

Time-of-flight secondary ion mass spectrometry (TOF-SIMS):— versatility in chemical and imaging surface analysis

Rana N. S. Sodhi

Surface Interface Ontario, Department of Chemical Engineering & Applied Chemistry, University of Toronto, 200 College Street, Toronto, Ontario, Canada M5S 3E5

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) has emerged as one of the most important and versatile surface analytical techniques available for advanced materials research. This arises from its excellent mass resolution, sensitivity and high spatial resolution providing both chemical and distributional (laterally and depth) information for a wide variety of materials and applications. Understanding the various modes of operation and the information that each provides is crucial to the analyst in order to optimise the type of data that is obtained. New developments in primary ion sources and the application of multivariate analysis techniques, which can only extend the versatility and applicability of the technique, are also discussed.

Introduction

The surface and near surface regions control many of the properties of solids that interest us. Knowledge of the surface and understanding its interaction with its environment is of fundamental importance. Of primary interest is the composition at the surface, such as: (i) chemical functionality; (ii) segregation of constituents / impurities – both laterally and with depth; and (iii) cleanliness.

Utilisation of modern methods of surface analysis is an important step towards achieving these goals. Techniques such as X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) are well established as surface analytical methods for advanced material research, however, recent advances in instrumentation have made these techniques even more powerful. Indeed, XPS and time-of-flight SIMS (TOF-SIMS) can now be considered as the 2 major, yet complementary, analytical techniques for obtaining chemical information at a surface.

Whereas XPS is somewhat straightforward — a sample is bombarded with X-rays (typically Al or Mg K_{α} radiation) and the kinetic energy of the emerging photoelectron measured to obtain its binding energy,¹ the TOF-SIMS experiment is inherently more complex. This arises not only from the wealth of peaks the analyst may have to consider, but also in the choice of instrumental parameters that can be utilised, since each may emphasize different aspects in the analysis. Without correctly structuring the analysis, TOF-SIMS can actually pose more questions than it can answer. However, in spite of these factors, TOF-SIMS may yield significantly more useful information than that obtainable from XPS alone. For example, fragmentation patterns obtained by TOF-SIMS on related systems can be very different, whereas the XPS spectra could be similar, if not identical.

Further, the sensitivity for a range of species is significantly better than that for XPS.

As with XPS, TOF-SIMS is a UHV technique, which adds a complexity to the apparatus. However, the need for UHV conditions is probably more stringent than for XPS since the ion beam will directly affect the surface composition and reactivity. This will be particularly important for analysis which go beyond the “static limit” — see below, such as for elemental imaging or depth profiling.

In this article the principles behind TOF-SIMS will be outlined and the various experimental configurations described with emphasis on the type of information they yield, both chemically and spatially. Methodologies simplifying the analytical problem will briefly be discussed.

Secondary ion mass spectrometry

In the SIMS experiment, a focused ion beam (primary ions) is used to bombard the surface. Atomic collisions transfer the primary ion energy to the target atoms thereby setting up a “collision cascade”. Part of the energy is transferred back to surface allowing surface atoms and molecular fragments to overcome surface binding energy. While most secondary particles come off neutrally charged, a small proportion comes off either as positive or negative ions which can be mass analysed.² Depending on the ion dose, the technique can be very surface sensitive — 1–2 monolayers, and with a finely focused primary ion beam, have a high lateral resolution of the order of a few tens of nanometers. Ion dose is an important parameter and leads to two different modes of SIMS, namely: (i) static SIMS — low primary ion dose ($< 10^{13}$ cm^{-2}), low flux (10 pA–5 nA) sputters up to ~0.1% of top monolayer — the “static limit”, yielding elemental and molecular distribution and (ii) dynamic SIMS — high

flux (μA), rapid erosion rates yielding elemental distribution / depth profiles.

Since the likelihood of the same area, or even the near vicinity receiving more than one primary ion strike when operated under static conditions, this mode of operation, for all practical purposes, yields chemical and molecular information of the original, unperturbed surface. Clearly, this would not be the case for the dynamic mode, where the high flux rate is essentially eroding the surface, however, this may not be an important factor when imaging a surface for elemental distribution.

There are different instruments, the capabilities of which depend on the types of analyser and ion guns utilised. For this article, however, only TOF-SIMS will be discussed.

Time-of-flight secondary ion mass spectrometry

General

TOF-SIMS probably constitutes the major evolving capability for SIMS instrumentation. While developments have occurred for other types of SIMS analysis, such as NanoSIMS,³ their applications are somewhat more specialised, whereas TOF-SIMS has a much broader basis, providing chemical information for a vast number of applications.⁴ Much of the landmark work within this area has come out of Benninghoven's group at Münster.⁵

In TOF-SIMS, a pulsed primary ion beam is used which generates secondary species (Fig. 1). Whilst most species emitted are neutral, a small percentage comes off as either a positive or negative secondary ion. These secondary ions are extracted into an analyser by a high voltage potential and their mass is determined by measuring their time-of-flight from the sample to the detector. The mass spectrum and secondary ion images can then be used to obtain composition,

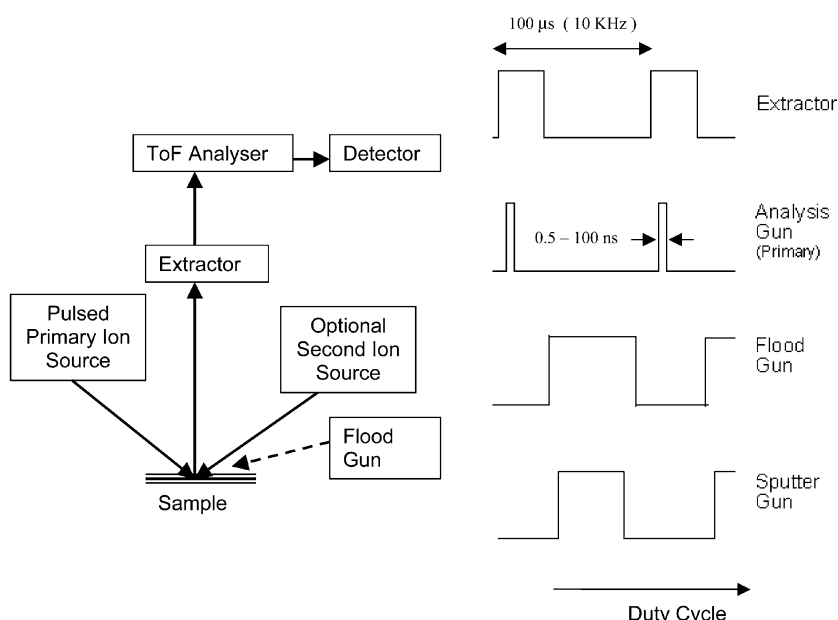


Fig. 1 Schematic of the TOF-SIMS experiment. The duty cycle of the extractor and analysis gun is shown as well as those for the flood and sputter guns, if necessary. See text for more a more specific description of operation.

distribution and molecular information of surface constituents. **The use of a time-of-flight analyser allows for:**

- Parallel detection of all ions, allowing for great sensitivity with a low ion dose, thereby ensuring that the static conditions are met.
 - **High mass range (up to 10k Daltons)**
 - Excellent mass resolution and sensitivity
 - Effective charge compensation for insulators which is allowed for by the **pulsed mode of the primary ion source.**
- In addition, TOF-SIMS allows:**
- **High spatial resolution**
 - (Shallow) depth profiling capabilities with good resolution
 - Monolayer sensitivity

However, the experimental conditions have to be carefully chosen to obtain the required information. Typically, an instrument will consist of multiple ion sources, have depth profiling capabilities, allow effective charge compensation by use of an electron flood gun, enable positive ion yield enhancement with use of an O_2 gas bleed, and have full computer control for operation, data work-up and full retrospective analysis. Thus a number of questions have to be asked

- Which gun or combination thereof should be used?
- **With which mode is the gun to be operated — for high mass resolution, spatial resolution or a compromise?**
- Is more information obtainable from positive or negative secondary ion mass spectra?

Ion sources

In order to design the experiment properly, it is important to have basic understanding on what information the various primary ion sources enhance and on the modes of gun operation. Table 1 lists the commonly available primary ion sources. **While all sources can result in high mass resolution, which is a function of the analyser, the Ga liquid metal ion gun (LMIG) has become the standard gun because of its ability for rapid submicron imaging.** This may become superseded by other LMIGs, such as the newly developed Au cluster gun,^{6–8} which keeps the submicron imaging yet

has other advantages. It **must be noted, which is not always apparent in the manufacturers' literature, that there is a compromise between good mass resolution and good spatial resolution.** **Optimisation of these parameters depends on the mode of operation of the LMIG gun, which will be discussed later, as it dictates on how the experiment will be performed.**

From Table 1, one can see that use of the various ion sources can affect the yield of different secondary ions. **Thus Cs enhances the yield of more electronegative ions, whereas oxygen will enhance that of electropositive ions.** In effect, the use of these ions affects the matrix (*i.e.* the molecular environment) of the surface thereby changing the secondary ion yields. Matrix effects, which arise from the chemical state of the surface, can be very large — several orders of magnitude for a metal oxide over the metal for example, which explains the action of an oxygen primary ion (and indeed the use of an O_2 bleed). Heavier mass can enhance the formation of heavier fragment yields and this has been accomplished with In in place of Ga in an LMIG. This effect is further enhanced by use of polyatomic clusters such as with the use of SF_5^+ ions,⁹ which can greatly increase yield without a concurrent increase in surface damage. New developments with the introduction of Au cluster LMIG^{6–8} and C_{60} guns^{8,10} greatly enhance the ion and high molecular weight yields. The former gun allows for submicron imaging at a performance level close to that of Ga, while the latter, because of the decrease in surface damage, opens up the possibility of performing *molecular depth profiling*.

In addition to the Ga source, when used as the primary ion source, the other guns

Table 1 Ion sources commonly used in TOF-SIMS.

<p>Ga – liquid metal ion gun (LMIG) – main work horse, various modes^a</p> <ul style="list-style-type: none"> • high mass resolution (bunch mode) • high spatial resolution (burst alignment (200 nm), collimated 100 nm)) • combination (burst mode (250 nm)) <p>Cs – enhances yield of electronegative ions</p> <ul style="list-style-type: none"> • implantation reduces work function allowing 2° electrons to overcome this • use as sputter source for cleaning or profiling for negative species <p>O – enhances yield of electropositive ions</p> <ul style="list-style-type: none"> • high electron affinity — metal more likely to give up electron • explains great increase (as much as 10^4) in M–O signal over M (equivalent can be accomplished by use of O_2 bleed) <p>Ar – neutral</p> <ul style="list-style-type: none"> • use as sputter source for cleaning or profiling for positive species <p>SF_6 – enhances heavier fragment yields + monolayer depth resolution</p> <ul style="list-style-type: none"> • higher mass + polyatomic species <p>Cluster Guns – latest developments</p> <ul style="list-style-type: none"> • Au LMIG – Au, Au_2 & Au_3 — combines mass/cluster enhancement yet maintains LMIG imaging capabilities • C_{60} — High mass/cluster – possibility for <i>molecular depth profiling</i> <p>^aSee text for explanation of the gun operating modes.</p>	
--	--

can be utilised for dual-beam depth profiling.¹¹ In this mode of operation, the Ga gun is used for data collection, whilst the second gun is used to actually produce the sputter crater. The spectra are collected from about the middle third of the crater so as to avoid crater edge effects. The timing of the guns is shown in Fig. 1, which also illustrates the pulsing of the primary ion source. Again, the choice of gun for producing the sputter crater is important and can be used to advantage, as it will affect the yields obtained by the Ga primary beam. Thus, use of Cs enhances the profile of the electronegative species, whilst oxygen enhances that of electropositives. Use of these beams for sputter pre-cleaning can also be beneficial to enhance yields for subsequent high spatial resolution imaging with the LMIG. Use of SF₆ for profiling is advantageous for ultra-thin layers as monolayer depth resolution can be obtained. Fig. 2 shows

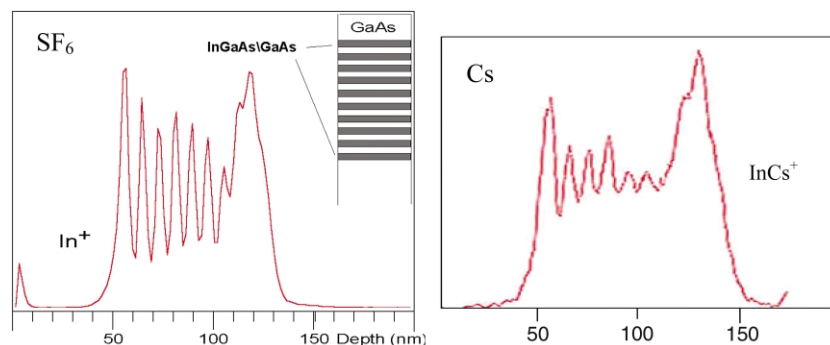


Fig. 2 Dual beam depth profile of InGaAs/GaAs quantum well structure (5 nm layer) using SF₆ and Cs as sputtering sources. Ga is primary source. Ion profiled are indicated in the respective diagrams.

depth profiles of a quantum well layered structure (InGaAs/GaAs – 5 nm layers) using Cs and SF₆ as the sputter sources. The profile is obtained by following InCs⁺ for the former, whilst In⁺ is better when using the latter source.

Modes of operation – mass spectra versus imaging

Fig. 1 shows a schematic of the TOF-SIMS experiment and illustrates the pulsing cycle of the primary ion source. Pulsing not only allows for time-of-flight, but also allows for effective charge-compensation for insulators, and efficient depth-profiling by use of a second gun when operated in an interlaced mode. These are also illustrated in Fig. 1. The pulse timing will dictate the mass resolution. The shorter the pulse, the higher the mass resolution. By “bunching” the raw pulse, high mass resolution can be attained without concurrent loss of counts, however, this is at a cost of spatial resolution, which, in this mode, will be no better than 2–5 μm. Fig. 3a illustrates the

high-mass resolution capabilities of TOF-SIMS. Si (27.977 amu) is well resolved from C₂H₄ (28.032 amu) with 2 other peaks (AlH and CH₂N) clearly distinguishable. It should be noted that surface topography can also have an effect on the ultimate mass resolution obtainable, arising from slight differences in the extraction field seen. Thus, for best results, a relatively flat area is required within the analysing region.

To obtain submicron spatial resolution, the gun is operated in a non-bunched mode. The various modes of operation are summarised in Fig. 3. Imaging (“Burst Alignment”) (Fig. 3b), and with further narrowing of the beam *via* apertures – “Collimated” modes, allow for the best spatial resolution. This, however, is at a serious cost to the mass resolution, which is now only nominal. While this may not pose a problem for well-separated peaks with no serious interferences, it can pose a

effectively lost. In addition to choosing the correct experimental conditions to obtain the required information, one has to design the experiment properly and in essence pose the right question. A full treatment of this topic goes well beyond the scope of this article and the reader is directed to relevant chapters in the TOF-SIMS book¹² and references therein.

A TOF-SIMS spectrum consists of numerous peaks arising from the fragmentation of the molecules at the surface thereby providing a useful fingerprint. A breakdown of the fragmentation pattern can allow identification of materials at a surface. This can be done either by comparison to model compounds or with the aid of library spectra, such as the Static SIMS Library.¹³ However, it is not necessary, or even efficient, to identify all fragments. A few characteristic peaks are often all that is needed, either to identify the compound, or to follow its distribution at a surface. Some *a priori* knowledge of the surface would also help. One simple example is the presence of peaks at 28, 43, 73, 147, 207, 221 and 281 amu in the positive spectrum which is highly indicative of polydimethylsiloxane (PDMS), a common surface contaminant. An alternative method of simplifying the spectrum has been advocated by Gilmore and is termed G[entle]-SIMS.¹⁴ This greatly simplifies the spectrum by “removing” the fragments and emphasizing the parent ion. Spectra are collected with 2 different sources, each of which will have a different “surface energy”. This can be extrapolated back to “zero plasma surface temperature” thereby suppressing the fragments and emphasizing the parent.

In spite of these approaches, analysis of TOF-SIMS spectral data can still be overwhelming. Recently, multivariate analysis methods have been applied. Principal component analysis (PCA) has been the most commonly applied technique. This is a statistical method used to find the combination of the variables that describe the most important trends in the data sets. PCA results are displayed mainly by score plot and loading plot.^{15, 16} The score plots allow classification of similar species, whilst the loadings give an indication as to which peaks are contributing to the particular PC. PCA allows a fair degree of automation to analysing a set of data, and can allow distinction between spectra which nominally look very similar. Castner’s group has successfully applied PCA analysis to identifying various adsorbed protein films, separating them out from very similar spectra, which would be virtually impossible to separate out visually.^{17–19} Vanden Eynde and Bertrand have also applied PCA analysis for the

Spectral interpretation

The wealth and extent of information that TOF-SIMS provides can itself be problematic. There can be too much and hence some of the information is

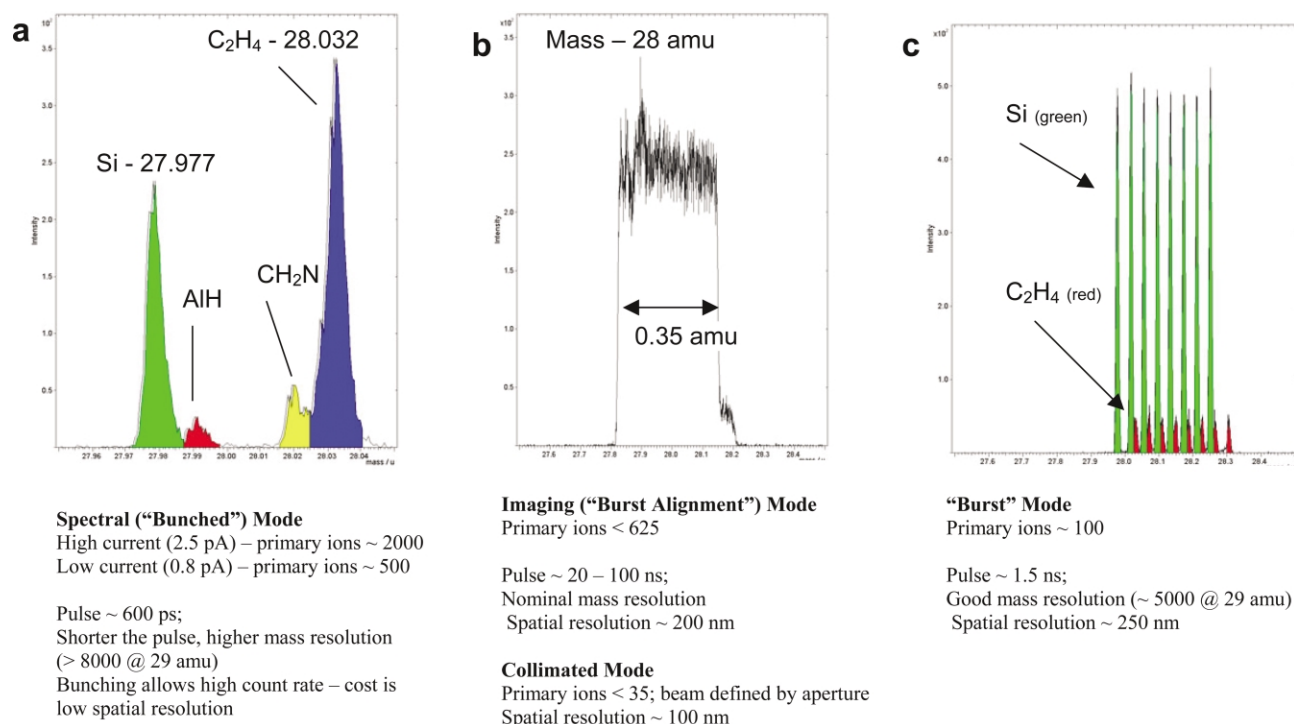


Fig. 3 Positive ion spectra of paper surfaces at mass 28 produced with Ga (25 keV) primary ion beam. (a) Spectral ("bunched") mode showing high mass resolution; (b) Imaging ("Burst alignment" mode (coated paper surface) — high spatial resolution but nominal mass resolution, collimating beam further improves spatial resolution; (c) "Burst mode" (same sample as (b)) — repetition of primary pulse without bunching allows good mass and spatial resolution with reasonable S/N and count rate.

quantification of polystyrene spectra.²⁰ While PCA generally is an "unsupervised" variational recognition technique, "supervised" pattern recognition techniques such as discriminant PCA²¹ can further enhance the ability to distinguish between various spectra. Other multivariate techniques such as neural networks are also showing great promise in analysing data,²² and these techniques can only expand the application and usefulness of TOF-SIMS to the study of various systems, in particular, polymeric and organic systems.

Multivariate techniques have also proved valuable in analysing and improving contrast in TOF-SIMS image analysis. By grouping together all spectral features for a component one can greatly increase the S/N and acquire meaningful images from spectra which still fall within the static limit. Further, topographic effects are easily extracted (typically from the first PC) allowing the chemical variations within the image to be separated out. For example, Biesenger *et al.* have applied PCA image enhancement to Langmuir–Blodgett films where it was essential that the static limit was not exceeded.²³ Fig. 4 further illustrates the enhancement in TOF-SIMS chemical image contrast achievable by PCA treatments. Fig. 4a shows the optical image of 4 pairs of semi-colons printed on paper, the total ion yield and a false colour image of the first 3 PCs. No contrast between the ink distribution and the paper surface is

discernable from the total ion yield. While individual components could be used to ascertain distribution, this can be time consuming. PCA provides an easy way of improving the image contrast as can be seen in the false colour image. The principal components, first 3 of which are shown in Fig. 4b, were calculated from a data set of 186 peaks (generated by an automated peak search) using MATLAB 6.5 / PLS Tool box 3.0 (Eigenvector Research Inc., Manson, WA). PC1

separates out the topography, while PC2 distinguishes between the ink components and the paper surface, and PC3 further distinguishes between the black and the other inks. From the loadings it should be possible to identify what is contributing to the chemical differences.

Finally quantification in TOF-SIMS must be considered. This is not as straightforward as for other techniques since the intensity not only depends on the amount of material but also on the ion

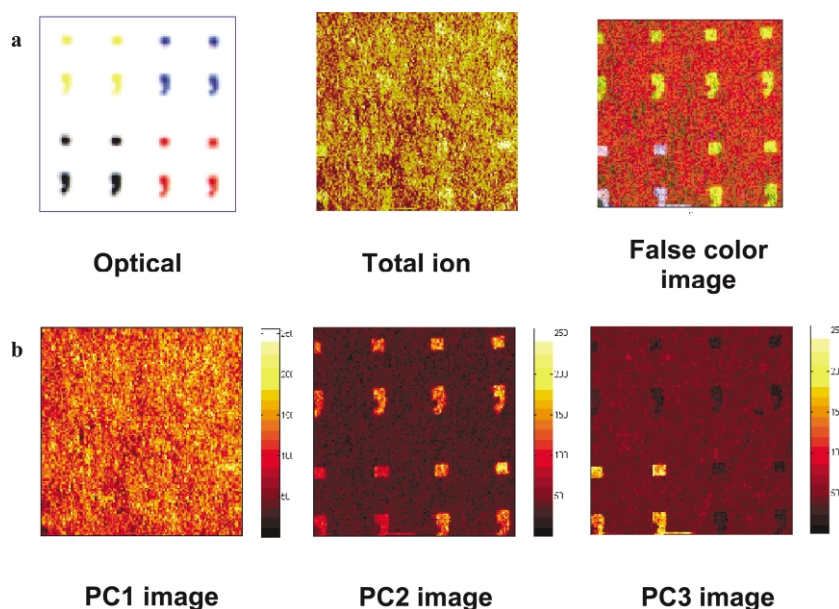


Fig. 4 PCA image enhancement of ink on paper surface — see text for details.

yield which will vary with the matrix. Thus standards will have to be used with a similar matrix to the analyte as well as the selection of several peaks characteristic of the material. In a complex system such as a polymer this can be very difficult. The reader is directed to pertinent chapters in ref. 4, e.g. X. Vanden Eynde, ch. 20, p. 543.

Summary

TOF-SIMS is a very powerful and versatile technique applicable to many types of systems. It has a high degree of sensitivity, both in detection limits and for depth and spatial resolution, yielding molecular and chemical information, and providing information to a level that other surface analytical techniques cannot furnish. An understanding of the instrumental factors behind the technique is important so as to design the experiment properly and to yield the required information. Multivariate analysis methods hold much promise in simplifying data analysis thereby allowing application of the technique to a wider range of problems.

References

- 1 *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, ed. D. Briggs and J. T. Grant, IM Publications, Chichester, 2003.
- 2 *Practical Surface Analysis, Vol. 2 Ion and Neutral Spectroscopy*, ed. D. Briggs and M. P. Seah, Wiley, Chichester, 2nd edn., 1992.
- 3 G. Slodzian, F. Hillion, F. J. Stadermann and F. Horreard, *Appl. Surf. Sci.*, 2003, **203–204**, 798.
- 4 *TOF-SIMS — Surface Analysis by Mass Spectrometry*, ed. J. C. Vickerman and D. Briggs, IM Publications, Chichester and SurfaceSpectra Ltd, Manchester, 2001.
- 5 A. Benninghoven, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 1023.
- 6 B. Hagenhoff, R. Kersting, D. Rading, S. Kayser and E. Niehuis, *SIMS XII*, Elsevier, Amsterdam, 1999, p. 833.
- 7 N. Davies, D. E. Weibel, P. Blenkinsopp, N. P. Lockyer, R. Hill and J. C. Vickerman, *Appl. Surf. Sci.*, 2003, **203–204**, 223.
- 8 D. G. Castner, *Nature*, 2003, **422**, 129.
- 9 F. Kotter and A. Benninghoven, *Appl. Surf. Sci.*, 1998, **133**, 47.
- 10 S. C. C. Wong, P. Blenkinsopp, N. P. Lockyer, D. E. Weibel and J. C. Vickerman, *Appl. Surf. Sci.*, 2003, **203–204**, 219.
- 11 E. Niehuis and T. Grehl, in *TOF-SIMS — Surface Analysis by Mass Spectrometry*, ed. J. C. Vickerman and D. Briggs, IM Publications, Chichester and SurfaceSpectra Ltd, Manchester, 2001, ch. 28, p. 753.
- 12 D. Briggs, in *TOF-SIMS — Surface Analysis by Mass Spectrometry*, ed. J. C. Vickerman and D. Briggs, IM Publications, Chichester and SurfaceSpectra Ltd, Manchester, 2001, ch. 16, p. 447 and ch. 18, p. 497.
- 13 The Static SIMS Library, Version 3, ed. J. C. Vickerman, D. Briggs and A. Henderson, SurfaceSpectra, Manchester, 2003.
- 14 I. S. Gilmore and M. P. Seah, *Appl. Surf. Sci.*, 2000, **161**, 465.
- 15 P. Geladi and H. Grahn, *Multivariate Image Analysis*, Wiley, New York, 1996.
- 16 B. M. Wise and N. B. Gallagher, *PLS_Toolbox User's Guide*, Eigenvector Research Inc., Manson, WA, 1998.
- 17 J.-B. Lhoest, M. S. Wagner, C. D. Tidwell and D. G. Castner, *J. Biomed. Mater. Res.*, 2001, **57**, 432.
- 18 S. L. McArthur, M. S. Wagner, P. G. Hartley, K. M. McLean, H. J. Griesser and D. G. Castner, *Surf. Interface Anal.*, 2002, **33**, 924.
- 19 M. S. Wagner and D. G. Castner, *Langmuir*, 2001, **17**, 4649.
- 20 X. Vanden Eynde and P. Bertrand, *Surf. Interface Anal.*, 1997, **25**, 878.
- 21 M. S. Wagner, B. J. Tyler and D. G. Castner, *Anal. Chem.*, 2002, **74**, 1824.
- 22 O. D. Sanni, M. S. Wagner, D. Briggs, D. G. Castner and J. C. Vickerman, *Surf. Interface Anal.*, 2002, **33**, 715.
- 23 M. C. Biesinger, P.-Y. Paepegaey, N. S. McIntyre, R. R. Harbottle and N. O. Petersen, *Anal. Chem.*, 2002, **74**, 5711.