## 4 Ion Beam Techniques: Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

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### CONTENTS

4.1 Introduction: The Analytical Question .................................................................65
4.2 Definitions of Important Terms ..............................................................................66
4.3 Physical Effects of Ion-Induced Sputtering ............................................................69
   4.3.1 Sputtering ........................................................................................................69
   4.3.2 Ionization ..........................................................................................................70
   4.3.3 Formation of Molecular Species ......................................................................70
   4.3.4 Polyatomic Primary Ion Bombardment .........................................................71
4.4 Instrumentation .......................................................................................................72
   4.4.1 Primary Ion Generation ....................................................................................73
      4.4.1.1 Ion Guns for Surface Analysis .................................................................73
      4.4.1.2 Ion Guns for Sputtering .........................................................................74
   4.4.2 Mass Analyzer ..................................................................................................75
   4.4.3 Charge Compensation ......................................................................................75
4.5 Operational Modes ..................................................................................................76
   4.5.1 Surface Spectrometry ......................................................................................77
      4.5.1.1 Typical Characteristics of SIMS Spectra .................................................77
      4.5.1.2 Quantification of SIMS Spectra ...............................................................79
   4.5.2 Surface Imaging ...............................................................................................83
   4.5.3 Depth Profiling .................................................................................................84
   4.5.4 3D Microarea Analysis ......................................................................................85
4.6 Performance Summary ............................................................................................86
4.7 Problem Solving .....................................................................................................87
   4.7.1 Defects in Car Paint .........................................................................................87
   4.7.2 Chlorine Diffusion in Polymer Materials .......................................................87
   4.7.3 Residues on Glass ............................................................................................89
   4.7.4 Monitoring of Cleaning Efficiencies ..............................................................91
4.8 Summary and Outlook ............................................................................................92
References ...................................................................................................................94

### 4.1 INTRODUCTION: THE ANALYTICAL QUESTION

A universally applicable surface analysis technique for the characterization of chemical composition should be able to (a) locate points and areas of interest on the surface as well as in deeper layers, (b) identify any elements and molecules found there, and (c) determine their concentrations with an overall sensitivity of at least parts per million (ppm) for surfaces and parts per billion (ppb) for the bulk.
Figure 4.1 shows schematically the various types of external and internal structures that an analyst might want to characterize. Unfortunately, no known analytical technique can satisfy all these requirements. Nevertheless, the performance of a technique in the three areas of location, identification, and quantification may be used as a measure of its usefulness in routine analysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS), to which this chapter is dedicated, has confirmed its position as a sought-after tool for surface characterization amongst the better-known analytical techniques. This position has been achieved over the last 20 years because of its supreme capabilities in the areas of location (imaging and depth profiling) and identification (spectrometry). Not only can elements be detected but molecules as well, usually simultaneously. Lateral resolution has improved to below 100 nm, while depths down to several micrometers can be analyzed at the same time as the lateral distributions of species (three-dimensional [3D] microarea analysis) are probed. It is therefore a tool well suited to failure analysis and sample screening. New options, in particular for the analysis of organic materials, have arisen with the advent of cluster-ion sources for the polyatomic bombardment of surfaces. The latter approach has improved the detection limit for organic materials by several orders of magnitude, and the first steps into organic depth profiling have been taken.

Given its strong positions in the areas of location and identification, the inferior performance of ToF-SIMS with respect to quantification is unfortunate but can often be overcome by the use of, for example, internal and external standards. Additionally, the last few years have shown that semi-quantitative information can be obtained without much effort for use in failure analysis.

4.2 DEFINITIONS OF IMPORTANT TERMS

In the following paragraphs definitions are given, and explained; these are either used later in the chapter or are commonly used in the SIMS community. It serves as reference and can be skipped at first reading.

Secondary ion yield $Y_i(X_q)$ (general)

$Y_i(X_q) = \text{number of detected secondary ions } X \text{ in charge state } q \text{ per number of primary ions}$, where $Y_i$ is dependent on the particular instrumental conditions used (e.g., transmission and detection efficiency). For measurements performed with the same instrument under near-identical operational conditions, the yield determination is the easiest way to compare different spectra quantitatively.

Useful yield $Y_u(X_q)$ (general)

$Y_u(X_q) = \text{number of detected secondary ions } X \text{ in charge state } q \text{ per number of sputtered species M}$. $Y_u$ is also dependent on instrumental parameters, as above. For determination of $Y_u$ the total number of sputtered species must be determined by some independent technique.
Energy distribution (general)
As a consequence of ion bombardment, elements and molecules are desorbed with different energy distributions. For elements the maximum in the distribution is at about 5–10 eV, with a slow decrease toward higher energies (proportional to $E/(E + E_b)^3$, where $E$ is the energy of the desorbing species, and $E_b$ the surface-binding energy [1]). The maximum for molecules is at lower energies, ca. 1 eV, and the distribution decreases exponentially with increasing energy (proportional to $\exp(-E/E_m)$, where $E_m$ is the maximum in the distribution [2,3]). This spread in energy must be compensated for in mass analyzers in order to achieve high mass resolution.

Angular distribution (general)
For primary ion bombardment perpendicular to the target surface, the sputtered material is ejected in a cosine distribution [4], $dY/d\Omega \propto \cos \nu$, where $\nu$ is the emission angle with respect to the surface normal. For other angles of incidence the cosine distribution shows an anisotropy in the direction of the reflected primary ions [5]. Just as for the energy distribution of the desorbed particles, the angular distribution must also be taken into account in the design of suitable mass analyzers. For example, it influences the analyzer performance with respect to topographically demanding samples (e.g., wires, balls, and edges).

Disappearance yield $Y_D(M)$ (organic materials)
$Y_D(M) = \text{number of surface species M having disappeared per number of primary ions}$. This quantity refers to those surface species that have disappeared from the surface as a result of primary ion bombardment, irrespective of their fate (i.e., due to sputtering, fragmentation, thermal desorption, etc.).

Disappearance cross-section $\sigma$ (organic materials)
$\sigma$ is defined as the area from which surface species have disappeared under primary ion bombardment, irrespective of their fate; the magnitude of $\sigma$ is a function of the particular species M being analyzed (i.e., $\sigma = \sigma(M)$). Typical values are $10^{-13}$ to $10^{-14}$ cm$^2$. It is used mainly in connection with organic monolayers.

Static limit (organic materials)
In general, the probability $P$ of collecting data from an already damaged area must be kept very small, that is,

$$P = \sigma_{tot}/A \ll 1$$

(4.1)

where

$A$ is the bombarded area

$\sigma_{tot}$ is the total area of damage

If $P$ is sufficiently small, then the bombardment processes can be assumed to be independent of each other, i.e.,

$$\sigma_{tot} = \sum \sigma = \text{PID} \times \sigma$$

(4.2)

where

$\sigma$ is the disappearance cross-section

PID is the primary ion dose

Then

$$P = \text{PID} \times \sigma/A = \text{PIDD} \times \sigma \ll 1$$

(4.3)
where PIDD (=PID/A) is the primary ion dose density. Thus, for $P = 0.01$ and $\sigma = 10^{-13}$ to $10^{-14}$ cm$^2$, the consequence is that $(PIDD)_{\text{max}} = 10^{11}$ to $10^{12}$ ions/cm$^2$, while for $P = 0.1$, $(PIDD)_{\text{max}} = 10^{12}$ to $10^{13}$ ions/cm$^2$. It must be emphasized that the static limit $(PIDD)_{\text{max}}$ depends on $\sigma$, which itself depends on the particular species.

**Transformation probability** $P(M \rightarrow X_q)$

$P(M \rightarrow X_q) = \text{number of emitted secondary ions } X_q \text{ per number of sputtered surface species } M = Y_i(X_q)/Y_D(M)$. $P(M \rightarrow X_q)$ is the probability of a surface species $M$ being transformed into an ion $X$ in charge state $q$. The transformation probability can be determined by evaluation of a plot of $N_d(t)$ versus $t$ if $N(M)$ is known. $P(M \rightarrow X_q)$ is used mainly for the description of monolayers. It is assumed that desorbed ions are stable. For metastable ions, measured values of $P(M \rightarrow X_q)$ are too low.

**Number of detectable ions** $N_d$ (organic materials)

$$N_d(t) = N_d(0) \exp(-\sigma I/Ae)t$$  \hspace{1cm} (4.4)

where

- $N_d(0)$ is the number of detectable ions at $t = 0$
- $I$ is the primary ion current
- $A$ is the bombarded area
- $\sigma$ is the disappearance cross-section

From a plot of $N_d(t)$ versus $t$, $\sigma$ can be found. $N_d(0)$ itself is given by

$$N_d(0) = N(M)P(M \rightarrow X_q)TD$$  \hspace{1cm} (4.5)

where

- $N(M)$ is the number of molecules $M$ present at the surface
- $T$ is the transmission of the analyzer
- $D$ is the detection efficiency
- $P(M \rightarrow X_q)$ is the transformation probability (see previous paragraph)

**Ion generation efficiency** $E(X_q)$ (organic materials)

$$E(X_q) = Y_i(X_q)/\sigma$$  \hspace{1cm} (4.6)

$\approx N(M) P(M \rightarrow X_q)TD$, for monolayers

where

- $Y_i(X_q)$ is the secondary ion yield
- $\sigma$ is the disappearance cross-section

$E(X_q)$ describes the maximum number of secondary ions that can be detected from the unit surface area (typically 1 cm$^2$) if the whole area were to be consumed. It therefore refers to the effectiveness with which ions can be generated. $E(X_q)$ depends on the primary ion species and is also used for the analysis of multilayers.

**Useful lateral resolution** $\Delta l$ (organic materials)

Estimation of $\Delta l$ is based on the area $\sigma$ that has to be damaged to detect $n$ secondary ions:

$$(\Delta l)^2 = \sigma = n/E(X_q)$$
\[ \Delta l = \left( n / E(X_q) \right)^{1/2} \]  

(4.7)

The dependency of \( \Delta l \) on \( E(X_q) \) is such that a good lateral resolution requires very efficient secondary ion generation independent of the physical properties of the analytical instrument (e.g., focus of the primary ion gun, transmission of the analyzer).

### 4.3 PHYSICAL EFFECTS OF ION-INDUCED SPUTTERING

SIMS is based on the initially unexpected observation that the bombardment of a surface with ions of kiloelectronvolt energy leads to the emission (sputtering) of a secondary species characteristic of the surface chemical composition, an effect that was first discovered by Thomson in 1910 [6]. A small fraction of the sputtered particles was found to be charged (secondary ions).

Even now, almost 100 years later, the physical effects that lead to the eventual desorption* of secondary particles are not yet completely understood. Whereas the desorption of secondary neutrals from elemental targets can be described fairly well, an explanation of the emission of charged particles and, in particular, of the emission of molecular species is still being sought. Nevertheless, there is a consensus that sputtering is based primarily on the formation of a collision cascade in the target caused by the impinging primary ion [7,8].

#### 4.3.1 SPUTTERING

When a primary ion hits a solid, it loses its energy and momentum by elastic and inelastic collisions with target atoms, which are then displaced. These moving atoms (i.e., primary recoils) themselves induce the movement of further target atoms (i.e., secondary recoils), so that the paths of the primary ion and of the highly energetic primary recoil atoms are surrounded by a cloud of recoil particles of lower energies (i.e., a collision cascade; see Figure 4.2). Recoil atoms can leave the solid if their

* Although the term “desorption” is now used mainly to describe the spontaneous disappearance of a species from a surface, in this chapter it will also be used to describe sputter-induced particle emission from surfaces.

FIGURE 4.2 Schematic of the sputtering process.
momenta are directed at least partially toward the surface, and if their energies are sufficient to over-
come the surface binding energy.

The greatest number of recoils is produced near the end of the collision cascade and their aver-
age energy is consequently comparatively low. Only recoils originating in the outermost monolayer
of the solid can overcome the surface energy barrier and contribute to the sputtered flux. The low-
energy of the secondary recoils is sufficient to cause the ejection of not only atoms into the gas phase
but also intact molecules (see Section 4.3.3). The total sputtered flux is therefore characteristic of
both the elemental and molecular composition of the uppermost monolayer of the bombarded sur-
face (see Refs. [2,7–11] for detailed descriptions).

4.3.2 Ionization

By far the greatest proportion of the sputtered flux has zero charge, i.e., consists of neutrals. The
fraction desorbed as ions is only $10^{-1}$ to $10^{-6}$. The number of sputtered ions per incident primary ion
(i.e., the secondary ion yield) can also vary tremendously with the chemical environment in the near-
surface layers, a phenomenon known as the matrix effect. Examples of the secondary ion yield
enhancement, which in some cases can reach several orders of magnitude, are described in Refs.
[12,13] for positive metal ions in oxidic environments.

With such yield variations direct quantification of surface species based on the number of des-
orbed secondary ions (i.e., from the SIMS data) is difficult (see Section 4.5.1). Sputtered neutrals
suffer much less from changes in the chemical matrix. However, the analytical technique, secondary
neutrals mass spectrometry (SNMS), that makes use of these neutrals, has so far been applied far
less often than SIMS for the simple reason that mass analysis can be achieved only if the species is
charged. Sputtered neutrals must therefore be ionized prior to mass analysis (i.e., postionization).
This process not only complicates the experimental setup but also reduces the number of surface
species that can be detected to such an extent that only for specific applications does the SNMS
approach the levels of sensitivity (in terms of minimum detectable surface species) of SIMS.

4.3.3 Formation of Molecular Species

Whereas the desorption of atoms and small molecular clusters by ion bombardment can be described
in a satisfactory way by the formation of collision cascades, it is surprising that large molecular spe-
cies, and even molecular constituents that are thermally unstable and cannot be vaporized, are also
emitted from the first monolayer of a surface as intact neutral particles and as positive or negative
secondary ions. This phenomenon provides the basis for the mass spectrometric analysis of molecu-
lar surfaces first described by Benninghoven [14,15]. An early summary of emission models for the
desorption of organic species can be found in Ref. [16].

As mentioned, the entire energy of the impinging primary ion is transferred in the collision
cascade. Those areas affected by the cascade therefore undergo dramatic changes in their com-
position, including the breaking and reformation of chemical bonds. If information on the
molecular structure of a surface is required, collection of data from already damaged areas must
be avoided. From a statistical point of view this can be achieved if the PIDD (i.e., the number
of primary ions per bombarded area) is reduced to such an extent that a maximum of only 1%
of the atoms in the surface suffer primary knock-on collisions. For such an operational mode
the term static SIMS (SSIMS) is used in contrast to dynamic SIMS (DSIMS). In the dynamic
versions the operational conditions are such that successive atom layers are removed com-
pletely and rapidly under the primary ion bombardment, and the sputtered flux is used to obtain
a “depth profile” of the elements present [2]. The static limit, i.e., the highest PIDD that can be
tolerated without causing significant surface damage, is of the order of $10^{11}$ to $10^{13}$ ions/cm$^2$, depending on the size of the species analyzed (see also Section 4.2).

During the last 10 years it has transpired that the efficiency with which secondary ions of organic materials can be generated (secondary ion formation efficiency $E$; see Section 4.2) is strongly dependent on the nature of the primary ion. In particular, the use of polyatomic primary ions, or clusters, has lead to dramatic increases in formation efficiency. As the formation efficiency influences not only the ultimate detection limit, but also the achievable lateral resolution (useful lateral resolution $\Delta l$, see Section 4.2), the advent of cluster ion sources has allowed the expansion of analytical applications in organic analysis.

### 4.3.4 Polyatomic Primary Ion Bombardment

Polyatomic bombardment refers to a cluster of atoms jointly reaching the target and thus allowing cooperative phenomena in the substrate. Currently, SF$_5$ [17,18], Au$_x$ [19], Bi$_x$ [20], as well as C$_{60}$ [21–23], are in use.

Whereas the emission behavior of elemental ions remains almost unchanged when switching from monatomic to polyatomic bombardment, the ion generation efficiency $E$ for organic materials is enhanced by up to three orders of magnitude. In Figure 4.3, a systematic study of the emission behavior of the polymer additive Irganox 1010 (mass 1176 amu) under bombardment with different primary ion species is shown. The additive was prepared as a monolayer on low-density polyethylene (LDPE). As a result of this method of preparation, secondary ions from the additive can originate only in the uppermost monolayer, and therefore disappearance cross-sections (necessary for the determination of $E$; see Section 4.2) can be measured exactly. Furthermore, the physical effects leading to the emission of secondary ions take place entirely in an organic substrate.

From Figure 4.3a it can be concluded that the formation efficiency increases with the mass of the primary ion for monatomic bombardment. When using Au$^+$ or Bi$^+$ instead of Ga$^+$ the efficiency increases by more than a factor of 10. An even more dramatic increase is observed when switching to polyatomic bombardment. Compared to the efficiency of Ga$^+$, the efficiencies of Bi$_3^+$ or C$_{60}^+$ are higher by more than three orders of magnitude. As the useful lateral resolution has a square root dependency on $1/E$ (see Section 4.2), the enhancement in ion formation efficiency leads to a corresponding improvement in the useful lateral resolution of more than one order of magnitude. Whereas under Ga$^+$ bombardment an area with a diameter of at least 8$\mu$m must be removed in order to generate four intact molecular ions, a diameter of 200 nm is sufficient under polyatomic bombardment. Thus, for the first time, organic imaging in the submicrometer range becomes possible [24].

Apart from enhancing the ion formation efficiency in the uppermost monolayer, polyatomic bombardment also leads to reduced damage in the deeper layers of an organic substrate. Therefore, not only does the uppermost monolayer contribute to the organic secondary ions signals, but signals from deeper layers can also be used. In some cases it is even possible to obtain stable secondary ion signals of organic species under prolonged primary ion bombardment, allowing the monitoring of the distribution of organic material as a function of sputtering depth (organic depth profiling) [25–27]. Several factors seem to influence the possibility of organic depth profiling, including the target chemistry [28,29] and the surface temperature [30,31].

The underlying physical and chemical effects are currently a topic of intense discussion. Explanations considered include a deposition of collision energy closer to the surface [32] and cooperative phenomena in overlapping collision cascades [33]. The first review on the current status in cluster ion bombardment is given in Ref. [34]. However, the field is still in development and new insights and developments can be expected over the next years.
**4.4 INSTRUMENTATION**

In general the instrumentation for a SIMS experiment can be divided into two parts, (I) and (II), as follows:

(I) Primary ion generation (primary ion column)

(Secondary ion generation, target)

(II) Mass analysis and detection (secondary ion column).

In the primary ion column the primary ions are generated, focused, and transported toward the target; in the secondary ion column the desorbed species are extracted, sorted by mass, and detected. Mass detection in ToF analyzers requires pulsed operation of the primary ion column. The primary

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**FIGURE 4.3** (a) Ion generation efficiency for the emission of the intact molecular ion of Irganox 1010 prepared as a monolayer on LDPE, as a function of primary ion species and primary ion energy. (b) Useful lateral resolution for detection of four intact molecular ions of Irganox 1010, as a function of primary ion species and primary ion energy.

<table>
<thead>
<tr>
<th>Projectile</th>
<th>Mass/u</th>
<th>PI energy range/keV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga⁺</td>
<td>69</td>
<td>5..25</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>133</td>
<td>4..10</td>
</tr>
<tr>
<td>SF₅⁺</td>
<td>127</td>
<td>5..10</td>
</tr>
<tr>
<td>Au⁺</td>
<td>197</td>
<td>8..25</td>
</tr>
<tr>
<td>Au₂⁺</td>
<td>394</td>
<td>8..25</td>
</tr>
<tr>
<td>Au₃⁺</td>
<td>591</td>
<td>12..25</td>
</tr>
<tr>
<td>Bi⁺</td>
<td>209</td>
<td>25</td>
</tr>
<tr>
<td>Bi₃⁺</td>
<td>627</td>
<td>25</td>
</tr>
<tr>
<td>C₆₀⁺</td>
<td>720</td>
<td>10..20</td>
</tr>
</tbody>
</table>
ions in fact reach the target in the form of ion packages with well-defined arrival times, a prerequisite for the measurement of the flight time of the generated secondary ions toward the detector.

### 4.4.1 Primary Ion Generation

In general, primary ion guns can be distinguished between those used for the analysis of the uppermost monolayer (analysis guns) and those used for subsequent sputter removal of surface species (sputter guns). The selection of a suitable ion gun for SIMS depends on the type of application intended and the particular operational mode (see Section 4.5).

#### 4.4.1.1 Ion Guns for Surface Analysis

A primary ion gun for surface analysis by ToF-SIMS should provide high lateral resolution, high mass resolution, and fast measurement times. For high mass resolution the pulse length of the primary ion packages must be very small (<1 ns). Good lateral resolution requires good focus ability in the ion column, while the measurement time is influenced by the rate at which data can be acquired, which is dependent principally on the achievable primary ion current. Unfortunately, the fundamental laws of physics decree that in any one ion optical arrangement the three decisive parameters, pulse length, focus diameter, and data rate, cannot all be optimized at the same time. The possible options fall within a parameter triangle as shown in Figure 4.4. For example, having a high mass resolution and a high lateral resolution will be possible only at the cost of data rates, i.e., measurement time, while, on the other hand, fast production of ion images with high lateral resolution requires a compromise with respect to mass resolution (i.e., primary ion pulse length). Depending on the ion gun used, either the whole parameter triangle can be accessed or special fixed points can be predefined.

Today, the two groups of ion guns most used in ToF-SIMS are liquid metal ion guns (LMIG) and gas-phase electron impact (EI) ionization guns. These two types of ion guns will now be discussed briefly.

In an LMIG a small needle is wetted by a liquid metal (e.g., Ga, Au, Bi). A positive voltage of some 10 kV is applied to the needle and a spray process (ion formation by field emission) occurs at the needle tip. This field-induced stream of positively charged ions (or jet) is used as the primary ion beam [35–37]. Because the ion production volume at the tip is very small, and the energy distribution in the emission solid angle is very narrow, LMIG sources have high brightness, and consequently the ion beam can be focused to a small area with high current density. The necessary use of liquid metals means that chemical reactions at the surface cannot be completely excluded, although they have not been reported so far. Generally, LMIGs allow fast switching between monatomic and polyatomic primary ions (e.g., \( \text{Au}^+_1, \text{Au}^+_3, \\text{Bi}^+_1, \\text{Bi}^+_3, \ldots, \text{Bi}^+_7 \)) and are therefore well suited to both elemental and molecular surface analyses. They are easy to use and the pulse length can be kept very short. They are currently the “universal workhorse” guns in ToF-SIMS surface analysis.

Before the advent of LMIGs, gas-phase ionization guns were the most used in surface analysis, usually operated with noble gas ions such as \( \text{Ar}^+ \) or \( \text{Xe}^+ \), and almost always involving EI. In an EI gun gas atoms are ionized by collisions with electrons of some 10 eV energy (i.e., five to six times the ionization potential) attracted to an anode from a heated filament. The gas ions so generated are
accelerated toward an extraction electrode and can then be focused onto the target \[2,38,39\]. The use of noble gases offers the advantage that there are no chemical reactions between the primary ion and the target species that could affect the correct determination of the surface composition. Although EI guns can deliver very high data rates, the focus quality and the achievable pulse length are limited. As a result, they are now not used as often as LMIGs. Recently, EI guns have found new interest because they allow the production and application of large polyatomic cluster ions such as \(C_{60}^+\) and \(SF_5^+\).

Figure 4.5 summarizes the performance data of primary ion guns used for analysis. It can be seen clearly that at a given beam current the focusing capability of LMIGs (liquid metal ion source [LMIS] in Figure 4.5) is more than one order of magnitude better than that of gas-phase ionization guns (duoplasmatron: the gas-phase ionization gun with the best focus quality \[40\]). Additionally, data have been added for Cs primary ions produced in a surface ionization gun (for operating principles see Ref. \[2\]). Please note that the data refer to unpulsed operations of the guns. Pulsing will reduce further the focus quality, making it difficult to reach a submicrometer focus quality with EI guns.

### 4.4.1.2 Ion Guns for Sputtering

For surface erosion in ToF-SIMS, either EI (\(O_2^+\)) or surface ionization ion guns (Cs\(^+\)) are used. These ions are used because, on the one hand, \(O_2^+\) stabilizes the chemical environment for the emission of positively charged secondary ions and, on the other, Cs\(^+\) does the same for negatively charged secondary ions (see Chapter 10). Their use thus guarantees high secondary ion yields even from deep layers. Recently, \(C_{60}^+\) and \(SF_5^+\) have also been used (gas-phase ionization) in context with organic depth profiling (see Section 4.5.3).
4.4.2 MASS ANALYZER

In a ToF-SIMS experiment, a ToF analyzer is used for mass separation of the desorbed secondary ions. In a ToF analyzer (Figure 4.6), the ions desorbed are accelerated to a common energy $qU$ (where $q =$ ion charge and $U =$ applied voltage), and the time $t$ taken by each type of ion to reach a detector, after traveling along a field-free drift path of given length $s$, is measured, according to

$$m s^2/2t^2 = qU$$

which can be rearranged to

$$t^2 = ms^2/2qU \propto mlq$$

(4.9)

The $m/q$ ratio can then be calculated from the flight time. Because a very well-defined start time is required for the flight time measurement, the primary ion gun has to be operated in a pulsed mode in order to be able to deliver discrete primary ion packages [41]. Electric fields (using, e.g., ion mirrors [41,42] or electrical sectors [43,44]) can be introduced into the drift path in order to compensate for different incident energies and angular distributions of the ions (see also Section 4.2).

The main features of a ToF analyzer are

- Quasi, simultaneous detection of all masses of one polarity
- High geometrical transmission
- High mass resolution

ToF analyzers therefore offer excellent sensitivity and have become the analyzer of choice for organic analysis and for screening purposes.

![Figure 4.6 Schematic of a ToF analyzer. The flight path length is $s$ and the extraction voltage $U$.](image-url)

4.4.3 CHARGE COMPENSATION

The primary ion bombardment leads not only to the desorption of sputtered elements and molecules but also to the emission of further secondary species, among the electrons. The number of emitted electrons per primary ion (the so-called ion-induced secondary-electron coefficient) can be as large...
as 10 depending on the particular material. Ion bombardment of insulating surfaces therefore leads to the build-up of positive charge at the surface that can severely disturb the secondary ion extraction. The charge can be compensated by auxiliary electron bombardment. Low-energy electrons are generally used (<20 eV) because, firstly, at those energies the electron-induced secondary-electron coefficient is <1 (if the electron-induced secondary-electron coefficient is less than unity, then every incoming electron leads to less than one outgoing electron and an existing positive charge can be compensated) and, secondly, because sensitive organic molecules are hardly affected by the additional bombardment. For the latter reason high-energy electrons (e.g., >3 keV, for which the electron-induced secondary-electron yield coefficient would also be below unity) are less suitable for charge compensation purposes.

When ToF analyzers are used for mass determination, low-energy electrons can easily be injected into the target zone in the period between secondary ion extraction and the next primary ion pulse. During that period all high voltages near the target zone, which might deflect low-energy electrons, can be switched off. With this arrangement, stable spectra of both polarities can be obtained even for extremely insulating materials, including powders (for details see Ref. [45]).

### 4.5 OPERATIONAL MODES

Depending on whether or not the primary ion beam is focused and rastered across the surface, and on whether or not the surface is continuously eroded during the SIMS experiment, four operational modes can be distinguished. These modes are pictured in Figure 4.7, and described below.

In surface spectrometry (see Section 4.5.1), an area of interest is bombarded by the primary ion beam and the mass spectra are recorded for all secondary ions originating from the entire bombarded area. The mass spectrum so obtained then contains information on the chemical composition in the area of interest. Such an experiment is normally performed under static or near-static conditions, i.e., the information originates from the uppermost monolayers of the sample.

![Figure 4.7 Operational modes.](image-url)
In surface imaging (Section 4.5.2) the primary ion beam is focused to a very small diameter (typically <1 μm) and is rastered across the surface point-by-point. The whole bombarded area is divided into so-called pixels that are interrogated step-by-step by the primary ion beam (ion probe mode of imaging). As a result, a mass spectrum is obtained from every pixel addressed, and therefore chemical maps can be acquired for any secondary ion of interest [46]. Alternatively, when operating a ToF analyzer with imaging capabilities, an unfocused primary ion beam is directed onto the sample surface, and a position-sensitive detector is used to deduce the point of origin of the secondary ions (ion microscope mode of imaging [43]). In general, the microprobe mode is used more often due to the better lateral resolution and higher data rates that can be obtained.

In depth profiling (Section 4.5.3) the PID density is increased to the point at which continuous sample erosion occurs during the SIMS experiment; the masses of the desorbed secondary ions are then analyzed as a function of sputter time. Since the sputter time is correlated with the eroded depth, a mass spectrum as a function of depth is recorded.

In 3D microarea analysis (Section 4.5.4) the combination of surface imaging with depth profiling allows any position within a 3D volume (voxel) to be addressed, thus providing access to the chemical compositions in the bombarded and eroded volumes.

### 4.5.1 Surface Spectrometry

Surface spectrometry is one of the oldest operational modes. Since all other modes require the detection of a spectrum in any case, this mode is described in detail below.

#### 4.5.1.1 Typical Characteristics of SIMS Spectra

Figure 4.8 shows the positive secondary ion mass spectrum (“positive” refers to the detection of positively charged secondary ions) from an isolated oligomer of polydimethylsiloxane (PDMS) prepared as a monolayer on an etched silver substrate (solution: 0.1 mg/mL in toluene, 1 μL spread over 80 mm²). This particular material is used here as an example since it allows most of the typical spectral features of SIMS spectra to be described. In contrast to polymer preparations containing more than one oligomer, spectra of isolated oligomers, though technically irrelevant, do not suffer from peak interferences with other oligomers, and the fragments can arise from only one type of molecule instead of from the whole molecular weight distribution. The chosen molecule was kindly provided by Wacker Chemie AG (München, Germany). PDMS molecules, known also as silicone oils or rubbers, are among the most troublesome contaminants in adhesion problems (see Chapter 18).

The spectrum can be divided into three general regions: elements and fragments (1–500 amu), quasimolecular ions (1150–1350 amu), and an intermediate region, in which almost no secondary ions can be detected.

The term “quasimolecular ions” refers to those ions that are formed either by the attachment of low-molecular-weight cations and anions (e.g., salt and metal ions) to the parent mass, or by the loss of small fragments (mostly functional groups such as CH₃, OH, etc.). The most intense group of peaks among the quasimolecular ions can be attributed to the attachment of silver to the intact molecule (i.e., (M + Ag)⁺) confirmed by a comparison of the calculated and measured isotopic patterns. Almost the same holds for the peak at mass 701.1 amu. Here, cationization has been achieved by the attachment of two Ag ions. Consequently, the ion is doubly charged and appears at half the mass of the parent molecule (1402.2 amu) (cf. detection of m/q). (The low intensity of this peak shows that formation of a doubly charged species is not a dominant process in SIMS.) Further, quasimolecular ions can be attributed to (M–CH₃)⁺ M⁺, and (M + H)⁺ (the isotopic patterns of M⁺ and (M + H)⁺ overlap), as well as (M + Na)⁺ and (M + K)⁺. The differences in the intensities of these ions, compared to that of the (M + Ag)⁺ peak, demonstrate the high formation probability of the cations. If a complete oligomer weight distribution were to be analyzed, the form of the distribution could be derived directly from the distributions of the respective quasimolecular ions.
The mass range up to 500 amu is dominated by element and fragment ions. Na, Si, and Ag are detected as elements. Na is due to a salt contamination, Si originates from the oligomer backbone, and Ag is a substrate ion. Four organic fragment series can be identified starting at masses 73, 103, 117, and 133 amu, respectively. All further fragments can be explained by the addition of the PDMS repeat unit (74 amu). The ion structures are given in Figure 4.9. With the exception of the primary ionization process, fragments in SIMS are nearly all formed according to the conventional rules of EI mass spectrometry (i.e., α and β cleavages, rearrangement processes [47]). As other polymers give rise to other fragment patterns, the type of polymer can be determined by evaluation of the low-mass fragments alone.

In the intermediate mass range, where the PDMS does not give rise to any characteristic secondary ions, large fragments can be observed originating from single or multiple main-chain scissions. In many cases these fragments are neutral and can therefore be observed only as (F + Ag)⁺ (where F is an appropriate fragment) from monolayer preparations on noble metals. From the mass separation between two fragment peaks the mass of the polymer repeat unit can be derived.

Of course, negatively charged secondary ions can also be formed, as quasimolecular ions (e.g., (M – H)⁻) as well as fragments. Small, negatively charged fragments are often more characteristic of a molecule than those positively charged, because charge stabilization is usually related to oxygen, a heteroatom having a profound influence on chemical behavior. From PDMS, for example, no negative quasimolecular ions are formed, but a strong fragment series starting at mass 75 amu (CH₃SiO₂) is observed.

In summary, SIMS spectra provide not only evidence of all the elements present but also detailed insight into the molecular composition. Quasimolecular ions can be desorbed intact up to 3,500 amu.
and sometimes even up to 15,000 amu, depending on the particular molecule [48] and on whether or not an effective ionization mechanism is present. Larger molecules tend to fragment under the SIMS excitation conditions due to stronger intra- and intermolecular bonds. If no quasimolecular ions are formed, due to steric hindering during desorption (large molecules), or hindered ionization (e.g., thick molecular overlayers without contact with cations), small-fragment ions still appear, because they can be formed even if strong intra- and intermolecular bonds exist, and because they carry an intrinsic charge. The observed fragment peak patterns are characteristic of the particular molecules and of the mass range up to 500 amu; the term “fingerprint region” is thus used. Whereas quasimolecular ions are comparatively easy to identify, the interpretation of the fingerprint region requires much experience and should best be left to the expert. Meanwhile, some spectral libraries have been published [49]. However, the number of substances represented in these libraries is still comparatively small. To date no material has been reported from which SIMS spectra could not be obtained, provided that it is stable in a vacuum environment, making SIMS a universal analysis technique.

4.5.1.2 Quantification of SIMS Spectra

Generally, the matrix effect, i.e., the dependence of the secondary ion yields, transformation probability, and ion formation efficiency, on the nature of the chemical environment complicates quantification of SIMS data or makes it even impossible. Nevertheless, many cases exist where at least semiquantitative data can be obtained. The three most common ones will be discussed in the following because it is essential for the user of the technique to be aware of the options and limitations in this respect.

4.5.1.2.1 Use of Internal Standards

Internal standards are elements or molecules added to the analyte in known concentrations. If chemically identical (i.e., isotopically labeled) or chemically similar (i.e., same substance class) materials are used, the analyte and standard react in the same way to changes in the chemical environment, which means that the respective transformation probabilities change in the same
ratios. The evaluation of $I(\text{analyte})/I(\text{standard})$, with $I$ being the peak areas of the corresponding characteristic peaks, therefore allows quantification of the amount of analyte material if a calibration curve had previously been constructed from which the (fixed) ratios of the transformation probabilities could be derived [50]. Although the use of internal standards can be a very powerful approach for absolute quantification, there are several limitations to it in SIMS:

- **Choice of a suitable standard:** The standard (S) must mix homogeneously with the analyte (A). Both S and A must show the same behavior with respect to segregation or crystallization. If a sample has to be prepared specially prior to analysis, both materials must show the same behavior in all preparatory steps. All these requirements can be fulfilled for isotopically labeled materials, which are of course chemically identical, but problems can occur when using chemically similar materials. On the other hand, the latter are generally more readily available, more stable, and cheaper, compared to isotopically labeled materials.
- As A and S must be mixed prior to the measurement, the use of internal standards will usually be limited to solutions and subsequent droplet depositions onto substrates.
- **Best results can be achieved when S and A are present in approximately equal amounts, i.e., prior knowledge is required about the expected amount of A.**

### 4.5.1.2.2 (Sub)monolayer Coverages

If the analyte is present on a substrate at a submonolayer or single-monolayer coverage, quantification can be achieved by normalizing an analyte peak area to a substrate peak area. In this approach linear relationships can be found between the surface coverage and the analyte signal normalized in this way. Absolute quantification is possible if at least one coverage value can be determined by independent quantitative techniques.

As an example, Figure 4.10 compares normalized analyte signals with known coverages of sputter-deposited standards [51]. The quantification refers to Ni on a Si wafer. Ni can cause severe problems in semiconductor production and must be quantified even for extreme submonolayer coverages. The advantage of ToF-SIMS lies in the possibility of analyzing small areas with good detection limits.

For submonolayer coverages, quantification is possible because in such dilute systems the matrix of an analyte species is always that of the neighboring substrate, and therefore $P(M \rightarrow X_q)$ is stable. Nevertheless, it would be expected that deviations from linearity would occur when approaching monolayer coverage. The finding that the linear behavior extends even to monolayer coverage can

![FIGURE 4.10](image-url)
be explained in a simple way by the fact that desorption in SIMS is caused by the collision cascade, which in this case takes place entirely in the substrate and “pushes” the species from below the surface. Interactions in the vertical direction (between the layers) are thus much more important for desorption and ionization than interactions in the horizontal direction (within a layer). As long as the maximum coverage does not exceed one monolayer, a stable ion formation process (i.e., stable \( P(M \rightarrow X_q) \)) can be expected. This argument implies that severe problems could occur in quantification during the transition from monolayer to multilayer. In that case the collision cascade could take place partially in the substrate and partially in the analyte itself, which would affect principally the sputter yield. In addition, the ion formation process could also change during the transition. Coverage effects on the secondary ion yield can be observed even for those cases where a second monolayer has just started to be formed (i.e., submonolayer coverage of the second monolayer on a complete first monolayer); the effect on \((M + H)^+\) formation is an example. For the same reason quantification is also unreliable for isolated multilayer clusters (“island” nucleation) on an otherwise uncovered substrate.

4.5.1.2.3 Organic Multilayers

Quantification of organic multilayer systems is surprisingly successful in view of the enormous chemical varieties of organic materials. For quantification purposes a typical analyte molecule A (mostly a fragment from the “fingerprint” area) is first chosen, and its intensity is then normalized to either

- That of a fragment of a second compound or that of the sum of both compounds (in binary mixtures), or
- The total spectral intensity, or
- A sum over the intensities of peaks (including all relevant compounds), or
- That of an uncharacteristic hydrocarbon fragment, \( C_xH_y \)

An example is given in Figure 4.11, which shows the quantification of polybutadiene (PBD) in a binary system of PBD and polystyrene (PS). Both polymers are unsaturated hydrocarbons and quantification by other techniques is not easy. A peak typical of PBD is the \( C_4H_6^+ \) fragment at mass 54 amu. A linear relationship can be obtained if the peak area of this fragment, normalized to the total spectral intensity, is plotted against the PBD concentration in the particular sample. The quantification is achieved directly at the surface, allowing the monitoring of surface phenomena such as segregation, preferential adsorption, and diffusion.

Quantification in such a system is possible mainly because the chemical environment consists only of hydrocarbons, which from a physical (in contrast to a chemical) point of view do not vary much (only C, H, and few heteroatoms are present). If fragment ions are used, then the matrix is formed partially by the (larger) molecule itself, which helps to stabilize \( P(M \rightarrow X_q) \) further.

However, this quantification approach requires considerable experience with SIMS. First of all, the choice of a fragment is not always straightforward and not all characteristic peaks are suitable. In particular, the most intense peaks are not necessarily the most successful candidates for quantification purposes. Second, a suitable normalization procedure must be chosen. In reality it might prove necessary to try several combinations of fragments and normalization procedures while at the same time using any additional foreknowledge of the sample. The selection should then, in principle, be tested on a model system of known composition in order to establish adequate reliability. Fortunately, statistical procedures based on multivariate statistical modeling can help to select suitable normalization candidates. In particular, the use of partial least squares fitting has shown promising results [52–54]. Furthermore, reference spectra can be consulted in order to identify characteristic fingerprint peaks. Absolute quantification in multilayer systems is only rarely achieved, but semiquantitative information can be obtained in many cases.
In summary, it can be concluded that quantification of surface coverages is possible much more often than might be expected given the matrix effect in SIMS. Internal standards should be used whenever possible, since they give the most reliable results. When working with (sub)monolayer coverages, quantification by normalization to a substrate-related peak is always worth the effort. If the matrix is genuinely stable, then information on the surface coverage can be derived. If the matrix is varying (e.g., due to oxygen treatment in a plasma or from UV/ozone exposure), at least some new insight into the matrix effect itself might be gained. In this approach even a change in oxidation state can be monitored. For organic multilayers it is well worthwhile to attempt quantification. If there are no initial clues as to which peaks and normalization procedures might be suitable, then a start could be made by normalizing identified fragment ion intensities to those of uncharacteristic hydrocarbon fragments (e.g., $C_4H_9^+$, $C_3H_7^-$), which are always present on samples that have been in contact with ambient air. This is surprisingly successful in many cases and easy to apply. Further progress could then be made from spectral libraries and eventually multivariate statistical modeling. Quantification remains difficult for systems where there are only a few monolayers (one to five) cover the substrate.

It should be emphasized that the determination of surface concentrations and coverages is only one aspect of quantification. SIMS can also be used successfully for the determination of molecular

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**FIGURE 4.11** Positive ToF-SIMS spectra of PBD and PS. The lower part shows the calibration curve derived from the results.

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Polybutadiene (PBD) $\left[ CH_2 - \text{CH} = \text{CH} - \text{CH}_2 \right]$

Polystyrene (PS) $\left[ CH_2 - \text{CH} \right]$

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weight distributions and average molecular weights in polymers, for the determination of diffusion
costants (vertical and horizontal diffusion), and for the determination of surface coverages via the
evaluation of species portions from ion images. Some examples will be shown in Section 4.7.2.

4.5.2 Surface Imaging

In general, three factors are essential for the successful location of surface species, and they there-
fore govern the overall performance in imaging (i.e., the level of spatial resolution). They are the

1. Physics of the analysis process
2. Lateral resolution provided by the instrumentation
3. Achievable sensitivity of the particular surface analytical technique

In SIMS, secondary ions are formed in a collision cascade following the impact of the primary ion.
The diameter of this collision cascade therefore determines the ultimate limit of the accuracy with
which the original position of a surface species can be located. Depending on the type of primary
ion, on the bombardment energy, and on the particular surface species, the collision cascade diam-
eter is about 2–5 nm [55,56].

The lateral resolution offered by the instrumentation is determined mainly by the spot diameter
of the primary ion beam. When LMIGs are operated in a static mode, i.e., not pulsed, a focus dia-
meter of 10 nm can be achieved [57]. However, when modern, sensitive ToF analyzers are used for
mass determination and ion detection, the static operational mode of the LMIG only allows the
acquisition either of total secondary ion images or of total ion-induced secondary-electron images.
Mass information cannot be obtained. The total secondary ion and secondary-electron images nev-
ertheless do give valuable topographical information. The image quality nowadays is close to that
of dedicated SEM instruments. If mass information is required, then the LMIG must be pulsed,
resulting in an inferior focus diameter. With only a purely nominal mass resolution, however,
50–80 nm can still be achieved. A focus diameter of 200 nm allows the acquisition of spectra with a
reasonable mass resolution of \( \frac{m}{\Delta m} = 5000 \), which is sufficient to differentiate elements from
organic species reliably. For maximum mass resolution, an LMIG with a focused diameter of ca. 1 \( \mu \text{m} \) has to be used.

A small focus diameter, however, is not of much help if not even one secondary ion can be
detected from the bombarded area due to insufficient sensitivity. This is a problem mainly in the
analysis of organic materials. However, the use of polyatomic primary ions has improved the situa-
tion considerably (see Section 4.3.4). Figure 4.3b shows that intact organic species can indeed be
detected with submicrometer pixel sizes.

As an example of the lateral resolution obtainable with a ToF-SIMS instrument, Figure 4.12
shows negative secondary ion images of a Ba halide crystal coated with Sr. The image resolution is
better than 100 nm (with Bi\(^{3+}\) as the primary ion).

However, it is not only the small fields of views that are of interest with respect to problem solv-
ing. ToF-SIMS instruments can also allow imaging of large fields of view, up to almost 10 \( \times \) 10 cm\(^2\).
In this case, either the stage is moved continuously under the primary ion beam and the resulting
data stream is reduced to pixels (stage scanning), or several adjacent images of maximum field of
view of the particular ion gun are assembled or “stitched” together. Important applications include
screening for unknown contaminants on glasses, polymers, and wafers.

In summary, it can be stated that imaging performance has improved dramatically over the last
decade. Fields of view ranging from 10 \( \times \) 10 \( \mu \text{m} \)\(^2\) to 10 \( \times \) 10 mm\(^2\) can be addressed routinely. The
LMIG has developed into the ion gun of choice for ToF-SIMS imaging because it shows excellent
focus quality, high ion currents, and can be pulsed in very short intervals, while at the same time
being able to produce polyatomic primary ions. Nevertheless, the learning curve for this operational
mode is still steep and more progress can be expected in the future.
4.5.3 Depth Profiling

Depth profiling, i.e., the sputter erosion of a surface with the purpose of analyzing the sample composition as a function of depth (DSIMS), is not the main subject of this chapter. A more detailed description can be found in Chapter 10. Nevertheless, in the last decade the number of depth profiling applications with ToF-SIMS instruments has increased continuously for three reasons:

- The possibility of detecting all masses simultaneously allows the screening of samples without the necessity of having prior knowledge of the sample composition.
- Depth profiles can be acquired easily from insulating materials.
- The sputtering ion energy can be lowered to <200 eV, improving the achievable depth resolution toward atomic dimensions.

For ToF-SIMS depth profiling a dual beam mode is used, i.e., two ion guns, one for sputter erosion and one for analysis of the crater center. An electronic timing scheme switches between the two ion guns automatically. This approach allows the optimization of sputter and analysis conditions independently from each other. The sputter gun can be operated at ultra-low energies for good depth resolution, while the primary ion species can be selected for optimum ion yields (e.g., O$_2^+$ for enhancement of electropositive elements, Cs$^+$ for enhancement of electronegative elements, and cluster ions (C$_{60}^+$, SF$_5^+$) for organic materials). For the analysis gun an LMIG is the most frequently used because of its excellent performance characteristics. The sputter rate of the analysis beam should be at the most 0.5% of that of the sputter beam, in order to avoid degrading the depth resolution. Normally, the field of view of the analysis gun is chosen to be smaller than that of the sputter gun, because such an arrangement automatically ensures that crater edge effects are minimized. For a detailed description of ToF-SIMS depth profiling see Ref. [58] and references therein.

Applications are wide ranging and include semiconductor materials, ceramics, and glass. As mentioned in Section 4.3.4, even depth profiles of organic materials are possible if polyatomic primary ions are used. An example is presented in Figure 4.13, which shows a ToF-SIMS depth profile through a layer system consisting of polyvinylpyrrolidone (PVP)/Irganox 1010 (polymer additive)/polymethylmethacrylate (PMMA). As can be seen there, for the polymers the principal constituents
of the repeat units could be detected with significant signal intensities. For the Irganox 1010, the largest positively charged fragment could be used. Such results are promising for the future. But as mentioned in Section 4.3.4, organic depth profiling is not always successful and the underlying physical and chemical effects are still under discussion. Recently, organic depth profiling was successfully reported even without the use of polyatomic primary ions but with low-energy Cs bombardment [59]. The field is still emerging and much progress can be expected in the near future.

4.5.4 3D MICROAREA ANALYSIS

Three dimensional ToF-SIMS analysis is the simultaneous combination of imaging and depth profiling, in which it is possible to analyze a volume of $300 \times 300 \times 3 \, \mu m^3$ (with the smallest dimension in the $z$-direction). For any voxel within this volume a complete ToF-SIMS spectrum is written to the computer disk and, via retrospective analysis of the raw data, the following types of information are available:

- A spectrum for any lateral position and depth
- A depth profile for any lateral position and mass
- An image for any depth and mass

It is therefore well suited to screening applications. An example is given in Figure 4.14, which shows a diffusion study in a metal oxide with a Cr + Fe + Y overlayer. The 3D distribution of the substrate compound Mg is shown on the left and the distribution of Y from the overlayer is shown on the right.
From the data it can be concluded that diffusion of the overlayer metals into the substrate occurred along the grain boundaries, and not through the bulk. In addition, organic materials have been analyzed. For 3D imaging of single biological cells, see Ref. [60].

### 4.6 PERFORMANCE SUMMARY

Table below summarizes the performance data at the time of writing. Instrumental performance (e.g., mass resolution, lateral resolution, etc.) is always likely to improve progressively with time.

<table>
<thead>
<tr>
<th>Principle of measurement</th>
<th>Excitation of the surface with high-energy ions; determination of the mass of desorbed secondary species (atoms, molecules)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Obtained information</td>
<td>Chemical (elemental/molecular) composition for the surface; detection of all elements and stable isotopes; detection of molecules (intact for m &lt; 10,000 amu)</td>
</tr>
<tr>
<td>Excitation depth</td>
<td>Some 10 nm</td>
</tr>
<tr>
<td>Information depth</td>
<td>Outermost monolayer</td>
</tr>
<tr>
<td>Operational modes</td>
<td>Spectrometry, imaging, depth profiling, 3D microarea analysis</td>
</tr>
<tr>
<td>Maximum field of view</td>
<td>ca. 10 × 10 cm²</td>
</tr>
<tr>
<td>Lateral resolution</td>
<td>&lt;100 nm (slightly higher for molecules)</td>
</tr>
<tr>
<td>Maximum depth</td>
<td>10 μm (depth profiling); 500 μm (imaging of cross-sections)</td>
</tr>
<tr>
<td>Depth resolution</td>
<td>&lt;1 nm (depth profiling); 100 nm (imaging of cross-sections)</td>
</tr>
<tr>
<td>Mass resolution</td>
<td>&gt;10⁴</td>
</tr>
<tr>
<td>Quantification</td>
<td>Only using standard reference samples; semiquantitative information can be obtained without standards</td>
</tr>
<tr>
<td>Detection limits</td>
<td>A few 10 ppb (elements), fmol (molecules)</td>
</tr>
<tr>
<td>Identification of compounds</td>
<td>Yes (including screening for unknown compounds)</td>
</tr>
<tr>
<td>Sample requirements</td>
<td>Compatible with vacuum conditions, including insulators and powders</td>
</tr>
</tbody>
</table>
4.7 PROBLEM SOLVING

It will be shown here, taking four selected examples, how ToF-SIMS can be used to solve surface-related problems. All examples have either originated directly from a production site or are related closely to development and production problems.

4.7.1 DEFECTS IN CAR PAINT

As one of the last steps in car production, visual checks are performed with respect to the quality of the car paint layers. If defects are observed, then that car cannot be processed further and paint repair is necessary. For quality and cost reasons it is therefore essential to find the cause of paint defects occurring at various stages of the production process, even if that means cutting samples from the (rather expensive) cars themselves.

One example of such a defect is described in Figure 4.15. On the left-hand side a sum image of all paint-related secondary ions is shown. Image intensities have been translated into a gray-scale color and height code. As can be seen, in the crater center hardly any paint-related ions were detected. Bearing in mind the information depth of ToF-SIMS of one monolayer, this means that at the crater position the uppermost monolayer must have consisted of something other than paint. On the right-hand side a sum image of the ions characteristic of a perfluorinated polyether is shown, indicating the presence of this material in the uppermost monolayer at the crater center. The identification was possible because perfluorinated polyethers have a characteristic ToF-SIMS spectrum consisting of $\text{C}_x\text{F}_y\text{O}_z$ fragment ions. Such polyethers are used, for example, as high-performance temperature-stable lubricants. Detailed discussions with the line engineers responsible for the painting process revealed that the lubricant originated from the transport belts used in the production. Lubricant droplets can fall into the paint bath and prevent adhesion of the paint to the metal. Tests in which the metal was deliberately contaminated by the lubricant proved that typical craters were indeed produced.

ToF-SIMS was decisive in solving the crater problem because it gave organic information about the various species present. It was thus possible to exclude polysiloxane as the cause of the defect although it often gives similar problems. Furthermore, the sensitivity was sufficient to detect sub-monolayer coverages of the lubricant at the crater bottom. The lubricant concentration was so low that neither EPMA nor SEM, imaging techniques normally applied to these kinds of problems, was able to detect the fluorine in the crater.

4.7.2 CHLORINE DIFFUSION IN POLYMER MATERIALS

Nowadays, products ranging from car bumpers to CD players to shavers consist of plastics covered by (colored) organic lacquers. One of the plastics generally used is polypropylene (PP). Unfortunately, not every lacquer adheres well to PP-based substrates. In order to overcome the problem either the PP surface can be modified (e.g., by corona or plasma treatment) or adhesion
promoters can be used. For PP, chlorinated polyolefines (CPO) have proved to be very useful for adhesion improvement. However, not much is known about the underlying adhesion mechanism. Furthermore, experience shows that the improvement is also dependent on the nature of the PP substrate.

One mechanism proposed is the diffusion of CPO into the PP substrate [61]. Differences in adhesion behavior based on this mechanism should then arise from different diffusion constants for CPO in the various PP substrates. In order to test this hypothesis, a 50 μm CPO layer was deposited onto two different substrates (the ethylene-propylene-diene terpolymers Keltan and Hifax). From the samples prepared in that way cryosections were cut, and the PP–CPO interfaces (as revealed by the surfaces of the sections) were analyzed with imaging ToF-SIMS. The chlorine distribution (originating from the CPO molecules) in the interface was monitored as a function of time in order to observe possible diffusion processes. Figure 4.16 shows the Cl⁻ image of the CPO-treated Hifax interface after 57 days. Broadening of the interface can be seen clearly, a first hint of the occurrence of diffusion. Linescans across this image, and across another taken after 8 days, are shown in Figure 4.17, demonstrating the broadening of the interface with storage time. A mathematical evaluation of the interface broadening based on diffusion theory (i.e., determination of the distance at which the original Cl concentration in CPO had decreased to one-tenth of its value as a function of the storage time, according to Fick’s second law) for the two substrates (Figure 4.18) showed not only that diffusion of CPO into the PP had indeed occurred but also that the diffusion constant in Keltan was significantly greater than in Hifax. This was in very good agreement with the empirical finding that lacquer adhesion was better on Keltan than on Hifax [61].

Imaging ToF-SIMS was used to investigate the adhesion mechanism because the values of the diffusion constants were not known in advance, and it was feared that collisional mixing, as occurs unavoidably in sputter depth profiling, could have destroyed the effect to be measured. Sectioning of samples instead of sputter depth profiling is a very useful methodology for the determination of depth distributions in those cases where the collision cascade would destroy sensitive material (e.g., organic layer systems).

![Cl-ToF-SIMS image of a cryosection of a CPO layer deposited on a PP substrate (diffusion time: 57 days). A color code is used to represent image intensities (see left color bar; pink and red correspond to low and high intensities, respectively). (From Rulle, H., PhD thesis, Münster, Germany, 1996.)](image-url)
FIGURE 4.17 Cl− line images across the image from Figure 4.16 and also across a similar image after 8 days of CPO diffusion time. The data were recorded by adding up all ion intensities over 10 lines in the center of the image in Figure 4.16. (From Rulle, H., PhD thesis, Münster, Germany, 1996.)

FIGURE 4.18 Cl diffusion profile (10% definition) as a function of sample storage time (room temperature) for the PP substrates Keltan (substrate 1) and Hifax (substrate 2). From the slopes of the curves the diffusion constants could be determined. (From Rulle, H., PhD thesis, Münster, Germany, 1996.)

4.7.3 RESIDUES ON GLASS

This example is taken directly from a production site for consumer electronics. The product in question consists mainly of plastic materials and glass held together by various glues. The product also contains moving and rotating metal parts that need to be lubricated. Unfortunately, the process...
technology of the product is confidential and therefore cannot be shown, but the example demonstrates how ToF-SIMS can be used to solve real production problems.

By optical inspection of the glass parts of products that had failed in a lifetime test, a contamination layer was detected, which in some areas was as thick as a few micrometers. In order to characterize the contaminant, infrared (IR) and x-ray photoelectron spectroscopy (XPS) measurements were performed. ToF-SIMS was not chosen in the first place because the problem seemed neither to require very sensitive analysis nor to be related in any way to the outer monolayer of the glass. The analyses showed that the material must be organic in origin, most probably based on aliphatic hydrocarbons (single Cls peak in the XPS spectrum, CH vibrations in the IR spectrum), but no further information could be obtained (no loss features or chemical shifts in the XPS spectra, no typical bonds in the IR spectra). The diagnosis “aliphatic hydrocarbon” included several glues and fats as possible contamination sources.

More information on the organic structure was therefore required. With the prior information from XPS and IR spectroscopies, it was clear that to record a ToF-SIMS spectrum directly from the material on the underlying glass would not be advisable. First of all the large amount of contamination present could pollute the vacuum system of the ToF-SIMS instrument (SIMS is sensitive to readsorbed submonolayer coverages and can therefore suffer severely from memory effects), and, second, aliphatic hydrocarbons need an effective ionization mechanism in order to be visible in a SIMS spectrum. Preparation was therefore carried out simply by rubbing a freshly etched silver substrate over the contamination, outside the vacuum system, thus transferring about a monolayer of the material to the silver. Noble metal substrates are well suited to this type of analysis because organic materials adsorbed on them can be ionized intact in the form of (M + NMe)+, with M being the molecule of interest and NMe the noble metal. This ionization mechanism works almost independently of the molecule chemistry [62]. For reference purposes the procedure was repeated for a component that had not failed.

The respective spectra are compared in Figures 4.19 and 4.20. Whereas the spectrum from the contaminated product showed a distinct peak pattern above 500 amu, this pattern was completely absent from the spectrum of the properly working product (note the enlarged section in the latter spectrum). The peaks in the spectrum of the contamination have a mass separation of 140 amu,
indicating some kind of polymer-like material. The isotopic pattern of the peaks is mainly that of silver, indicating that the spectra originated from neutral molecules cationized by silver from the substrate (i.e., (M + Ag)+ formation). From evaluations of the absolute masses it could be concluded that the repeat unit of the material must have the base composition C_{10}H_{20}. The first peak of the distribution would then correspond to a trimer of the repeat unit with hydrogen end groups, so that the contamination must have been a purely aliphatic hydrocarbon.

After further analysis of six glues and three fats used in the production (all dissolved in suitable solvents and deposited as monolayers on silver substrates), one particular fat was found to have the same characteristic peak pattern as the contamination. The fat formula is based on polyalphaolefines (Figure 4.21 shows the spectrum of the extracted base oil). Intact molecules cationized by silver produced the characteristic peak pattern in the spectrum. By comparing Figures 4.19 and 4.21 it can be concluded that the contamination must have occurred via the gas phase, because the contamination and the fatty base oil have significantly different molecular weight distributions. Low-mass molecules (n = 3, 4) are more pronounced in the contaminant compared to the base oil. This difference is caused by the fact that low-molecular-weight molecules can desorb more easily into the gas phase than those of higher molecular weights, and the shifted distribution is found after readsorption of the desorbed molecules on the glass. The mechanism was confirmed by storing some fat material together with a clean silver substrate in a closed environment for some hours. The base oil indeed desorbed into the gas phase and readsobered on the silver, where it could be detected by ToF-SIMS, showing the shifted molecular weight distribution. After the fat was replaced, the number of products failing the lifetime test was significantly reduced, and no further optically visible contamination of the glass surfaces was observed.

### 4.7.4 Monitoring of Cleaning Efficiencies

Molecular information from the outermost monolayer of a solid is decisive in the monitoring of cleaning efficiencies because most cleaning agents and many contaminants are organic in origin. The following two examples show how ToF-SIMS can provide useful information in this context.
Figure 4.22 shows ToF-SIMS data from a metal surface. The upper row shows the spectra before cleaning. On the left-hand side, positively charged secondary ions are shown and on the right-hand side negatively charged secondary ions. Clearly, the surface contamination by mineral oil and fatty acid residues can be seen, originating from the metal forming processes. Using ToF-SIMS it was possible not only to determine the average molecular weight of the mineral oil, which is related to its viscosity, but the various fatty acid residues could be distinguished as well. In the negative spectra, the most prominent ion, at mass 255 amu, is that originating from a palmitate residue. After cleaning, the peaks from the mineral oil and the fatty acid residues are diminished significantly, proving the success of the cleaning process. The peak around 485 amu belongs to the used surfactant (the active ingredient in the surfactant cleaning agent).

The use of surface analytical techniques such as ToF-SIMS allows not only the monitoring of the removal of surface contaminants, but also the visualization of the presence of cleaning residues. As an example, Figure 4.23 shows ToF-SIMS images of a Ni surface that had been treated using a water-based multibath cleaning step. All cleaned surfaces showed bad adhesion behavior in the next step in the manufacture, which was soldering. Even the additional use of a plasma cleaning step did not improve the adhesion strength.

The lateral distribution of some characteristic substrate ions is presented on the left-hand side of Figure 4.23. The right-hand side shows the lateral distribution of the cleaning agent dodecylbenzene-sulphonic (DDBS) acid. Taking into account that the information in ToF-SIMS is coming exclusively from the outermost one to three monolayers of the surfaces under investigation, it can be concluded that the Ni surface was contaminated by spot-like remnants of the cleaning agent, with a local coverage in the multilayer range. It is not surprising, therefore, that the additional plasma treatment was unsuccessful because it could not remove the locally thick cleaning remnants. The problem was solved, however, by optimization of the rinsing steps in the water-based cleaning cascades.

4.8 SUMMARY AND OUTLOOK

ToF-SIMS is a very powerful tool for the chemical characterization of surfaces. It is able to identify the presence of elements and molecules, it is sensitive down to the ppb and fmol levels, it is very
surface specific (information depth = the outermost monolayer), and it allows the determination of the lateral distributions of elements and molecules with submicrometer resolution. Furthermore it can be applied to almost any material in general without any special preparation (i.e., as-received). It should therefore be the method of choice in those cases where molecular information is requested or where the material available for analysis is very limited. With ToF-SIMS, screening of unknown

**FIGURE 4.22** Monitoring of cleaning efficiency by ToF-SIMS. Upper row: Data before cleaning. Lower row: Data after cleaning and rinsing. The amounts of mineral oil (left, positive polarity) and fatty acid residues (right, negative polarity) are clearly diminished after cleaning.

**FIGURE 4.23** Mass resolved ToF-SIMS images of a Ni surface after cleaning. Left: Substrate (Ni). Right: Signals characteristic of DDBS acid. mc: number of counts in the brightest pixel; tc: total number of counts; the field of view was 500 × 500 μm².
samples is possible; i.e., information on all elements and molecules present on the surface can be obtained simultaneously without any need for prior sample knowledge. The in-depth distribution of elements, and increasingly often molecules, can be probed with a depth resolution in the nanometer range. Combining imaging and depth profiling yields information on the 3D distribution of the species of interest. Here again, the screening capabilities of ToF-SIMS make it a sought-after tool, for example, production control and failure analysis.

On the negative side it must be said that SIMS is inherently a non-quantitative technique, although in many analytically important cases at least semiquantitative information can be obtained. The high sensitivity of surface mass spectrometry can sometimes be troublesome when dealing with production problems. Submonolayer coverages of possible contaminants are present virtually on all surfaces originating from production sites, and careful thought must always be given to whether or not a molecule that has been detected is really the one causing the problem. Working with surface mass spectrometry still requires considerable experience, although the use of the technique continues to expand rapidly and is becoming more user-friendly. Currently, more than 300 commercial instruments are installed worldwide, 60% of which are used in industrial laboratories. A German idiom says: “If the only tool you have is a hammer, you tend to think of every problem as a nail.” In this sense ToF-SIMS is not always the most suitable analytical tool for solving surface-related problems. Sometimes cheaper techniques (e.g., measurement of contact angle) can give information faster and more easily. Nevertheless, ToF-SIMS is currently the only technique available for the unambiguous identification of those organic molecules present at surfaces that so often cause problems in adhesion, wetting, corrosion, etc. It must therefore be regarded as a powerful tool that contributes several large and important pieces to the general analytical jigsaw puzzle that has to be solved by a combination of several techniques when dealing with complex surface-related problems.

ToF-SIMS is still developing very quickly. Whereas the last decade saw the development of dedicated depth profiling options, and the improvement of the performance of ion guns for imaging purposes, currently the use of polyatomic primary ions for applications in organic depth profiling and biological analysis is the main point of focus. Additionally, the level of automation for measurement and data evaluation is constantly increasing, making the technique available for high-throughput and routine applications. With the improvement in ion formation efficiency, for the first time organic imaging with submicrometer resolution has become possible, thus making ToF-SIMS a real nano-analytical tool.

REFERENCES

At the moment, there is only one commercial spectra library on the market. Information can be found at http://www.surfacespectra.com/simslibrary/index.html. Additionally, the ToF-SIMS instrument manufacturers and some service laboratories offer libraries with their systems or services.


