One of the key parameters characterizing the ion formation process in SIMS is the ionization probability $\alpha^{+,-}$, i.e. the probability that a sputtered particle leaves the surface in a positively or negatively charged state. Numerous theoretical models have been published describing $\alpha^{+,-}$, a fairly recent review of which can be found in [1]. An experimental determination of this quantity requires the detection of sputtered neutral species (besides the corresponding secondary ions), a task which adds complexity due to the fact that these particles must be post-ionized prior to mass and energy spectrometric detection. In order to permit a quantitative evaluation of $\alpha^{+,-}$, it is essential that i) the post-ionization probability must be precisely known and, even more importantly, ii) related neutral and ionic sputtering yields must be determined under otherwise identical experimental conditions. Particularly the latter condition is generally hard to fulfil, since most experiments employ post-ionization schemes which are sensitive to the number density of sputtered neutrals at a point located relatively far away from the surface, while the detection of secondary ions usually involves a direct measurement of the flux of charged particles leaving the surface, often even assisted by an accelerating electrostatic field. As a consequence, ion optical conditions and therefore the instrumental detection efficiency for secondary ions and post-ionized neutrals will in general be different.

In this paper, we describe an experimental method which avoids these problems. The technique is based on the in situ detection of sputtered secondary ions and the respective sputtered neutral species within the ionization region of a reflectron Time-of-Flight (ToF) mass spectrometer, which has been described in great detail earlier [2,3]. A schematic view of the setup is shown in Fig. 1. The sample is bombarded with a pulsed ion beam. During the primary ion pulse, the sample is held at ground potential in order to ensure that the spatial region between the surface and the extraction electrode $E_1$ is field-free. The sputtered neutral particles are ionized by an excimer laser operated at wavelengths of 248, 193 or 157 nm which is fired immediately...
after the primary ion pulse. The resulting photoions are extracted by an electric field which is switched on shortly (about 20 ns) after the ionizing laser pulse with a rise time short enough (< 10 ns) to ensure that motion of the ions during the slope of the extraction field is negligible. As a consequence, it is the leading edge of the field pulse (and not the exact firing time of the ionization laser) which determines the zero of the flight time measurement in the reflectron ToF mass spectrometer. Moreover, the use of this timing sequence ensures that the temporal width and shape of the flight time peak recorded for particles of a particular mass are exclusively determined by the time refocusing properties of the reflectron ToF spectrometer and, in particular, do not depend on either the timing jitter or the temporal width of the ionization laser pulse.

An important aspect of the technique concerns the ionization volume $V_{\text{ion}}$, i.e., the spatial volume within the extraction region from which ions are accepted and detected by the mass spectrometer. In the direction parallel to the sample surface, both the location as well as the extension of $V_{\text{ion}}$ are simply determined by ion optical conditions. In the direction along the surface normal, however, the situation is slightly more complicated. Here, both the exact location of the center of $V_{\text{ion}}$ as well as its spatial extension are determined by the time refocusing properties of the reflectron ToF spectrometer. In order to illustrate this, Fig. 3 shows the calculated flight time of ions as a function of their starting coordinate $z$ at the time when the extraction field is switched on for a typical set of experimental parameters. The shape of the measured ToF peak is to first order determined by the inverse derivative of the depicted curve, the peak will therefore be centered around a flight time corresponding to the local minimum in Fig. 3. The corresponding $z$-value determines the center of the ionization volume. The experimentally observed half width of the peaks is about 20 ns corresponding to a $z$-interval of about 1 mm (indicated by the shaded area in Fig. 3), ions starting farther away from the center are quickly dispersed in flight time and are

![Fig. 3 Calculated flight time vs. starting coordinate $z$ along the surface normal](image)

![Fig. 2 ToF signal of post-ionized sputtered neutrals vs. position of the ionizing laser beam](image)
therefore not detected in the peak, but rather contribute to a structureless background in
the ToF spectrum. The shape of curves like that displayed in Fig. 3 therefore acts as an
effective restriction of the sensitive volume of the mass spectrometer along the z-
direction. In order to demonstrate this, Fig. 2 shows the measured ToF signal of post-
ionized sputtered neutral particles vs. the position of a tightly focused ionization laser
beam which was translated in directions parallel and perpendicular to the sample surface.
It is clearly seen that the effective diameter of $V_{\text{ion}}$ is about 1 mm in both directions.

For the quantitative detection of sputtered neutrals, it is essential to eliminate the
influence of the generally unknown post-ionization cross sections. In our approach, this is
accomplished by saturating the photoabsorption process, thus leading to a complete
photoionization of all neutral particles within the ionization volume. In order to achieve
and identify this condition, it is essential that i) photoionization is accomplished by
absorption of only one single photon, since only in this case the laser intensity
dependence of the measured photoion signals is easily understood and ii) the ionizing
laser beam is defocused to the dimension of $V_{\text{ion}}$. A typical laser intensity dependence
measured under these conditions is depicted in Fig. 4, which clearly shows the saturation
behaviour expected for a single photon absorption process (dotted line fitted to the data).
In the present context, it is important to note that the saturated signal is representative of
the number density of sputtered neutral particles present within $V_{\text{ion}}$ at the firing time of
the laser.

For the detection of secondary ions, the ionization laser is simply switched off, while
all other parameters of the experiment remain unchanged. Under these conditions, all of
the above arguments with respect to the extension of $V_{\text{ion}}$ and the generation of a ToF
spectrum remain valid, and the instrument therefore detects sharp flight time peaks of
secondary ions which are present within $V_{\text{ion}}$ at the switching time of the extraction field.
Fig. 5 shows an example which was obtained on sputtered neutral Ge atoms. For
comparison, a spectrum taken with the ionization laser switched on is included, which
clearly shows that the mass spectral characteristics of secondary ions
and post-ionized neutrals are identical. It should be explicitly
noted at this point that this way of
generating a secondary ion mass
spectrum is fundamentally different
from the usual way ToF-SIMS
spectra are acquired. In particular,
the width of the flight time peaks is
independent of the primary ion
pulse length and, hence, long pulses
(several $\mu$s) can be employed which
ensure that the ionization volume is
completely filled with sputtered
particles (ions and neutrals) of all
emission velocities. Under these
conditions, the measured ion signals
are representative of the number

\[ \lambda = 157 \text{ nm} \]

Fig. 4 ToF signal of post-ionized sputtered neutral Al atoms vs. peak power density of the ionizing laser
density of secondary ions within the ionization volume (instead of the flux as in usual ToF-SIMS spectra) and, as such, are directly comparable to the respective post-ionized neutral signals. Moreover, since the instrument cannot distinguish between post-ionized neutrals and secondary ions present within $V_{ion}$, the transmission and detection efficiency for both species are identical. As a consequence, the method presented here allows the detection of secondary neutrals and ions of the same mass under exactly the same experimental conditions, and the ionization probability for the formation of positively charged secondary ions can therefore be directly determined as

$$\alpha^+ = \frac{S(X^+)}{S_{tot}(X^0) + S(X^+)}$$

without any further corrections. As an example, Table 1 shows the resulting ionization probability of Ge and Ag atoms sputtered from the respective clean surfaces under UHV conditions. It should be stressed again that the absolute magnitude of $\alpha^+$ is a direct outcome of the experiment and contains no further correction for instrument transmission, post-ionization efficiency etc. For comparison, data taken from ref [4] is included which was obtained in a non mass resolved manner by comparing absolute secondary ion yields with known total sputtering yields. Further examples in which the method is used to determine the ionization probability of sputtered clusters are presented elsewhere in this volume [5].

References