A personal perspective on the development of quadrupole and time-of-flight SIMS

1969-1992

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20th Anniversary of Annual Workshops on SIMS
The beginnings of “static” SIMS

“We discovered a number of different anion species in the spectrum, atomic ones like F\(^-\), Cl\(^-\) or Br\(^-\), but in addition molecular cluster ions like CO\(_3\)\(^-\), NO\(_3\)\(^-\) and SO\(_4\)\(^-\). Most surprising, however, was the appearance of organic anion complexes like \(\text{CH}_3(\text{CH}_2)_n\text{COOH}^-\) with high intensities. These unexpected results told us that sputtering was much softer than anybody expected at that time. It should be possible to generate characteristic molecular secondary ions from even larger or more fragile molecular surface species by ion bombardment.” *Spectra taken from Phys. Status Solidi 34, 169 (1969).*

UHV Quadrupole SIMS instrument

Implications for catalysis

M. Barber, J.C. Vickerman and J. Wolstenhome, Faraday Trans., 72, 40 (1976)

DETECTION OF HIGH MASS CLUSTER IONS SPUTTERED FROM BI SURFACES

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⇒ Recombination model for some molecular clusters
The desorption of undestroyed molecular ions can be explained only by the assumption of another type of secondary ion emission process. It is assumed that this process is the result of a collective electronic excitation in an area near the surface by the impinging primary ion. In addition, the molecular ion is supposed to be bound on the surface by electrostatic forces which are perturbed by this collective electronic excitation. In this way the desorption of an unfragmented particle can be explained.

“The appearance of molecular ions in the secondary ion spectra of the organic molecules investigated was completely unexpected.”

Cationization of Organic Molecules in Secondary Ion Mass Spectrometry

Sir,

We show that organic molecules can be ionized from the solid by cationization in secondary ion mass spectrometry (SIMS) and that such ionization shows significant similarities to recently developed methods of ionizing organic compounds in the solid state. Observed in the SIMS spectra are organometallic ions which are formally due to (i) addition of cations (Ag⁺, Pt⁺) to the intact organic molecule (M), (ii) fragmentation of the cationized species by loss of simple neutral molecules, and (iii) processes yielding more complex surface-derived entities containing several metal atoms. These novel observations may have importance in the theory of secondary ion emission as well as in the analysis of thermally sensitive organic compounds.

Figure 1 shows the high mass region of the spectrum of p-aminobenzoic acid supported on silver. The argented molecule (M + Ag)⁺, m/e 244 and 246 is clearly present in good yield. Other ions of interest are m/e 236 and 238 (loss of water

Figure 1. Secondary ion mass spectrum (SIMS) of p-aminobenzoic acid on silver. The primary ion current was 3 × 10⁻⁵ A cm⁻² and the scan time ~20 min.

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PDMS (1976) and FAB (1979) opened mass spectrometry to biomolecules, setting the stage for MALDI and electrospary MS in 1985.
TOF-SIMS enters the scene

A time-of-flight mass spectrometer for measurement of secondary ion mass spectra
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Received 25 March 1981.

Abstract
A time-of-flight mass spectrometer has been constructed at the University of Manitoba. In this instrument, bursts of alkali-metal ions of 10 ns duration strike a thin layer of organic material deposited onto a metal backing. The secondary ions produced are accelerated across a fixed potential 10 kV, then travel down a flight tube 1.6 m long. Measurement of the time of flight determines the mass-to-charge ratio of the ions. Mass spectra from biomolecules with masses up to 1355 Dalton have been measured with the instrument. They exhibit significant quasimolecular ion peaks.
With competition from Germany and USA

In Munster, Bennighoven completed a TOF-SIMS I machine in 1979, which eventually morphed into the modern reflectron-based instrumentation TOF-SIMS 2. Currently marketed by Ion-TOF. The TRIFT I was developed in about 1984 at Evans and Associates. VG and Kratos??

Sub-micron Molecular Imaging. A Viability Study by Time-of-flight SIMS

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yields. At the risk of stating the obvious, a particular set of mass channels must deliver 65.5 k counts to populate, on average, each pixel in a 256 × 256 pixel image with a single count. An image with sufficient contrast to realize 1 μ resolution requires, on average, at least 10 counts per pixel.

Plate 2. As for Plate 1 but with a 20μ × 20μ imaged area.
SIMS XIII - 1992

Quantification (of stuff in Si) - 70 pages
Instrumentation (microbeam analysis) – 100 pages
Depth Profiling (of stuff in Si) – 180 pages
Polymers and organics (mostly tof) – 50 pages
Metals, semiconductors, geology – 130 pages
Dynamic SIMS bioimaging – 40 pages
Static SIMS represented about 20% of the talks