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**Semi-quantitative analysis of microstructures
by secondary ion mass spectrometry**

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Abstract

The focus of this review is on trace-element quantitation of microstructures in solids. This review is aimed at the non-specialist who wants to know how SIMS quantitation is achieved. Despite 35 years of SIMS research and applications, SIMS quantitation remains a fundamentally empirical enterprise and is based on standards. The most used standards are “bulk standards” – solids with a homogeneous distribution of a trace element – and ion-implanted solids. The SIMS systematics of bulk standards and ion-implanted solids are reviewed.

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Introduction

Trace-element quantitation of microstructures by secondary ion mass spectrometry (SIMS) has been an important and dominant tool of microanalysis for about 35 years. In today's research-and-development environment, SIMS quantitation is being applied to a broad range of disciplines: semiconductor electronics, materials science, metallurgy, geochemistry, biology and medicine, diffusion studies, nuclear science, and particle characterization.

In simple language, SIMS is sputtering-source mass spectrometry. Applications of SIMS can be divided into two sputtering-rate regimes: static SIMS and dynamic SIMS. Static SIMS utilizes very low sputtering rates, such that sample material is removed on a monolayer scale. On the other hand, dynamic SIMS is characterized by much higher sputtering rates — typically involving removal of material to depths $\geq 100\text{nm}$ below sample surfaces. The lion's share of trace-element quantitation by SIMS is done with dynamic SIMS; and such quantitation is the focus of this review.

The microstructures in view for this paper are solids with characteristic dimensions from $\sim 100\text{nm}$ to $\sim 250\mu\text{m}$. Macrostructures (i.e., structures with characteristic dimensions greater than $\sim 250\mu\text{m}$) generally can be analyzed by other techniques with more efficiency and accuracy than SIMS.

For the purposes of this review, trace elements are defined as elements with concentrations less than 100 atomic parts per million (ppma). Most SIMS instruments have been designed with high collection efficiency and high transmission for sputtered ions and are thus well suited for trace-element determinations. Detection limits for SIMS range from 0.1 to 1000 atomic parts per billion (ppba) for all elements in the Periodic Table. The SIMS sensitivity for each element depends on many factors; some of the more important factors are the ionization potential/electron affinity, the chemistry and atomic structure of the host matrix, and the chemical activity of sputtering beam.

A note on concentration units. Many SIMS researchers utilize units of concentration based on numbers of atoms; e.g., atom density (atoms/cm^3), atomic % (atoms/100 atoms of the host matrix), and ppma (atoms/ 10^6 atoms of the host matrix). Other SIMS researchers use mass-based concentration units; e.g., mass density (g/cm^3), weight % (g/100g of the host matrix), and parts per million by weight – commonly abbreviated ppm – ($\text{g}/10^6\text{g}$ of the host). The atom-based and mass-based units can be calculated from each other provided that the mass density and the chemical composition of the host matrix are known.

The citation of the “chemical composition of the host matrix” in the foregoing paragraph is a reminder that SIMS analysis is complementary to and dependent upon other micro-analytical techniques, particularly electron microscopy (for mapping) and electron-microprobe analysis (for major and minor element composition). Since SIMS is destructive analysis, it is always prudent to extract as much information from non-destructive, electron-beam-based techniques as possible before SIMS analysis.

It is also worthwhile to point out that SIMS trace-element quantitation has been driven in large measure by the technical requirements of the semiconductor electronics industry and the research efforts to meet these requirements. Most of the present day “infrastructure” of SIMS quantification — terminology, analytical techniques, and “tricks of the trade” for interpreting SIMS results — was developed and refined in the successful application of SIMS to semiconductor-electronics challenges^[1].

Trace-element quantitation by SIMS - - the specifics

A central construct in trace-element of quantitation by SIMS is *useful yield*. Useful yield is identified with a constituent *i* sputtered from the host matrix; i.e.,

$$\square = \frac{D_i}{S_i}$$

where \square = the useful yield of species *i*

D_i = the number of ions of species *i* detected by the SIMS instrument

S_i = the number of atoms of species *i* sputtered from the host matrix by the SIMS instrument.

The useful-yield parameter can be calculated on any time-scale of a SIMS analysis; all that is required is that the ions detected are correlated with atoms sputtered. For quantitation applications, the useful yield is calculated by summing the detected ions and sputtered atoms over an entire analysis. Useful yield is thus based purely on experimentally determined quantities. Useful yield has units of [ions/atoms] for species *i*.

The experimental context for SIMS determination of useful yield is depth-profile analysis. In depth-profile analysis the sputtering beam is tightly focused and rastered over the surface of the sample. Rastering in this way creates a sputtered crater with a flat bottom. If the sputtering-beam intensity is constant, the depth of the crater’s flat bottom at any time *t* after the start of the analysis is proportional to *t*. This proportionality allows for a time-to-depth conversion for characterizing the depth dependence of the sputtered-ion intensity of species *i*. The dimensions of the crater at the end of the analysis are determined, typically, by surface profilometry or optical-interference microscopy. Knowing the crater dimensions allows the analyst to calculate the volume of the host matrix sputtered during the profile. Knowing in turn the atom density (or concentration) of species *i*, the analyst can calculate number of atoms of *i* corresponding to the sputtered volume.

In a typical depth profile, the sputtered ions of species *i* are sampled at regular intervals with a fixed integration time. In the time between the sampling intervals for species *i*,

other species in the host matrix are usually sampled. In this setting, a duty factor is used to represent the fraction of the time of the depth-profile analysis that is actually utilized for counting sputtered ions of species i . The total number of sputtered ions for the analysis is thus the number of ions actually counted, divided by the duty factor.

The useful-yield parameter has scant utility for quantitation because it depends not only on the intrinsic sputtering properties of species i from the host matrix but also on extrinsic properties of the SIMS instrument (e.g., aperture diameters, slit widths, and voltages on lenses and other ion-optical elements). The value of the useful-yield concept is rather as a stepping-stone to a related parameter — called relative useful yield (RUY) — which is largely independent of SIMS-instrument conditions while retaining the dependence on the intrinsic sputtering properties of species i from the host matrix .

The defining relationship for RUY is:

$$[RUY]_{ij} = \frac{\varpi_j}{\varpi_i}$$

where

$[RUY]_{ij}$ is the relative useful yield of species i with respect to species j ,

ϖ_i is the useful yield of i ,

ϖ_j is the useful yield of j .

For purposes of quantitation, species j is chosen from the major-element species of the host matrix. This choice is made because the concentrations of major elements can be accurately determined on a microscale at the same locations where SIMS analyses are planned, usually by electron-microprobe analysis. The RUY is a dimensionless parameter.

Relative useful yield — application to quantitation

Consider a microstructure with the following compositional parameters:

(1) a matrix atom density n

where

$$n = \frac{\left[\begin{array}{l} \text{total number of atoms in the matrix} \\ \text{unit volume} \end{array} \right]}{\left[\begin{array}{l} \\ \end{array} \right]}$$

(2) a major-element species j with a known concentration $C_j \left[\begin{array}{l} \text{atoms } j \\ \text{atoms matrix} \end{array} \right]$

and atom density $n_j \left[\begin{array}{l} \text{atoms } j \\ \text{unit volume} \end{array} \right]$

(3) a trace-element species i with an unknown concentration of $C_i = \frac{\text{atoms } i}{\text{unit volume}}$

and atom density $n_i = \frac{\text{atoms } i}{\text{unit volume}}$

(4) a known $[RUY]_{ij}$ for species i and j .

Using the definition of $[RUY]_{ij}$, the relationships $C_i = n_i/n$ and $C_j = n_j/n$, and some algebra, the unknown C_i can be expressed as:

$$C_i = \frac{[\text{ions detected}]_i}{[\text{ions detected}]_j} * [RUY]_{ij} * C_j$$

The right-hand side of this expression contains only quantities that are determined in a SIMS measurement or are known from other, prior measurements. This expression is therefore the defining relation for applying RUY to SIMS quantitation.

A useful property of RUY can be exhibited for species i and j when i and j are isotopes of multi-isotope elements I and J , respectively. Namely,

$$[RUY]_{ij} = [RUY]_{JI}$$

This follows formally from the fact that $\square = \square$ and $\square = \square$.

Relationship of RUY to Relative Sensitivity Factor

For SIMS analysis in semiconductor-electronics applications, quantitation is usually achieved with a parameter called Relative Sensitivity Factor (RSF). For a trace-element species i and a major-element species j , the defining relation for SIMS quantitation with the RSF parameter is:

$$n_i = \frac{[\text{ions detected}]_i}{[\text{ions detected}]_j} * [RSF]_{ij}$$

where n_i is the atom density of species i in (atoms/unit volume) and $[RSF]_{ij}$ is the RSF parameter of species i with respect to species j for the matrix in view. The units of RSF are (atoms/unit volume). The RSF for a matrix is related to the corresponding RUY by:

$$[RSF]_{ij} = [RUY]_{ij} * n_j$$

where n_j is the atom density (atoms/unit volume) of major-element species j in the matrix. The RSF's for isotopes of multi-isotope elements are different from each other according to the relative proportions of the isotopes.

Measurement of RUY by SIMS

For practical purposes, there are two methods for measuring RUY's by SIMS:

- (1) measurements of compositionally homogeneous matrices with trace-element species which are known to be homogeneous on a microscale, such matrices are commonly called “bulk standards”.
- (2) Measurements of ion implants in homogeneous matrices, these are commonly called “ion-implanted standards”.

The almost exclusive reliance on these two methods nowadays is part of the legacy of SIMS quantitation for semi-conductor electronics and is the result of years of effort to find the most reliable and reproducible SIMS-quantitation techniques.

- (1) RUY for bulk standards.

A bulk standard for trace-element species i in a matrix with major-element species j is characterized by a number density n_i for species i and a number density n_j for species j . Under normal SIMS operating conditions the count-rates of species i and j are constant, except for counting statistical fluctuations — these fluctuations can be minimized by summing the detected-ion signals over a large number of sampling periods (called “cycles” in SIMS parlance). The RUY in this setting is thus given by

$$[RUY]_{ij} = \frac{(\text{sum of detected ions})_j}{(\text{sum of detected ions})_i} * \frac{n_i}{n_j}$$

- (2) RUY for ion-implanted standards

In an ion-implanted standard, the major-element species j is characterized by atom density n_j , as it was for the bulk-standard case. On the other hand, species i is characterized by a calibrated implant Fluence, F_i (atoms/unit area).

A SIMS depth-profile analysis of an ion-implanted standard is represented schematically in Figure 1. For this technique to succeed, it is imperative that the depth d_0 for the onset of the appearance of the implant profile be sufficiently below the sample surface for steady-state sputtering conditions to be established. Similarly, the “disappearance depth” d_1 of the implant profile must be well-defined.

The number of detected ions of species j is summed over the cycles corresponding to the interval from d_0 to d_1 . The number of detected ions for species i is obtained by numerical integration of the species – i profile from d_0 to d_1 .

The number of sputtered atoms of species j is

$$n_j * A * (d_1 - d_0)$$

where A is the analyzed area.

The total number of sputtered atoms of species *i* is

$$F_i * A$$

Thus, the RUY for species *i* and species *j* is

$$[RUY]_{ij} = \frac{(\text{sum of detected counts from } d_1 \text{ to } d_0)_j}{(\text{integral of detected counts from } d_1 \text{ to } d_0)} * \frac{F_i}{n_j * d_1 - d_0}$$

Dependence of SIMS quantitation on matrix composition

There is as yet no first-principles formulation for quantitative prediction of sputtering yields of elements from a matrix of arbitrary composition. This means that SIMS quantitation is fundamentally empirical; i.e., RUY's must be determined on an element-by-element basis for each distinct matrix. This observation notwithstanding, theoretical considerations allow many useful estimates of RUY's for trace elements and matrices where direct measurements have not been made. However, such estimates are at best semi-quantitative and can be improved only by measurements, such as those outlined in this review.

References

[1] R. G. Wilson, F. A. Stevie, and C. W. Magee, *Secondary Ion Mass Spectrometry*, John Wiley & Sons, Chichester, UK, 1989.

Note: The proceedings volumes of the biennial International Conference on Secondary Ion Mass Spectrometry — specifically, SIMS II through SIMS XIV — are an indispensable resource of diverse SIMS quantitation topics. Space limitations of this review prevent proper bibliographic citation of these volumes.

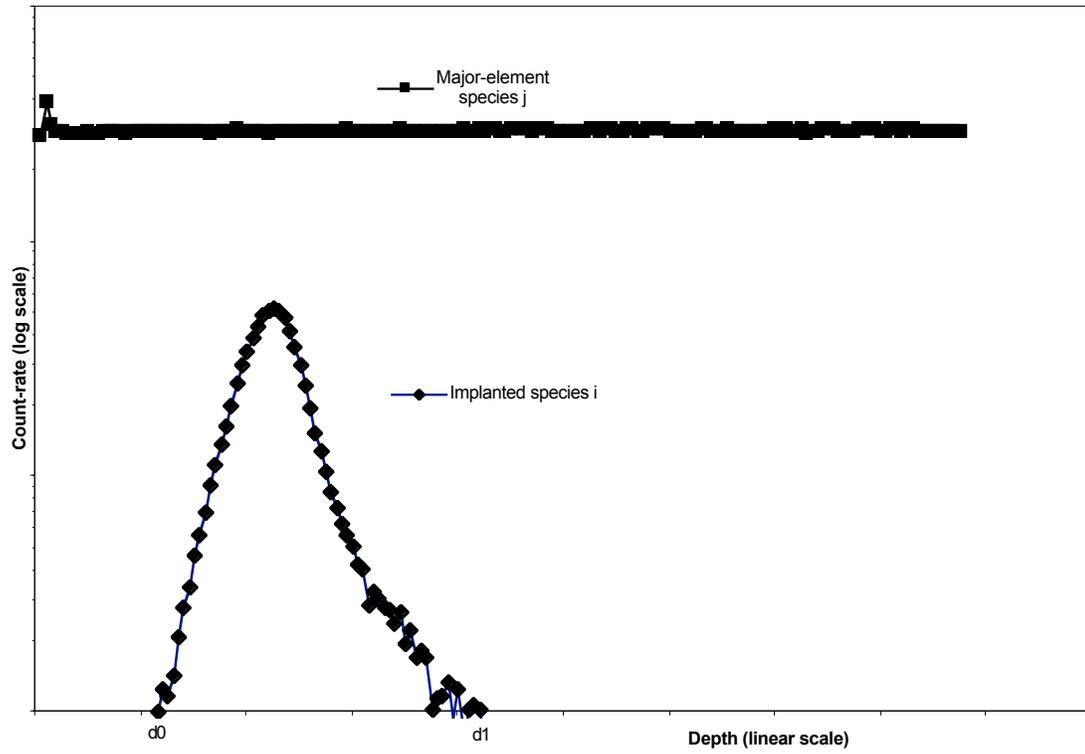


Figure 1. Schematic representation of a SIMS depth profile for an ion-implanted standard. Depth d_0 marks the "appearance depth" of implant species i ; d_1 marks the species- i "disappearance depth"