ion optical axis will not be transmitted if their starting velocity exceeds a certain threshold value. Therefore, $A_{\text{TOF}}$ may critically depend on the velocity distribution of the sputtered neutrals, and different geometry factors result for different elements. A thorough examination of this explanation of course requires further experiments, in which the relevant parameters such as laser beam dimensions, distance between laser beam and surface, ion optical acceptance volume etc. are varied systematically. Such investigations are currently under way in our laboratory.

IV Conclusion

For the elements studied here, the smallest RSF variation as a function of laser intensity is found for non-resonant
multiphoton ionization with 193 nm. Hence, at this wavelength the quantitation of measured Laser-SNMS signals is largely independent of the laser intensity as long as all detected particles are ionized by the same process. If different ionization mechanisms occur for different sputtered atoms, however, the RSF may vary over many orders of magnitude, and the reproducibility of the ionizing conditions such as laser pulse energy, beam profile etc. will be extremely crucial for quantitation. In principle, this situation is improved if all sputtered particles are ionized by a single photon absorption process. In this case, the RSF are shown to span a range of three orders of magnitude at low laser intensity, most of which is due to the variation of the ionization cross section. Consequently, this range is significantly narrowed due to the saturation of the ionization if the laser intensity is increased. Even under complete saturation an RSF scatter over about an order of magnitude remains which is attributed to differences in the effective ionization volume of different elements.

Acknowledgement. The authors are greatly indebted to Prof. Dr. H. Oechsner for providing funds to perform this work as well as for many stimulating discussions.

References

12. Thompson MW (1968) Phil Mag 18: 377