Quadrupole-based Dynamic SIMS: A Brief History with Personal Reminiscences

Charles W. Magee

Chief Scientist
I Introduction

A. History of Trace Analytical Mass Spectrometry

In 1913, J.J. Thompson became the first person to mass resolve an ion beam by passing the ions through a magnetic field and in so doing, invented the first mass spectrometer.
Hollow Cathode Ion Source for Solids Mass Spectrometry

Sir: Hollow cathode discharge tubes are well known as sharp line spectral sources which have long been useful in physics (1, 2) and more recently as source lamps for atomic absorption spectrometry. Demountable hollow cathode tubes may be utilized as atomic emission sources for trace element analysis (3–6) by placing the solid sample in the cathode or by evaporating a solution sample in the cathode cavity.

The surface sputtering action of the hollow cathode discharge yields excellent elemental sensitivity (7) by moni-

toring the excited atomic species. A large neutral population is, of course, also formed. It is further known, from ion microprobe mass spectrometry, that ion bombardment of a surface can produce secondary ions of the target species. Coburn and Kay (8, 9) have shown that both dc and rf discharges may be used in a planar diode sputtering system to determine major constituents in a surface film.

Our initial intent in interfacing a hollow cathode tube to a mass spectrometer was to gain a better understanding of the reactions and plasma conditions which exist in our hollow cathode emission source. Subsequent experiments have shown that the hollow cathode discharge may offer advantages as a mass spectrometry surface ionization source for solids, such as metals and alloys. It can also be used to provide survey analysis of the trace elements in a


ANALYTICAL CHEMISTRY. VOL. 46, NO. 3, MARCH 1974 • 461
My Experience in SIMS at RCA Laboratories (1973)

Worked on Si semiconductor problems using Cameca’s demonstration instrument (IMS-300) in Elmsford, NY

Figure 1. CAMECA IMS 300 ion microscope
• New Cameca was too expensive ($250,000) for RCA’s budget
• My boss, Richard E. Honig said: “Charles, I made my own in 1950, you can make your own now!”

Sputtering of Surfaces by Positive Ion Beams of Low Energy

Richard E. Honig
RCA Laboratories, Princeton, New Jersey
(Received October 28, 1957)

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My Experience in SIMS at RCA Laboratories (1973)

• State of quad-SIMS in 1973 literature was pretty rudimentary

Velocity Filtering for Secondary Ion Quadrupole Mass Spectrometer

Z. Šroubek
Institute of Radio Engineering and Electronics, Czechoslovak Academy of Sciences, Prague, Czechoslovakia
(Received 16 January 1973)

A simple method of secondary ion velocity filtering for sputter ion mass spectroscopy is described. The experiments on Ni surfaces show that the method allows sorting of secondary ions according to their adsorption energies and thereby enhances the analytic capabilities of the spectrometer.


Fig. 1. Target assembly of SIM3 which allows velocity filtering of sputtered ions.
Other early quad SIMS instruments in the 1970s:

90° cylindrical electric sector

Direct Comparison of Ion Scattering and Secondary Ion Emission as Tools for Analysis of Metal Surfaces

M. Grundner, W. Heiland, and E. Tuglauer

Received 22 October 1973/accepted 16 April 1974

Other early quad SIMS instruments in the 1970s:

90° cylindrical mirror mirror analyzer

A Simple, Inexpensive SIMS Apparatus*

R. Schubert† and J. C. Tracy

Bell Laboratories, Murray Hill, New Jersey 07974
(Received 15 November 1972; and in final form, 8 January 1973)
Other early quad SIMS instruments in the 1970s:

Parallel plate capacitor
My Experience in SIMS at RCA Laboratories (1974)

Other early quad SIMS instruments in the 1970s:

Klaus Wittmaack’s early instruments

A VERSATILE IN-DEPTH ANALYZER

K. Wittmaack, J. Maul and F. Schulz

Gesellschaft für Strahlen- u. Umweltforschung mbH
Physikalisch-technische Abteilung
D-85569 Neuharlang
Germany

Proc. Sixth Int. Conf.
Electron and Ion Beam Science and Technology
San Francisco, May 13-16, 1974

Specialists in Materials Characterization
Other early quad SIMS instruments in the 1970s:

Klaus Wittmaack’s early instruments

Fig. 1. Construction of the UHV in-depth analyzer
My Experience in SIMS at RCA Laboratories (1974)

Other early quad SIMS instruments in the 1970s:

Klaus Wittmaack’s early instruments

First Depth Profile

First Ion Image

Materials Characterization
Model A: Line-of-sight, no energy analyzer

First page of notes from my SIMS research notebook

Model A of our SIMS instrument consists of a UTI quadrupole mass spectrometer, PHI argon ion gun and simple linear motion sample manipulator mount. After bakeout at 150°C, the base pressure is 1.5x10^-8 torr. Without

“This geometry was simplest to try and it yielded results”

This geometry was the simplest to try and it yielded results.
Model A: Line-of-sight, no energy analyzer
Model A: Line-of-sight, no energy analyzer

First mass spectrum: Aluminum
**Model A:** Line-of-sight, no energy analyzer

First depth profile: Cu/Mo/Si
My Initial Efforts at Making a SIMS Instrument at RCA Laboratories (1974-76)

Model B: Parallel-plate capacitor energy analyzer (made on 3M Ion Scattering Spectrometer chamber)
My Initial Efforts at Making a SIMS Instrument at RCA Laboratories (1974-76)

**Model B:** Parallel-plate capacitor energy analyzer (made on 3M Ion Scattering Spectrometer chamber)
My Initial Efforts at Making a SIMS Instrument at RCA Laboratories (1974-76)

Model C: Energy analysis through modulation off low-energy ions: analog detection with lock-in amplifier

SIMS with a standard quadrupole residual gas analyzer

G. E. Thomas and E. E. de Kluizenaar

Philips Research Laboratories, Eindhoven, Netherlands
(Received 15 October 1973)

Model C: Energy analysis through modulation off low-energy ions: Analog detection with lock-in amplifier

Fig. 1. SIMS spectra of Al using 5 keV Ar⁺ primary ions. The upper curve was recorded with all electrodes in the QRGA ion source grounded and with dc amplification. The lower curve was recorded with modulation and with tuned ac amplification. The probable identities of the most intense peaks are indicated. The inset shows the mass 16–20 region with the QRGA operating in the normal electron impact mode.
**Model C:** Energy analysis through modulation off low-energy ions:
Analog detection with lock-in amplifier

Overlay of modulated and un-modulated signals
My Initial Efforts at Making a SIMS Instrument at RCA Laboratories (1974-76)

Model D: Cylindrical mirror energy analyzer

“Results were promising in that the resolution was quite impressive with a FWHM of ~0.3amu which is equal to that obtained by K. Wittmaack (Int. J. Mass Spec. 11, 23-35 (1973).”
My Initial Efforts at Making a SIMS Instrument at RCA Laboratories (1974-76)

Model D: Cylindrical mirror energy analyzer
Model D: Cylindrical mirror energy analyzer
Model E: Re-designed parallel-plate capacitor energy analyzer
My Initial Efforts at Making a SIMS Instrument at RCA Laboratories (1974-76)

Model E: Re-designed parallel-plate capacitor energy analyzer
Model E: Re-designed parallel-plate capacitor energy analyzer
Model F: 90° cylindrical electrostatic energy analyzer

“Model F…is a 90° electric sector in front of the quadrupole field. ….
The ion beam is passed through the outer ESA plate, though the α aperture of the ESA and strikes the sample along the surface normal. Secondary ions are “looked at” normal to the surface.”
My Initial Efforts at Making a SIMS Instrument at RCA Laboratories (1974-76)

Model F: 90° cylindrical electrostatic energy analyzer
My Initial Efforts at Making a SIMS Instrument at RCA Laboratories (1974-76)

Model F: 90° cylindrical electrostatic energy analyzer
Model F: 90° cylindrical electrostatic energy analyzer
And then came my **BIG INSPIRATION!**
My Experience in SIMS at RCA Laboratories (1975)

Other early quad SIMS instruments in the 1970s:

QMAS from Applied Research Laboratories

Specialists in Materials Characterization
My Experience in SIMS at RCA Laboratories (1975)

Other early quad SIMS instruments in the 1970s:

**QMAS from Applied Research Laboratories**

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Specialists in Materials Characterization
My Experience in SIMS at RCA Laboratories (1975)

Other early quad SIMS instruments in the 1970s:
QMAS from ARL

Now THIS is what I was after!
Other early quad SIMS instruments in the 1970s:

QMAS from ARL.
Other early quad SIMS instruments in the 1970s:

**QMAS from Applied Research Laboratories**

You may be asking yourself; “Why have I never heard of this instrument?”

….because it never sold even one instrument! It was not sufficiently cheaper than ARL’s larger Ion Microprobe Mass Analyzer (IMMA)
My Initial Efforts at Making a SIMS Instrument at RCA Laboratories (1974-76)

Model G: 180° spherical electrostatic energy analyzer

Secondary Ion Quadrupole Mass Spectrometer (SIQMS)
Secondary ion quadrupole mass spectrometer for depth profiling—design and performance evaluation

Charles W. Magee, William L. Harrington, and Richard E. Honig

RCA Laboratories, Princeton, New Jersey 08540
(Received 1 September 1977; in final form, 25 October 1977)

A quadrupole-based secondary ion mass spectrometer designed for depth profiling is described which combines ultrahigh vacuum construction with high sputtering rate, detection sensitivity, depth resolution, mass spectral purity, and abundance sensitivity. Impurities such as B and Al implanted in Si can be profiled to levels below one part per million atomic (ppma), at a depth resolution equal to that obtained by commercial ion microprobes. The primary beam consists of 5 keV, mass-analyzed $^{40}$Ar$^+$ ions, focused to about 70 $\mu$m in diameter. Its high current density (>25mA/cm$^2$) permits adequate beam rastering and electronic signal-gating to optimize depth resolution. A secondary ion extraction lens and spherical energy filter are responsible for achieving abundance sensitivities of five to six orders of magnitude on the low mass side of a matrix peak. The ultrahigh vacuum environment of the sample dramatically reduces molecular peaks containing H, C, and O, allowing even hydrogen to be profiled to concentrations below 10 ppma. Because large amounts of data are generated by multi-element depth profiling, means for automated instrument control and data acquisition have been developed.

Secondary ion optics design

The potential of the inner sphere is $V_1 = [1 - 2(R_0/R_1)]$, and the potential of the outer sphere is $V_2 = [3 - 2(R_0/R_1)]$. In general, the two dividers resistors used to establish the potential of the incident electron beam with respect to the spheres are unequal.

Let $a$ be the radial distance of an incident electron measured from the path of radius $R_0$, and let $\theta$ be the angle the incident electron makes with the path of radius $R_0$. Let $e$ be the radial distance of the outgoing electron measured from the path of radius $R_0$. Then

$$\frac{e}{R_0} = -\frac{a}{R_0} + 2\left(\Delta E/E_0\right) = 2\epsilon,$$

where $\Delta E = E - E_0$. The absence of a term linear in $\epsilon$ shows that the spherical deflector has first order angle focusing.

To obtain the energy resolution of the spherical deflector, one must calculate the transmission of electrons as a function of energy, taking into account the distribution of the incident electrons over space and angle. With entrance and exit slits of equal width $w$ (or with virtual slits), such a transmission function, neglecting the $\epsilon^2$ term, would be a triangle whose width at half height $\Delta R_1$ is given by

$$\Delta R_1 = w/2R_0.$$

Use of a round entrance aperture instead of a slit would change the shape of the transmission function (line shape) without significantly changing $\Delta R_1$. Addition of the
Secondary Ion Quadrupole Mass Spectrometer (SIQMS)

Hemispheres from Chicago Float Company for “Toilet-Bowl” ESA
Secondary ion optics design

\[ \Delta E_o = \frac{3}{\beta} = 0.039 \text{, a spectrometer has 3.9% energy resolution} \]

\[ \frac{1}{2} \text{band width} \Delta E_p = \frac{100 \times 0.039}{3.5 \times 0.039 + 1.14V} = 0.039 \text{, a spectrometer has 3.9% energy resolution} \]

\[ V_o = V_0 \left[ 3 - 2 \frac{\Delta E_p}{\Delta E_o} \right] = 3 - 2 \left( \frac{0.039}{0.039} \right) = 3 \times 0.600 \text{ V}_{3} = -0.45 \text{ V}_{3} = -0.45 \text{ V}_{3} \]

\[ V_{5} = V_{0} \left[ 2 \frac{\Delta E_p}{\Delta E_o} \right] = 2 \times 2 \left( \frac{0.039}{0.039} \right) = 2 \times 2 \times 0.600 \text{ V}_{5} = +0.72 \text{ V}_{5} \]

Specialists in materials Characterization
Secondary Ion Quadrupole Mass Spectrometer (SIQMS)

Specialists in Materials Characterization
Secondary Ion Quadrupole Mass Spectrometer (SIQMS)

Selected-area transmission effectiveness of extraction lens

Effect of Sample-to-Extraction Lens Distance

Sample too far from lens

Correct sample-to-lens distance

Sample too close to lens

Secondary Ion Images

Specialists in Materials Characterization
Secondary Ion Quadrupole Mass Spectrometer (SIQMS)

Designed my own primary beam rastering circuit

Specialists in Materials Characterization
Secondary Ion Quadrupole Mass Spectrometer (SIQMS)

Designed my own primary beam rastering circuit boards
Demonstration of secondary ion imaging:
Polaroid picture, October 31, 1975

Mo image of Mo screen on stainless steel; 200um spacing
Secondary Ion Quadrupole Mass Spectrometer (SIQMS)
Secondary Ion Quadrupole Mass Spectrometer (SIQMS)
Secondary Ion Quadrupole Mass Spectrometer (SIQMS)
Well, how did it work?
Well, how did it work?
Well, how did it work?
Well, how did it work?
Well, how did it work?

Round Robin on profiling P layer in Ta$_2$O$_5$

*Equal to the best depth resolution of the study*
Could it depth profile?

- 200 keV $^{27}\text{Al}$ ion implanted into silicon

**Conditions for SIQMS profile:**
- Primary ion beam: 5 keV $^{40}\text{Ar}^+$
- Sputtering rate: 7.6 Å/sec
- Detected ion: $^{27}\text{Al}^+$
- Oxygen jet: OFF

Specialists in Materials Characterization
But we needed a Cs source for n-type dopants in semiconductors

Solution? Make my own, of course
Secondary Ion Quadrupole Mass Spectrometer (SIQMS)

Cs primary ion source
Secondary Ion Quadrupole Mass Spectrometer (SIQMS)

Cs primary ion source

Figure 2-8  Cesium-ion current density at the critical point versus the corresponding critical temperature for tungsten. Behavior of the ion current and neutral flux (curves A and B, respectively) is shown as a function of temperature for one value of cesium arrival rate at the ionizing surface. The curve at the right shows the corresponding increase in neutral cesium efflux as current density is increased.
Secondary Ion Quadrupole Mass Spectrometer (SIQMS)

Cs primary ion source
Secondary Ion Quadrupole Mass Spectrometer (SIQMS)

Cs primary ion source
Secondary Ion Quadrupole Mass Spectrometer (SIQMS)

Cs primary ion source

Depth Profiling of n-Type Dopants in Si and GaAs Using Cs⁺ Bombardment Negative Secondary Ion Mass Spectrometry in Ultrahigh Vacuum

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Reprinted from Journal of the Electrochemical Society
Vol. 126, No. 4, April 1979
Printed in U.S.A.
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Won “Young Author of the Year” from Electrochemical Society, 1979
Secondary Ion Quadrupole Mass Spectrometer (SIQMS)

SIQMS also cited in:

Secondary Ion Mass Spectrometry
BASIC CONCEPTS

4.4.2.2. SIQMS at RCA Corporation

The quadrupole ion probe developed by Magee, Harrington, and Honig [981] at RCA Laboratories approaches the capabilities of larger double focusing SIMS instruments in many specifications. Figure 4.117 shows the

A WILEY-INTERSCIENCE PUBLICATION
JOHN WILEY & SONS
New York Chichester Brisbane Toronto Singapore
Specialists in Materials Characterization
Other “milestones of the SIQMS instrument
The use of nuclear reactions and SIMS for quantitative depth profiling of hydrogen in amorphous silicona)


Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

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RCA Laboratories, Princeton, New Jersey 08540
(Received 20 July 1977; accepted for publication 16 August 1977)

Depth profiles for hydrogen in amorphous silicon have been determined by the use of resonant nuclear reactions \[^{1}H(^{14}N,\alpha\gamma)^{12}C\] and \[^{1}H(^{19}F,\alpha\gamma)^{16}O\] and by secondary ion mass spectroscopy (SIMS). Independent calibration procedures were used for the two techniques. Measurements were made on the same amorphous silicon film to provide a direct comparison of the two hydrogen analysis techniques. The hydrogen concentration in the bulk of the film was determined to be about 9 at.% H. The SIMS results agree with the resonant nuclear reaction results to within 10%, which demonstrates that quantitative hydrogen depth profiles can be obtained by SIMS analysis for materials such as amorphous silicon.

PACS numbers: 61.70.Wp, 82.80.Ms, 82.80.Jp
Depth profiling of sodium in SiO$_2$ films by secondary ion mass spectrometry

Charles W. Magee and William L. Harrington

RCA Laboratories, Princeton, New Jersey 08540
(Received 27 March 1978; accepted for publication 4 May 1978)

A focused beam of electrons in coincidence with a high current density Ar$^+$ sputtering beam and SIMS detection has been used to perform accurate depth profiling analyses of sodium in SiO$_2$ films. Conditions for exact charge compensation are described, and analyses of a 150-keV sodium implant in a 0.73-$\mu$m film of SiO$_2$ are presented. Without charge neutralization, 98% of the implanted sodium moved to the SiO$_2$/Si interface during SIMS analysis, whereas optimum charge compensation resulted in a basically unaltered implant profile with only 0.06% sodium at the interface.


Specialists in Materials Characterization
Commercially Available Quadrupole-based SIMS Instruments (attachments) in the 1980s

Most of these instruments were dedicated “SIMS-Only” tools that could depth profile dopants and impurities in semiconductors.
Commercially Available Quadrupole-based SIMS Instruments (attachments) in the 1980s

Atomika 3000, ~1982, Designed by Klaus Wittmaack
Commercially Available Quadrupole-based SIMS Instruments (attachments) in the 1980s

Riber MIQ256, ~198?, designed by Helmut Liebl

Specialists in Materials Characterization
Commercially Available Quadrupole-based SIMS Instruments (attachments) in the 1980s

Vacuum Generators SIMSLAB, ~1985

Specialists in Materials Characterization
Commercially Available Quadrupole-based SIMS Instruments (attachments) in the 1980s

Physical Electronics SIMS II Attachment, 1981, designed by Bob Gerlach

Two separate electronics packages can be selected for use with the revolutionary SIMS II detector. This first package is an all-digital option used when the customer already has, or is considering purchasing, a PHI Multiple-technique Analytical Computer System (MACS). With this version, MACS controls the entire SIMS II detector operation. All lens, energy filter, and quadrupole parameters are under computer control. Ion energy selection, energy resolution, mass selection, and mass resolution can be programmed. Further-

Photograph and schematic drawing of SIMS II detector.
Commercially Available Quadrupole-based SIMS Instruments (attachments) in the 1980s

Physical Electronics 6300, 1984, designed by David Welkie
New wide angle, high transmission energy analyzer for secondary ion mass spectrometry

M. W. Siegel
Extranuclear Laboratories, Pittsburgh, Pennsylvania 15238

M. J. Vasile
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 15 April 1981, accepted for publication 3 July 1981)

A conically tapered resistive disk with a single conducting hemisphere is used to effect the same energy selection as a pair of concentric hemispheres. The combination of this energy filter with a quadrupole mass spectrometer produces a secondary ion mass spectrometry (SIMS) instrument with a high total transmission attributable to its open geometry and lack of restricting apertures.
Commercially Available Quadrupole-based SIMS Instruments (attachments) in the 1980s

Extranuclear Laboratories SphericEL, ~ 1980

Specialists in Materials Characterization
Bessel Box  *The single biggest detriment to the use of quadruple mass spectrometers for SIMS that was ever invented!*

It was a line-of-sight device that allowed one to bolt a SIMS analyzer onto any port on a vacuum system that pointed directly at the sample: results were terrible…but they sold!

Commonwealth Scientific with bolt-on SIMS for SEMs
3M ISS/SIMS,
Leybold-Heraeus ESCA-SIMS

Specialists in Materials Characterization
One Last Example for my SIQMS

Ion imaging of implanted B in Si

Japanese for....... The End