10

MASS AND OPTICAL SPECTROSCOPIES

10.0 INTRODUCTION

The analytical techniques covered in this chapter are typically used to measure trace-level elemental or molecular contaminants or dopants on surfaces, in thin films or bulk materials, or at interfaces. Several are also capable of providing quantitative measurements of major and minor components, though other analytical techniques, such as XRF, RBS, and EPMA, are more commonly used because of their better accuracy and reproducibility. Eight of the analytical techniques covered in this chapter use mass spectrometry to detect the trace-level components, while the ninth uses optical emission. All the techniques are destructive, involving the removal of some material from the sample, but many different methods are employed to remove material and introduce it into the analyzer.

In Dynamic Secondary Ion Mass Spectrometry (SIMS), a focused ion beam is used to sputter material from a specific location on a solid surface in the form of neutral and ionized atoms and molecules. The ions are then accelerated into a mass spectrometer and separated according to their mass-to-charge ratios. Several kinds of mass spectrometers and instrument configurations are used, depending upon the type of materials analyzed and the desired results.

The most common application of dynamic SIMS is depth profiling elemental dopants and contaminants in materials at trace levels in areas as small as 10 μm in diameter. SIMS provides little or no chemical or molecular information because of the violent sputtering process. SIMS provides a measurement of the elemental impurity as a function of depth with detection limits in the ppm–ppt range. Quantification requires the use of standards and is complicated by changes in the chemistry of the sample in surface and interface regions (matrix effects). Therefore, SIMS is almost never used to quantitatively analyze materials for which standards have not been carefully prepared. The depth resolution of SIMS is typically between 20 Å and 300 Å, and depends upon the analytical conditions and the sample type. SIMS is also used to measure bulk impurities (no depth resolution) in a variety of materials with detection limits in the ppb–ppt range.

By using a focused ion beam or an imaging mass spectrometer, SIMS can be used to image the lateral distribution of impurities in metal grain boundaries, biological materials (including individual cells), rocks and minerals, and semiconductors. The imaging resolution of SIMS is typically 1 μm, but can be as good as 10 nm.

Static SIMS is similar to dynamic SIMS but employs a much less intense primary ion beam to sputter the surface, such that material is removed from only the top monolayer of the sample. Because of the less violent sputtering process used during static SIMS, the chemical integrity of the surface is maintained during analysis such that whole molecules or characteristic fragment ions are removed from the surface and measured in the mass spectrometer. Measured molecular and fragment ions are used to provide a chemical rather than elemental characterization of the true surface. Static SIMS is often used in conjunction with X-Ray Photoelectron Spectroscopy (XPS), which provides chemical bonding information. The bonding information from XPS (see Chapter 5), combined with the mass spectrum from static SIMS, can often yield a complete picture of the molecular composition of the sample surface.

Static SIMS is labeled a trace analytical technique because of the very small volume of material (top monolayer) on which the analysis is performed. Static SIMS can also be used to perform chemical mapping by measuring characteristic molecules and fragment ions in imaging mode. Unlike dynamic SIMS, static SIMS is not used to depth profile or to measure elemental impurities at trace levels.

In Surface Analysis by Laser Ionization (SALI) ionized and neutral atoms are sputtered from the sample surface, typically using an ion beam (like SIMS) or a

laser beam (like LIMS). However, SALI employs a high-intensity laser that passes parallel and close to the surface of the sample, interacting with the sputtered secondary ions and neutrals to enhance the ionization of the neutrals, which are then detected in the mass spectrometer. SALI, in the single-photon ionization mode (low-intensity laser), can be used to provide a chemical rather than elemental characterization of the true surface, like static SIMS. While in multiphoton ionization mode (intense laser), it can be used to provide enhanced sensitivity and improved quantification over dynamic SIMS in certain applications. Improved quantification is possible because ionization of the sputtered neutral atoms occurs above the surface, separate from the sputtering process, eliminating difficulties encountered during quantification of SIMS—especially at surfaces and interfaces. SALI can also be used in conjunction with other analytical techniques, such as LIMS, in which a laser is used to desorb material from the surface. Like static and dynamic SIMS, SALI can be used to map the distribution of molecular (organic) or elemental impurities.

In Sputtered Neutral Mass Spectrometry (SNMS), atoms are removed from the sample surface by energetic ion bombardment from an RF argon plasma (not an ion beam). Sputtered atoms are then ionized in the RF plasma and measured in a mass spectrometer. SNMS is used to provide accurate trace-level, major, and minor concentration depth profiles through chemically complex thin-film structures, including interfaces, with excellent depth resolution. Because ionization is separate from the sputtering process (unlike SIMS), semiquantitative analyses, through interfaces and multilayered samples, may be performed without standards; improved accuracy (± 5–30%) is possible using standards. One of the primary advantages of SNMS over other depth profiling techniques is the extremely good depth resolution (as good as 10 Å) achievable in controlled cases. The detection limits of SNMS are limited to the 10 ppm–pph range. The analytical area of an SNMS depth profile is typically 5 mm in diameter, rendering analysis of small areas impossible, while providing a more "representative" sampling of inhomogeneous materials.

Laser Ionization Mass Spectrometry (LIMS) is similar to SIMS, except that a laser beam, rather than an ion beam, is used to remove and ionize material from a small area (1–5 μm in diameter) of the sample surface. By using a high-intensity laser pulse, the elemental composition of the area is measured, by using a low-intensity pulse, organic molecules and molecular fragments are desorbed from the surface, sometimes providing results similar to those of static SIMS. The elemental detection limits of LIMS are in the 1–100 ppm range which are not as good as those of SALI or SIMS but better than most electron-beam techniques, such as EDS and AES. LIMS is not usually used to acquire depth profiles because of the large depth (0.25–1 μm) to which the high-intensity laser penetrates during a single pulse and because of the irregularity of the crater shape. LIMS is used in failure analysis situations because it samples a relatively small volume of material (1 μm^3), is relatively

independent of sample geometry (shape), and produces an entire mass spectrum from a single pulse of the laser (analysis time less than 10 minutes). LIMS mass spectra can be quantified using standards in certain cases, but LIMS data are usually qualitative only. Additionally, because LIMS employs a laser for desorption and ionization, it can be used to analyze nonconductors, such as optical components (glasses) and ceramics.

Spark-Source Mass Spectrometry (SSMS) is used to measure trace-level impurities in a wide variety of materials (both conducting and nonconducting specimens) at concentrations in the 10–50 ppb range. Elemental sensitivities are uniform to within a factor of 3, independent of the sample type, rendering SSMS an ideal tool for survey impurity measurements when standards are unavailable. SSMS is usually used to provide bulk analysis (no lateral or in-depth information) but can also be used to measure impurities on surfaces or in thin films with special sample configurations. In SSMS, a solid material, in the form of two conducting electrodes, is vaporized and ionized using a high-voltage RF spark. The ions from the sample are then simultaneously analyzed using a mass spectrometer.

Glow-Discharge Mass Spectrometry (GDMS) is used to measure trace level impurities in solid samples with detection limits in the ppb range and below, with little or no in-depth or lateral information. The sample, in the form of a pin measuring $2 \times 2 \times 20$ mm, forms the cathode of a noble gas DC glow discharge (plasma). Atoms sputtered from the surface of the sample are ionized in the plasma and analyzed in a high-resolution mass spectrometer. Depth profiles with a depth resolution poorer than 100 nm can be obtained from flat samples run in a special sample configuration.

GDMS is slowly replacing SSMS because of its increased quantitative accuracy and improved detection limits. Like SNMS and SALI, GDMS is semiquantitative without standards ($\pm$ a factor of 3) and quantitative with standards ($\pm 20\%$) because sputtering and ionization are decoupled. GDMS is often used to measure impurities in metals and other materials which are eventually used to form thin films in other materials applications.

In Inductively Coupled Plasma Mass Spectrometry (ICPMS), ions are generated in an inductively coupled plasma and subsequently analyzed in a mass spectrometer. Detection of all elements is possible with the exception of a few because of mass interferences due to components of the plasma and the unit mass resolution of most ICPMS units. Typical samples are introduced into the plasma as liquids, but recent developments allow direct sampling by laser ablation. Solids and thin films (including interfaces) are usually digested into solution prior to analysis. Detection limits from solution are in the ppt–ppb range; with typical dilutions of 1000, the detection limits from solids are in the ppb–ppm range. ICPMS is fast and reproducible; survey mass spectra can be obtained from a solution in minutes. Quantitative analyses are performed with accuracies better than $\pm 5\%$ using standards, while semiquantitative analyses are accurate to $\pm 20\%$ or better. Surface and thin film analyses

are performed by dissolving the surface or thin film into solution and analyzing the solution. This kind of methodology is often selected when the average composition of a surface or film over a large area must be measured, or when a thin film exceeds the thickness of the analytical depth of other analytical techniques.

ICP-OES is similar to ICPMS but uses an optical detection system rather than a mass spectrometer. Atoms and ions are excited in the plasma and emit light at characteristic wavelengths in the ultraviolet or visible region of the spectrum. A grating spectrometer is used for simultaneous measurement of preselected emission lines. Measurement of all elements is possible with the exception of a few blocked by spectral interferences. The intensity of each line is proportional to the concentration of the element from which it was emitted. Elemental sensitivities in the sub-ppb–100 ppb range are possible for solutions; dilutions of 1000 times yield detection limits in the ppm range. Direct sampling of solids is performed using spark, arc or laser ablation, yielding similar detection limits. By sampling a solid directly, the risk of introducing contamination into the sample is minimized. Like ICPMS, ICP-OES is quantified by comparison to standards. Quantitative analyses are performed with accuracies between 0.2 and 15% using standards (typically better than ±5%). ICP-OES is less sensitive than ICPMS (poorer detection limits) but is selected in certain applications because of its quantitative accuracy and accessibility. (There are thousands of ICP-OES systems in use worldwide and the cost of a new ICP-OES is half that of an ICPMS.)

10.1 Dynamic SIMS

Dynamic Secondary Ion Mass Spectrometry

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Introduction

Dynamic SIMS, normally referred to as SIMS, is one of the most sensitive analytical techniques, with elemental detection limits in the ppm to sub-ppb range, depth resolution (z) as good as 2 nm and lateral (x, y) resolution between 50 nm and 2 μm, depending upon the application and mode of operation. SIMS can be used to measure any elemental impurity, from hydrogen to uranium and any isotope of any element. The detection limit of most impurities is typically between 10^{12} and 10^{16} atoms/cm^3, which is at least several orders of magnitude lower (better) than the detection limits of other analytical techniques capable of providing similar lateral and depth information. Therefore, SIMS (or the related technique, SALI) is almost always the analytical technique of choice when ultrahigh sensitivity with simultaneous depth or lateral information is required. Additionally, its ability to detect hydrogen is unique and not possible using most other non-mass spectrometry surface-sensitive analytical techniques.

Dynamic SIMS is used to measure elemental impurities in a wide variety of materials, but is almost new used to provide chemical bonding and molecular information because of the destructive nature of the technique. Molecular identification or measurement of the chemical bonds present in the sample is better performed using analytical techniques, such as X-Ray Photoelectron Spectrometry (XPS), Infrared (IR) Spectroscopy, or Static SIMS.

The accuracy of SIMS quantification ranges from ±2% in optimal cases to a factor of 2, depending upon the application and availability of good standards. However, it is generally not used for the measurement of major components, such as silicon and tungsten in tungsten silicide thin films, or aluminum and oxygen in alumina, where other analytical techniques, such as wet chemistry, X-Ray Fluorescence (XRF), Electron Probe (EPMA), or Rutherford Backscattering Spectrometry (RBS), to name only a few, may provide much better quantitative accuracy (±1% or better).

Because of its unique ability to measure the depth or lateral distributions of impurities or dopants at trace levels, SIMS is used in a great number of applications areas. In semiconductor applications, it is used to quantitatively measure the depth distributions of unwanted impurities or intentional dopants in single or multilayered structures. In metallurgical applications, it is used to measure surface contamination, impurities in grain boundaries, ultratrace level impurities in metal grains, and changes in composition caused by ion implantation for surface hardening. In polymers or other organic materials, SIMS is used to measure trace impurities on the surface or in the bulk of the material. In geological applications, SIMS is used to identify mineral phases, and to measure trace level impurities at grain boundaries and within individual phases. Isotope ratios and diffusion studies are used to date geological materials in cosmogeochemical and geochronological applications. In biology and pharmacology, SIMS is used to measure trace elements in localized areas, by taking advantage of its excellent lateral resolution, and in very small volumes, taking advantage of its extremely low detection limits.

Basic Principles

Sputtering

When heavy primary ions (oxygen or heavier) having energies between 1 and 20 keV impact a solid surface (the sample), energy is transferred to atoms in the surface through direct or indirect collisions. This creates a mixing zone consisting of primary ions and displaced atoms from the sample. The energy and momentum transfer process results in the ejection of neutral and charged particles (atomic ions and ionized clusters of atoms, called molecular ions) from the surface in a process called sputtering (Figure 1).

The depth (thickness) of the mixing zone, which limits the depth resolution of a SIMS analysis typically to 2–30 nm, is a function of the energy, angle of incidence,
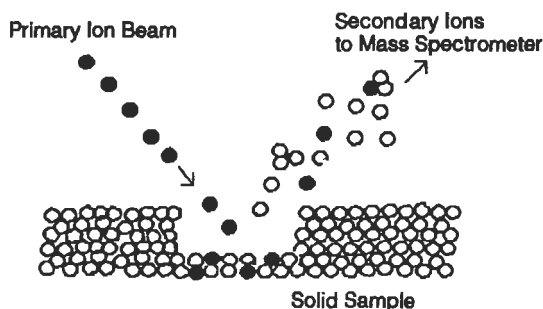
Primary Ion Beam

Secondary Ions
to Mass Spectrometer

Solid Sample

Figure 1   Diagram of the SIMS sputtering process.

and mass of the primary ions, as well as the sample material. Use of a higher mass primary ion beam, or a decrease in the primary ion energy or in the incoming angle with respect to the surface, will usually cause a decrease in the depth of the mixing zone and result in better depth resolution. Likewise, there is generally an inverse relationship between the depth (thickness) of the mixing zone and the average atomic number of the sample.

During a SIMS analysis, the primary ion beam continuously sputters the sample, advancing the mixing zone down and creating a sputtered crater. The rate at which the mixing zone is advanced is called the sputtering rate. The sputtering rate is usually increased by increasing the primary ion beam current density, using a higher atomic number primary ion or higher beam energy, or by decreasing the angle at which the primary ion beam impacts the surface. The primary ion beam currents used in typical SIMS analyses range from 10 nA to 15 μA—a range of more than three decades.

The depth resolution of a SIMS analysis is also affected by the flatness of the sputtered crater bottom over the analytical area; a nonuniform crater bottom will result in a loss in depth resolution. Because most ion beams have a Gaussian spatial distribution, flat-bottomed craters are best formed by rastering the ion beam over an extended area encompassing some multiples of beam diameters. Moreover, to reject stray ions emanating from the crater walls (other depths), secondary ions are collected only from the central, flat-bottomed region of the crater through the use of electronic gating or physical apertures in the mass spectrometer. For example, secondary ions are often collected from an area as small as 30 μm in diameter, while the primary ion beam sputters an area as large as 500 × 500 μm. Unfortunately, no matter what precautions and care are taken, the bottom of a sputtered crater becomes increasingly rough as the crater deepens, causing a continual degradation of depth resolution.

Detection Limits

The detection limit of each element depends upon the electron affinity or ionization potential of the element itself, the chemical nature of the sample in which it is contained, and the type and intensity of the primary ion beam used in the sputtering process.

Because SIMS can measure only ions created in the sputtering process and not neutral atoms or clusters, the detection limit of a particular element is affected by how efficiently it ionizes. The ionization efficiency of an element is referred to as its ion yield. The ion yield of a particular element A is simply the ratio of the number of A ions to the total number of A atoms sputtered from the mixing zone. For example, if element A has a 1:100 probability of being ionized in the sputtering process—that is, if 1 ion is formed from every 100 atoms of A sputtered from the sample—the ion yield of A would be $1/100$. The higher the ion yield for a given element, the lower (better) the detection limit.

Many factors affect the ion yield of an element or molecule. The most obvious is its intrinsic tendency to be ionized, that is, its ionization potential (in the case of positive ions) or electron affinity (in the case of negative ions). Boron, which has an ionization potential of 8.3 eV, looses an electron much more easily than does oxygen, which has an ionization potential of 13.6 eV, and therefore has a higher positive ion yield. Conversely, oxygen possesses a higher electron affinity than boron (1.5 versus 0.3 eV) and therefore more easily gains an electron to form a negative ion. Figures 2a and 2b are semilogarithmic plots of observed elemental ion yields relative to the ion yield of iron (M^+/Fe^+ or M^-/Fe^-) versus ionization potential or electron affinity for some of the elements certified in an NBS 661 stainless steel reference material. From these plots, it is easy to see that an element like zirconium has a very high positive ion yield and, therefore, an excellent detection limit, compared to sulfur, which has a poor positive ion yield and a correspondingly poor detection limit. Likewise, selenium has an excellent negative ion yield and an excellent detection limit, while manganese has a poor negative ion yield and poor detection limit. The correlation of electron affinity and ionization potential with detection limits is consistent in most cases; exceptions due to the nature of the element itself or to the chemical nature of the sample material exist. For example, fluorine exhibits an anomalously high positive ion yield in almost any sample type.

One of three kinds of primary ion beams is typically used in dynamic SIMS analyses: oxygen (O_2^+ or O^-), cesium (Cs^+), or argon (Ar^+). The use of an oxygen beam can increase the ion yield of positive ions, while the use of a cesium beam can increase the ion yield of negative ions, by as much as four orders of magnitude. A simple model explains these phenomena qualitatively by postulating that M–O bonds are formed in an oxygen-rich mixing zone, created by oxygen ion bombardment. When these bonds break in the ion emission process, oxygen tends to become negatively charged due to its high ionization potential, and its counterpart
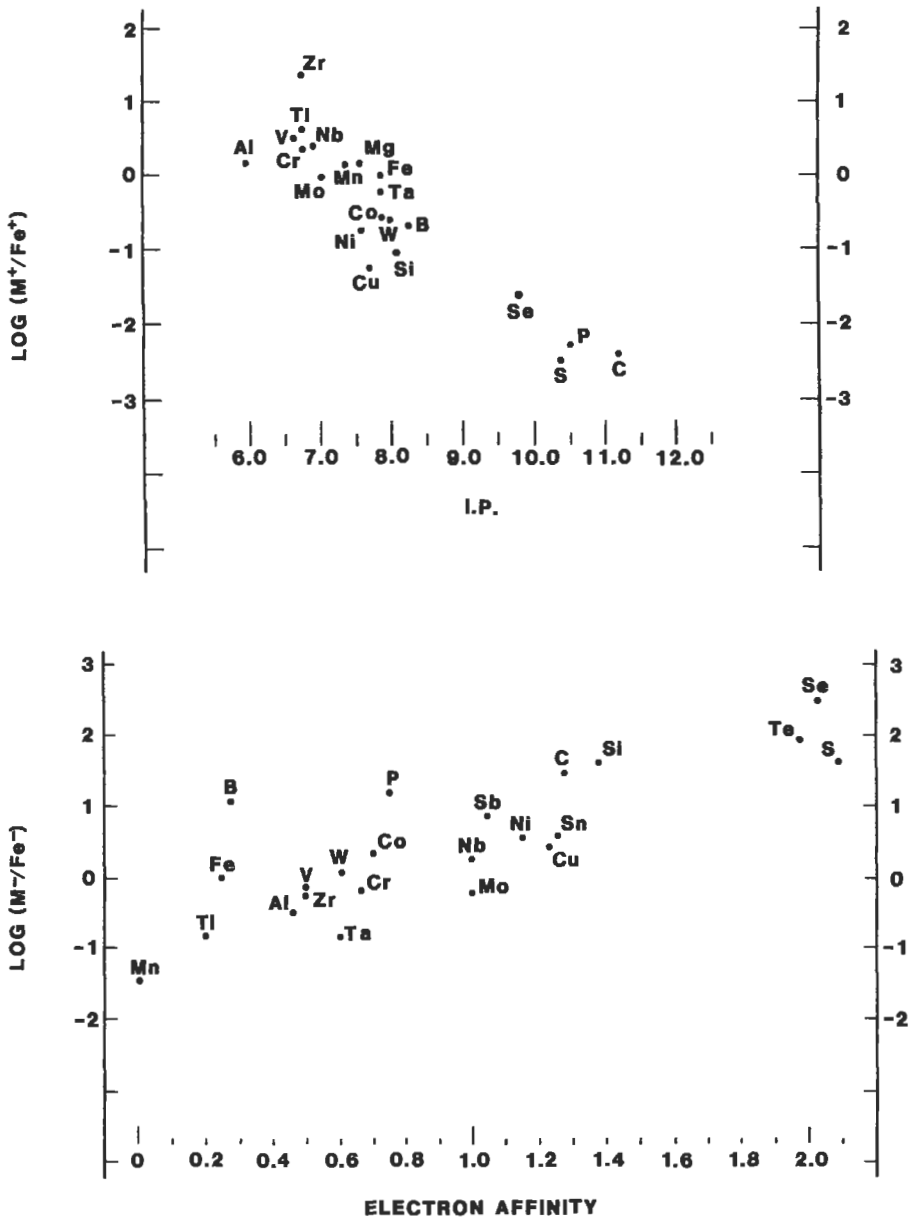
Figure 2 (a) Semilogarithmic plot of the positive relative ion yields of various certified elements (M^+/Fe^+) in NBS 661 stainless steel reference material versus ionization potential. (b) Semilogarithmic plot of the negative relative ion yields of various certified elements (M^-/Fe^-) in NBS 661 stainless steel reference material versus electron affinity.

M dissociates as a positive ion.[1] Conversely, the enhanced ion yields of the cesium ion beam can be explained using a work function model,[2] which postulates that because the work function of a cesiated surface is drastically reduced, there are more secondary electrons excited over the surface potential barrier to result in enhanced formation of negative ions. The use of an argon primary beam does not enhance the ion yields of either positive or negative ions, and is therefore, much less frequently used in SIMS analyses.

Like the chemical composition of the primary beam, the chemical nature of the sample affects the ion yield of elements contained within it. For example, the presence of a large amount of an electronegative element like oxygen in a sample enhances the positive secondary ion yields of impurities contained in it compared to a similar sample containing less oxygen.

Another factor affecting detection limits is the sputtering rate employed during the analysis. As a general rule, a higher sputtering rate yields a lower (better) detection limit because more ions are measured per unit time, improving the detection limits on a statistical basis alone. However, in circumstances when the detection limit of an element is limited by the presence of a spectral interference (see below), the detection limit may not get better with increased sputtering rate. Additionally and unfortunately, an increase in the sputtering rate nearly always results in some loss in depth resolution.

Common Modes of Analysis and Examples

SIMS can be operated in any of four basic modes to yield a wide variety of information:

1 The depth profiling mode, by far the most common, is used to measure the concentrations of specific preselected elements as a function of depth (z) from the surface.

2 The bulk analysis mode is used to achieve maximum sensitivity to trace-level components, while sacrificing both depth (z) and lateral (x and y) resolution.

3 The mass scan mode is used to survey the entire mass spectrum within a certain volume of the specimen.

4 The imaging mode is used to determine the lateral distribution (x and y) of specific preselected elements. In certain circumstances, an imaging depth profile is acquired, combining the use of both depth profiling and imaging.

Depth Profiling Mode

If the primary ion beam is used to continuously remove material from the surface of a specimen in a given area, the analytical zone is advanced into the sample as a function of the sputtering time. By monitoring the secondary ion count rates of selected
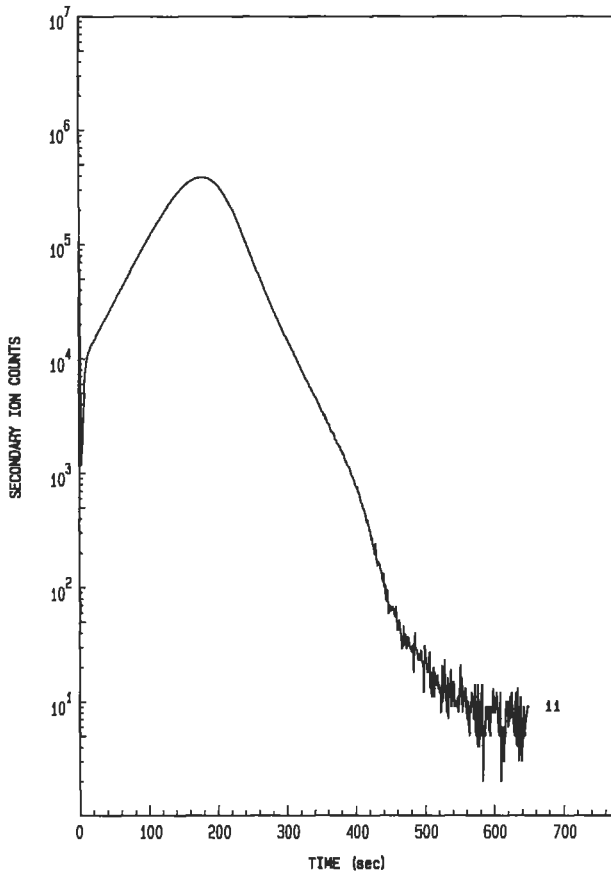
Figure 3a   **Unprocessed depth profile (secondary ion intensity versus sputtering time) of a silicon sample containing a boron ion implant.**

elements as a function of time, a profile of the in-depth distribution of the elements is obtained. The depth scale of the profile is commonly determined by physically measuring the depth of the crater formed in the sputtering process and assigning that depth to the total sputtering time required to complete the depth profile. A depth scale assigned in this way will be accurate only if the sputtering rate is uniform throughout the entire profile. For samples composed of layers that sputter at different rates, an accurate depth scale can be assigned only if the relative sputtering rates of the different layers are known. A typical SIMS depth profile is collected as secondary ion counts per second versus sputtering time (typically one second per measurement) and converted to a plot of concentration versus depth by using the depth of the sputtering crater and comparing the data to standards. Figure 3a is an unprocessed depth profile of a silicon sample containing a boron ion implant.
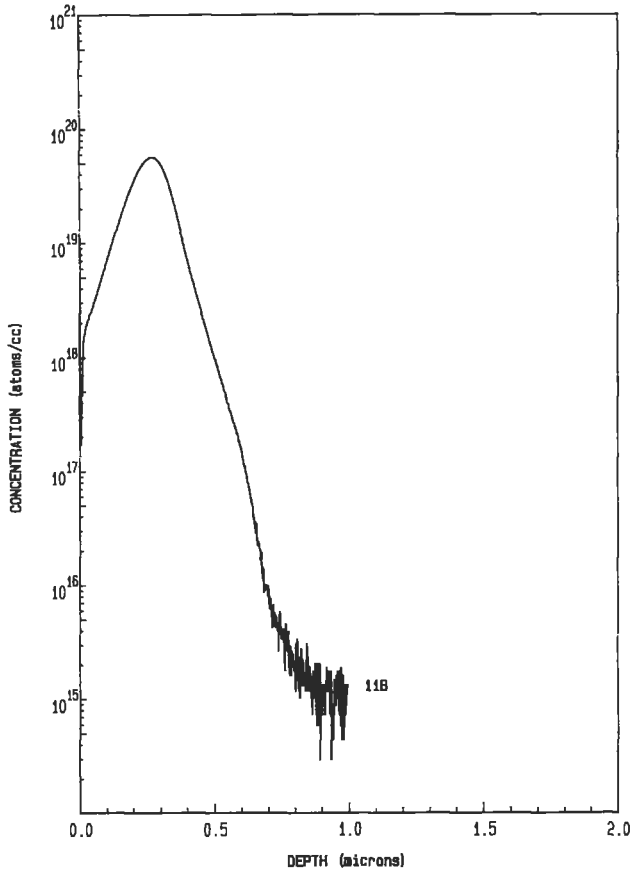
Figure 3b Depth profile in (a), after converting the sputtering time to depth and the secondary ion intensities to concentrations.

Figure 3b shows the same depth profile after converting to depth and concentration. Depth profiles can be performed to depths exceeding 100 μm and can take many hours to acquire; a more typical depth profile is several μm in depth and requires less than one hour to acquire.

Mass Scan Mode

A mass scan is acquired in cases when a survey of all impurities present in a volume of material is needed. Rather than measuring the secondary ion count rates of pre-selected elements as a function of sputtering time the count rates of all secondary ions are measured as a function of mass. Because a mass scan is continuously acquired over a mass range, no depth profiling or lateral information is available while operating in this mode. Figure 4 shows a mass scan acquired from a zirconia
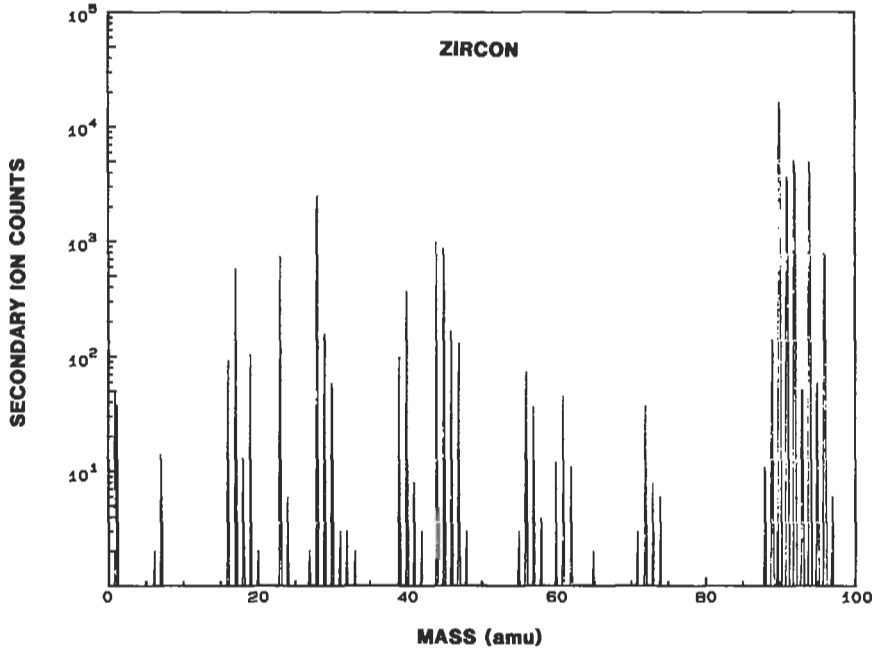
Figure 4   **Mass scan acquired from a zirconia crystal.**

crystal (geological sample). It shows peaks for many elements and molecules, but provides no information concerning the depth or lateral distribution of these impurities.

Bulk Analysis Mode

Bulk analysis mode is typically used to obtain the lowest possible detection limits of one or several elements in a uniform sample. This mode of operation is similar to a depth profile with the sputtering rate set to the maximum. This causes the crater bottom to lose its flatness and allows impurities from the crater walls to be measured, thereby sacrificing depth resolution. Therefore, accurate measurement of impurities is obtained only when they are uniformly distributed in the sample. This method of measurement usually results in at least a factor-of-10 improvement in detection limits over the depth profiling mode. As an example, the detection limit of boron in silicon using the bulk analysis mode is 5×10^{12} atoms/cm^3, several orders of magnitude better than the boron background acquired using the depth profiling mode (6×10^{14} atoms/cm^3), as shown in Figure 3b.

Imaging Mode

SIMS imaging is performed using one of two methods. The first, called ion micros-copy or stigmatic imaging, is only possible using specially constructed mass spec-trometers capable of maintaining the *x*–*y* spatial relationships of the secondary ions. These mass spectrometers are typically specially configured double-focusing mag-netic-sector spectrometers and are actually better termed secondary ion *microscopes*. The lateral resolution of microscope imaging is typically no better than 1 µm. The second method, scanning imaging, is performed by measuring the secondary ion intensity as a function of the lateral position of a small spot scanning ion beam. The lateral resolution of this type of imaging is largely dependent on the diameter of the primary ion beam, which can be as small as 50 nm.

Figures 5a and 5b are mass-resolved secondary ion images of gold (Au) and sul-fur (S) in a cross-sectioned and polished pyrite (gold ore) sample acquired using the microscope imaging method. The gray level is proportional to the secondary ion intensity measured at each location, i.e., more gold or sulfur is found in darker loca-tions. These images show that the gold, the geologist's primary interest, is localized in the outer few µm of the sulfur-containing pyrite grain.

By acquiring mass-resolved images as a function of sputtering time, an imaging depth profile is obtained. This combined mode of operation provides simultaneous lateral and depth resolution to provide what is known as three-dimensional analysis.

Sample Requirements

Most SIMS instruments are configured to handle samples less than 2.5 cm in diam-eter and 1 cm in thickness. The surface of the sample must be as smooth as possible because surface roughness causes a significant loss in depth resolution; cross sec-tions and other cut samples must be well polished before analysis. In SIMS instru-ments capable of stigmatic imaging, the sample should be planar, because it effectively is part of the secondary ion optics. Nonplanar samples are better ana-lyzed using a quadrupole SIMS instrument (discussed below) in which the sample shape does not affect the results as strongly. Samples composed of materials that are dielectric (nonconducting) must be analyzed using special conditions (see below). Quadrupole SIMS instruments are also less affected by sample charging and are often used to analyze dielectric samples.

Artifacts

Although SIMS is one of the most powerful surface analysis techniques, its applica-tion is complicated by a variety of artifacts.
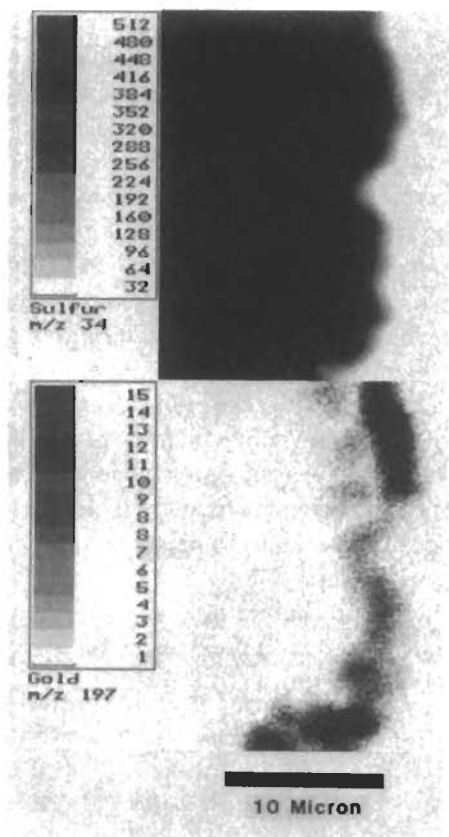
Figure 5 **Mass-resolved secondary ion images of sulfur and gold in a pyrite ore sample.**
A comparison of the two images clearly shows the gold is found in the outer
several μm of the sulfur-containing pyrite grain. These images were acquired
using a magnetic-sector mass spectrometer in the microscope-imaging mode.

Mass Interferences

The most frequent artifacts arise from interferences in the mass spectrum, that is, ionized atomic clusters (molecular ions) or multiply charged ions whose nominal mass-to-charge ratio equals that of the elemental ions of interest. Such interferences can cause erroneous assignment of an element not present in the sample or simply can degrade the detection limit of the element of interest. Figure 6 is a mass spectrum obtained from high-purity silicon, using oxygen ion bombardment. In addition to the $^{28}Si^+$, $^{29}Si^+$, and $^{30}Si^+$ isotope peaks, there exist numerous other peaks of atomic and molecular ions typically composed of primary ion species (oxygen), ions
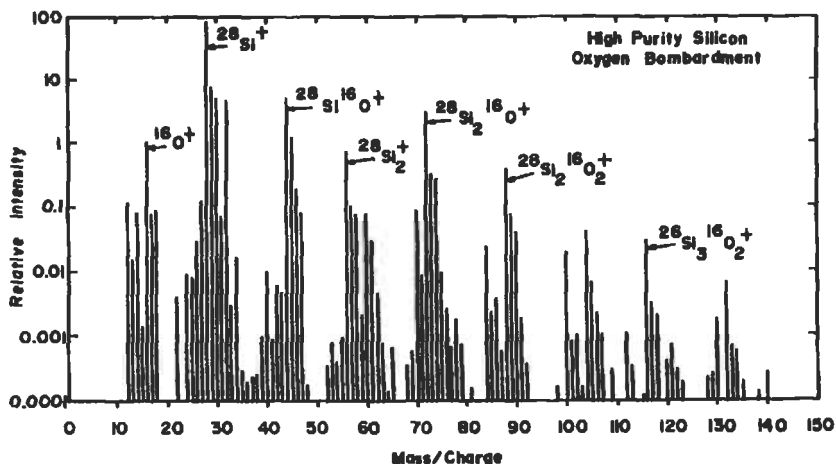
Figure 6   Typical secondary ion mass spectrum obtained from high-purity silicon using an oxygen ion beam. Major ion peaks are identified in the spectrum.

of the major components of the sample (silicon), or atmospheric species (hydrogen, carbon, oxygen, nitrogen, etc.) remaining in the high-vacuum sample chamber. Many of these peaks are sufficiently intense to produce a measurable background, which may preclude determination of a specific element (impurity), even in the ppm range.

Once identified, voltage offset and high mass resolution techniques may be used to reduce the detrimental effect of these interfering ions. In the voltage offset technique, the mass spectrometer is adjusted to accept only ions in a certain (usually higher) kinetic energy range. This technique is effective in discriminating against molecular ions because the energy distribution of atomic ions (typically the ions of interest) is broader than that of molecular ions at the same nominal mass. Figure 7 shows two SIMS depth profiles of the same silicon sample implanted with arsenic (^{75}As). These depth profiles were obtained under normal conditions (0-V offset) and under voltage offset conditions (50-V offset). The improvement in the detection limit of arsenic with the use of a 50-V offset results from discrimination of the $^{29}Si^{30}Si^{16}O$ molecular ion also at mass 75.

High mass resolution techniques are used to separate peaks at the same nominal mass by the very small mass differences between them. As an example, a combination of ^{30}Si and ^{1}H to form the molecular ion $^{30}Si^{1}H^{-}$, severely degrades the detection limit of phosphorous (^{31}P) in a silicon sample. The exact mass of phosphorous (^{31}P) is 31.9738 amu while the real masses of the interfering $^{30}Si^{1}H$ and $^{29}Si^{1}H_2$ molecules are 31.9816 amu and 31.9921 amu, respectively. Figure 8 shows a mass

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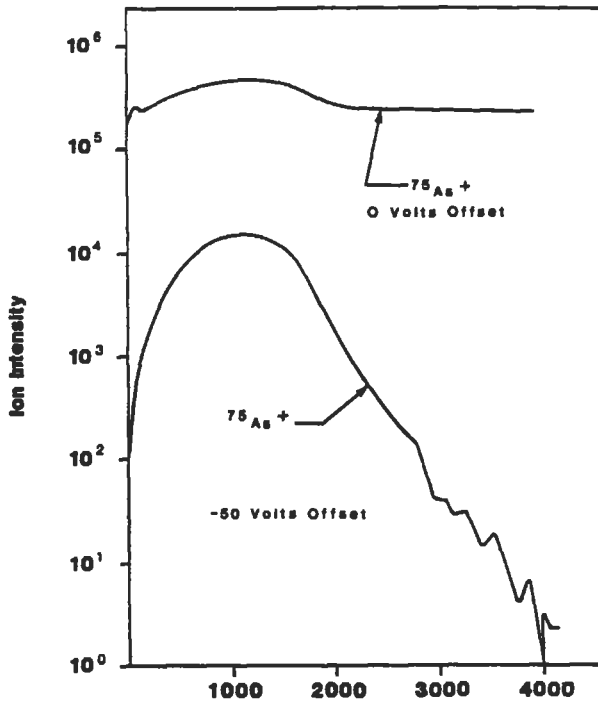
Figure 7   Depth profile of an arsenic (^{75}As) ion implant in silicon with and without use of voltage offset techniques. Voltage offset provides an enhanced detection limit for As in Si.

spectrum obtained from a phosphorus doped amorphous silicon thin film using high mass resolution techniques. The two mass interferences, $^{30}Si^1H^-$ and $^{29}Si^1H_2^-$, are completely separated from the $^{31}P^-$ peak. Quadrupole instruments are not usually capable of such high mass resolution.

Primary Ion Beam Sputtering Equilibrium

As explained above, the mixing zone contains a mixture of atoms from the primary ion beam and the solid sample. In the case of oxygen or cesium ion bombardment, these primary species become part of the material in the mixing zone and can significantly alter the ion yields of elements in the sample. However, when sputtering is first started (at the beginning of a depth profile), the mixing zone contains very few atoms from the primary ion beam, causing ions ejected from the mixing zone to be less affected by the enhancement process.

Crater Bottom Roughening

In polycrystalline solids or samples consisting of various phases, each grain may sputter at a different rate producing extensive roughness in the bottom of the cra-
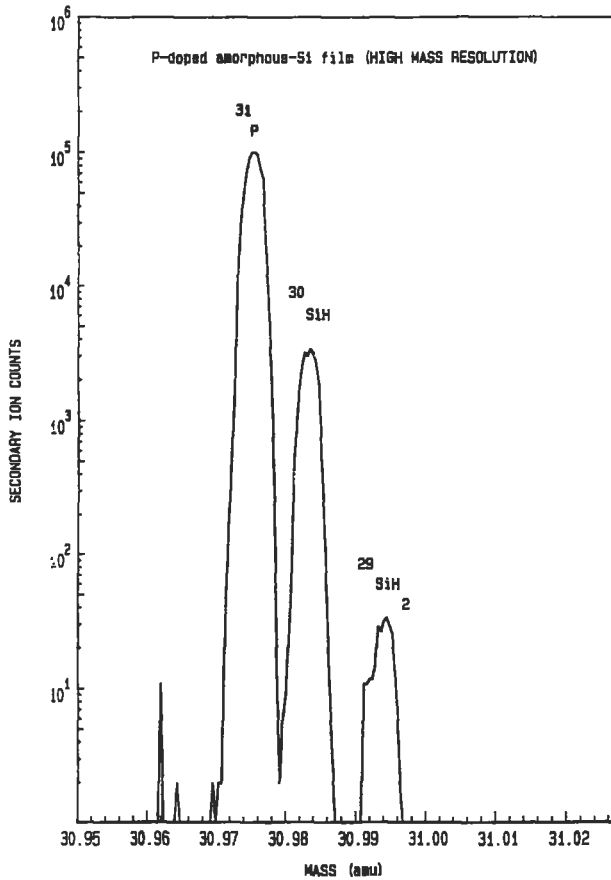
Figure 8   High mass resolution mass spectrum obtained from a phosphorus-doped amorphous silicon hydride thin film using a magnetic sector ion microanalyzer. The ^{31}P peak is well separated from the hydride interferences.

ter.[3] The roughness of the crater bottom will result in a loss in depth resolution and cause the depth profile to appear smeared in depth.

Surface Oxide

By enhancing the positive ion yield of most elements, the presence of an oxide on the surface of a sample can cause the first several points of a SIMS depth profile to be misleadingly high. Exceptionally large secondary ion signals for most elements are observed while profiling through the surface oxide, even though their concentrations are not higher. In these cases, the first several data points are corrected or simply disregarded.

Sample Charging

The charge carried by positive primary ions can accumulate on the surface of a non-conducting sample, causing the primary ion beam to be defocused or to move away from the analytical area of interest, thus preventing continued analysis. In addition, the accumulated charge can change the energy of the ejected ions, thereby affecting their transmission and detection in the mass spectrometer. This effect, called *sample charging*, is eliminated or reduced by flooding the sample surface with a low energy electron beam, providing compensation for the build-up of positive charge. As a general rule, samples with resistivities above 10^8 ohm/cm^2 require the use of electron flooding. In highly insulating samples, the use of a negative primary ion beam may also alleviate this charging problem.

Adsorption of Gaseous Species

During the sputtering process, residual atoms and molecules in the vacuum above the sample surface (typically containing hydrogen, carbon, nitrogen, and oxygen) are incorporated into the mixing zone by absorbing onto newly exposed and unsputtered reactive ions and molecules of the sample. The incorporated atmospheric species are eventually ejected from the mixing zone as elemental and molecular ions and detected as if they were originally present in the sample, complicating SIMS detection of these species and adding interfering molecular ions to the secondary ion mass spectrum. As an example, a mass interference between ^{31}P, and $^{30}Si^1H$ and $^{29}SiH_2$, all having mass 31, can be caused by hydrogen from the atmosphere in the sample chamber. The detrimental effects of these atmospheric species can be reduced by improving the vacuum in the sample chamber, but no matter how good the vacuum is, some adsorption will occur.

Impurity Mobility—Ion Beam-Induced Diffusion

Another difficulty is ion beam-induced diffusion of extremely mobile ions, such as lithium and sodium, in dielectric thin-film samples. This effect is normally observed when depth profiling a dielectric thin film on a conducting substrate with a positive primary ion beam. Diffusion occurs because the primary ion beam deposits a charge on the sample surface, creating a large electric field across the thin film, thereby driving the mobile ions away from the surface, to the interface between the thin film and substrate. In bulk insulators, this problem may be less severe because the electric field gradient is smaller. Nonetheless, the acquired depth profile no longer reflects the original composition of the sample. This effect is reduced or eliminated by flooding the sample surface with a low energy beam of electrons during sputtering. The current of electrons striking the sample surface must be carefully balanced against the build-up of charge due to the primary ion beam. Otherwise, distortion of the depth profile will still occur. As a general rule, quadrupole mass spectrometers have much less difficulty with impurity mobility artifacts

than do magnetic sector spectrometers, and they are almost always used in these applications.

Quantification

Ion yields of different elements vary by several orders of magnitude and depend sensitively on the type of primary beam and sample. Accurate quantification requires comparison to standards or reference materials of similar or identical major element composition that must be measured using the same analytical conditions, especially using the same type of primary ion beam. For example, an aluminum sample with a known content of copper is not a good standard to use for quantification of copper in stainless steel. Similarly, a standard analyzed using a cesium primary ion beam must not be used as a standard for quantification of an unknown sample analyzed using an oxygen ion beam. In some cases, semiempirical ion yield systematics are successfully used to quantify certain analyses; this method of quantification is accurate only to within an order of magnitude.

Ion implantation is often used to produce reliable standards for quantification of SIMS analyses.[4] Ion implantation allows the introduction of a known amount of an element into a solid sample. A sample with a major component composition similar to that of the unknown sample may be implanted to produce an accurate standard. The accuracy of quantification using this implantation method can be as good as ±2%.

Instrumentation

SIMS instruments are generally distinguished by their primary ion beams, and the kinds of spectrometers they use to measure the secondary ions. Several types of primary ion beams—typically, oxygen, cesium, argon, or a liquid metal like gallium—are used in SIMS analyses, depending on the application. Nearly any SIMS instrument can be configured with one or more of these ion-beam types. The majority of SIMS mass spectrometers fall into three basic categories: double-focusing electrostatic or magnetic sector, quadrupole, and time-of-flight. Time-of-flight analyzers are primarily used for surface and organic analyses (especially for high molecular weight species) and are mentioned in the article on static SIMS.

A double-focusing, electrostatic or magnetic-sector mass spectrometer achieves mass separation using an electrostatic analyzer and magnet. Secondary ions of different mass are physically separated in the magnetic field, with light elements making a tight arc through the magnet and heavy elements making a broad arc. Ions of different charge-to-mass ratios are measured by changing the strength of the magnetic field in the magnet to align the ions of interest with a stationary detector. Magnetic-sector systems provide excellent detection limits because of their high transmission efficiency, and are capable of high mass resolution. Some of these

spectrometers are capable of stigmatic imaging (also called ion microscopy) which is used to acquire mass-resolved ion images with a resolution as good as 1 μm.

In quadrupole-based SIMS instruments, mass separation is achieved by passing the secondary ions down a path surrounded by four rods excited with various AC and DC voltages. Different sets of AC and DC conditions are used to direct the flight path of the selected secondary ions into the detector. The primary advantage of this kind of spectrometer is the high speed at which they can switch from peak to peak and their ability to perform analysis of dielectric thin films and bulk insulators. The ability of the quadrupole to switch rapidly between mass peaks enables acquisition of depth profiles with more data points per depth, which improves depth resolution. Additionally, most quadrupole-based SIMS instruments are equipped with enhanced vacuum systems, reducing the detrimental contribution of residual atmospheric species to the mass spectrum.

The choice of mass spectrometer for a particular analysis depends on the nature of the sample and the desired results. For low detection limits, high mass resolution, or stigmatic imaging, a magnetic sector-based instrument should be used. The analysis of dielectric materials (in many cases) or a need for ultrahigh depth resolution requires the use of a quadrupole instrument.

Conclusions

SIMS is one of the most powerful surface and microanalytical techniques for materials characterization. It is primarily used in the analysis of semiconductors, as well as for metallurgical, and geological materials. The advent of a growing number of standards for SIMS has greatly enhanced the quantitative accuracy and reliability of the technique in these areas. Future development is expected in the area of small spot analysis, implementation of post-sputtering ionization to SIMS (see the articles on SALI and SNMS), and newer areas of application, such as ceramics, polymers, and biological and pharmaceutical materials.

Related Articles in the Encyclopedia

Static SIMS, SALI, SNMS, and Surface Roughness

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10.2   Static SIMS

Static Secondary Ion Mass Spectrometry

BILL KATZ

Contents

- Introduction
- Basic Principles
- Sample Preparation
- Instrumentation
- Qualitative Analysis
- Quantitative Analysis
- Chemical Mapping
- Conclusions

Introduction

With today's technology, the definition of the surface as it effects a material's performance in many cases means the outer one or two monolayers. It is the specific chemistry of these immediate surface molecules that determines many of the chemical and physical properties. Therefore, it is important to have available a tool that is able to characterize the chemistry of these layers. One such method that has met with considerable success is Static Secondary Ion Mass Spectrometry (SIMS).

Static SIMS entails the bombardment of a sample surface with an energetic beam of particles, resulting in the emission of surface atoms and clusters. These ejected species subsequently become either positively or negatively charged and are referred to as secondary ions. The secondary ions are the actual analytical signal in SIMS. A mass spectrometer is used to separate the secondary ions with respect to their charge-to-mass ratios. The atomic ions give an elemental identification (see

the article on dynamic SIMS), whereas the clusters can provide information on the chemical groups.

The mass spectrum of the clusters obtained represents a fingerprint of the compounds analyzed. The data show the various chemical functional groups as they fragment during analysis. The data may be acquired over relatively small areas (μm or less) for a localized analysis or larger areas (mm) for a macrocharacterization. Further, by monitoring a particular charge-to-mass ratio (i.e., a particular chemical group), one can obtain chemical maps depicting the lateral distribution of a specific fragment or compound.

Basic Principles

The analytical signal (he secondary ions) is generated by the interaction of an energetic particle with a sample surface. This interaction can be divided into two regimes by the total flux of primary particles used. In what is known as Dynamic SIMS, the incident flux of primary ions is large enough (above 5^{12} atoms/cm^2) that, statistically, a given area has a high probability of being repetitively bombarded, causing a crater to be formed in the sample. This mode of SIMS provides an in-depth analysis of any element (including H) and its isotopes with excellent detection limits (ppm to ppb atomic). The disadvantage is the large primary fluxes tend to alter or totally obliterate the chemistry, limiting dynamic SIMS to elemental analysis.

When the total flux is kept below 5^{12} atoms/cm^2, the probability of a primary ion striking a previously analyzed area is low, thus leaving the surface chemistry intact. This is the mode of operation used for Static SIMS. With respect to the primary beam, the total incident flux is the critical parameter for maintaining the chemical integrity of the material. Typically, static SIMS is performed using an inert gas beam operated at kinetic energies between 1 and 10 keV. The beam can be composed either of positively charged ions (Ar$^+$, Xe$^+$) or neutral particles (Ar, Xe) depending upon the type of ion source used.

In the SIMS process the energy of the incoming primary particles is dissipated by collisional cascades within the sample as the primary penetrates well into the material. The energy transferred to the sample is sufficient to cause atoms and molecules at the surface (within 1–3 atomic layers) to be ejected. A small fraction of these carry positive or negative charge, and are detected. In static SIMS, since one is primarily after chemical information, the identification of the cluster molecular ions is of particular interest as it allows one to identify the chemical compounds present at the surface. Unfortunately, in many-atom compounds severe fragmentation of the clusters takes place during the ejection and ionization process, with the parent ions rarely being observed. In most cases, therefore, identification of the parent species must rely on deductions made from the fragmentation patterns observed.

Sample Preparation

A major advantage of static SIMS over many other analytical methods is that usually no sample preparation is required. A solid sample is loaded directly into the instrument with the condition that it be compatible with an ultrahigh vacuum (10^{-9}–10^{-10} torr) environment. Other than this, the only constraint is one of sample size, which naturally varies from system to system. Most SIMS instruments can handle samples up to 1–2 inches in diameter.

In specialized cases, a treatment known as cationization sometimes is tried to improve the amount of molecular (chemical) information made available. If Ag or Na are deliberately introduced into the sample, they will often combine with the molecular species present to create Ag^+ or Na^+ molecular ions. These ions are more stable to fragmentation than the bare molecular ions, and can therefore be observed more easily in the mass spectrum. The identification of parent ion peaks in this manner aids in detailed chemical identification.

Static SIMS is also capable of analyzing liquids and fine particles or powders. A liquid is often prepared by putting down an extremely thin layer on a flat substrate, such as a silicon wafer. Particles are easily prepared by pressing them onto double-sided tape. No further sample preparation, such as gold- or carbon-coating, is required.

Because of the extreme surface sensitivity of static SIMS, care should always be exercised not to handle the samples. Clean tools and gloves should be used always to avoid the possibility of contaminating the surface. While it is possible to remove surface contamination with solvents like hexane, it is always desirable not to clean the surface to be analyzed.

Instrumentation

All commercially available SIMS systems have in common some type of computer automation, an ion source, a high-vacuum environment, and some type of mass spectrometer. While the specifics may vary from system to system, the basic requirements are the same. The hardware feature that tends to distinguish the various systems is the type of mass spectrometer used. These fall into three basic categories:[1]

- Quadrupole spectrometers. These are the least expensive mass spectrometers, and the easiest to operate. By applying AC and DC potentials to a set of four rods, ions are separated by mass as they pass through the quadrupole. The voltages can be changed quickly, allowing relatively rapid scanning of the mass range, which is usually limited to around 1000 amu. Because quadrupoles cannot effectively separate ions having a wide energy spectrum, an electrostatic filter is used between the sample and the quadrupole. Perhaps the major drawback to

quadrupoles is that they have only moderate mass resolution and cannot separate peaks of the same nominal mass.

- Magnetic-sector spectrometers. These spectrometers use an electrostatic analyzer for energy filtering and a magnetic sector for mass separation. They are capable of achieving high mass resolution, with typical mass ranges of 250 amu.

- Time-of-flight spectrometers. *Time-of-flight* (TOF) analyzers are capable of both high mass resolution and extended mass range. Their design requires that the ion beam be pulsed (1–10 ns) to ensure high mass resolution. After the ion beam strikes the sample surface, the extracted secondary ions travel through a drift tube to a detector having a large area. Mass separation is accomplished by noting that ions having different masses take different times to reach the detector. For example, lighter secondary ions take less time to traverse the drift tube and reach the detector faster. Using this type of mass analyzer enables the entire mass spectrum to be collected in a few μs.

Each type of mass spectrometer has its associated advantages and disadvantages. Quadrupole-based systems offer a fairly simple ion optics design that provides a certain degree of flexibility with respect to instrument configuration. For example, quadrupole mass filters are often found in hybrid systems, that is, coupled with another surface analytical method, such as electron spectroscopy for chemical analysis or scanning Auger spectroscopy.

Contrasted with the quadrupole filter, both magnetic-sector and TOF analyzers provide the advantage of high mass resolution. This enables the separation of fragments having similar masses into distinct peaks. These instruments are useful when dealing with analytical situations requiring more exact mass determination. If there is a requirement to measure to high mass (thousands of amu), such as may be the case when studying polymers, TOF analyzers become the only choice.

Qualitative Analysis

One of the most common modes of characterization involves the determination of a material's surface chemistry. This is accomplished via interpretation of the fragmentation pattern in the static SIMS mass spectrum. This "fingerprint" yields a great deal of information about a sample's outer chemical nature, including the relative degree of unsaturation, the presence or absence of aromatic groups, and branching. In addition to the chemical information, the mass spectrum also provides data about any surface impurities or contaminants.

Figure 1 shows a positive static SIMS spectrum (obtained using a quadrupole) for polyethylene over the mass range 0–200 amu. The data are plotted as secondary ion intensity on a linear y-axis as a function of their charge-to-mass ratios (amu). This spectrum can be compared to a similar analysis from polystyrene seen in Figure 2. One can note easily the differences in fragmentation patterns between the
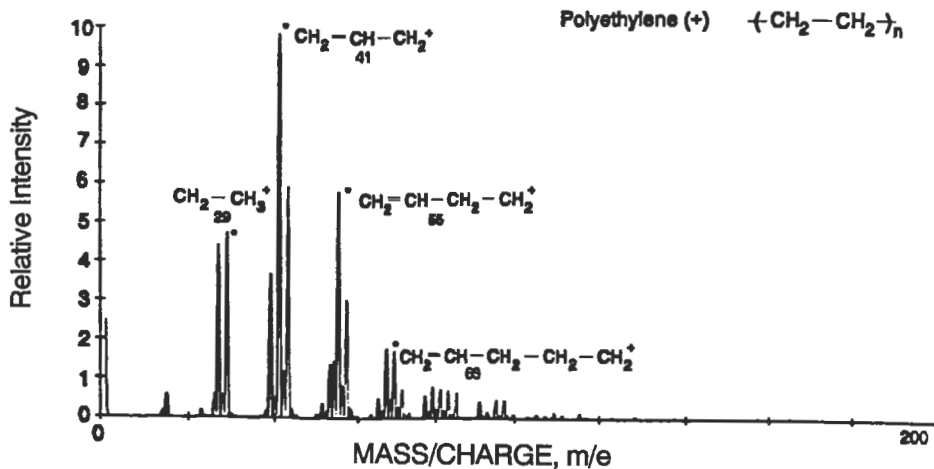
Figure 1   Positive mass spectrum from polyethylene, 0–200 amu.

two materials. Polystyrene is seen to have distinct fragment peaks characteristic of the aromatic nature of the compound. With the exception of the large peak at mass 91, most of the interesting information is found above 100 amu. Fragment peaks between 100 and 200 amu can be assigned to structures corresponding to rearrangements of the polystyrene backbone with one or more phenyl groups attached. This is seen to be dramatically different from the polyethylene spectrum, which is typical for a saturated short-chain hydrocarbon, with no significant peaks above 100 amu. This is a typical example of the current use of SIMS.
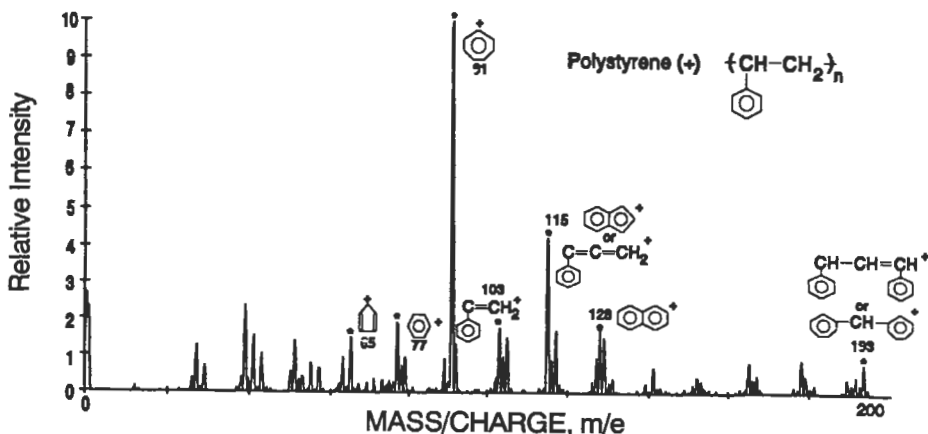
Figure 2   Positive mass spectrum from polystyrene, 0–200 amu.
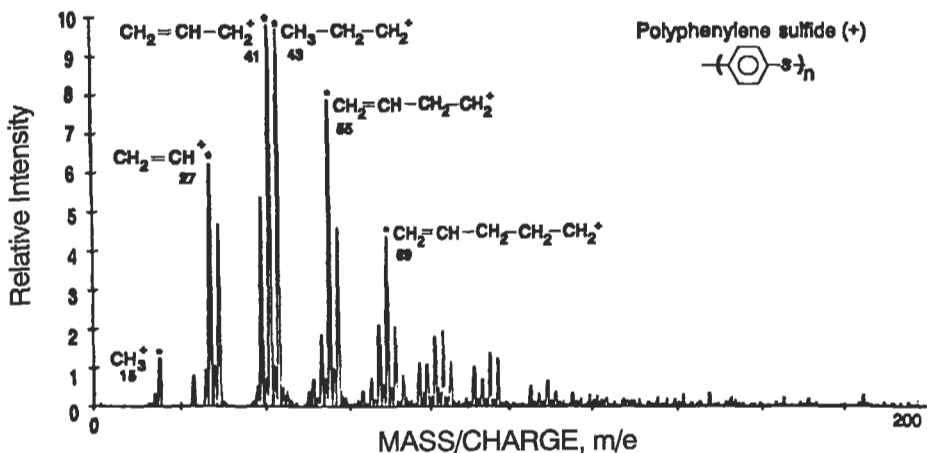
Figure 3   **Positive mass spectrum from polyphenylene sulfide, 0–200 amu.**

As mentioned earlier, the secondary ions ejected from a surface can be positively or negatively charged. Analytically, this is quite useful, as certain species are more readily ionized in one mode than another. The positive and negative mass spectra from polyphenylene sulfide shown in Figures 3 and 4, respectively, illustrate this point. The positive mass spectrum looks quite similar to that of polyethylene (Figure 1), with no indication of either the phenyl ring or the sulfur atom found in the polyphenylene sulfide. In marked contrast, the negative spectrum in Figure 4 clearly shows the presence of the phenyl group with the sulfur atom attached. This demonstrates how both positive and negative spectrometry may be needed to fully characterize a structure.
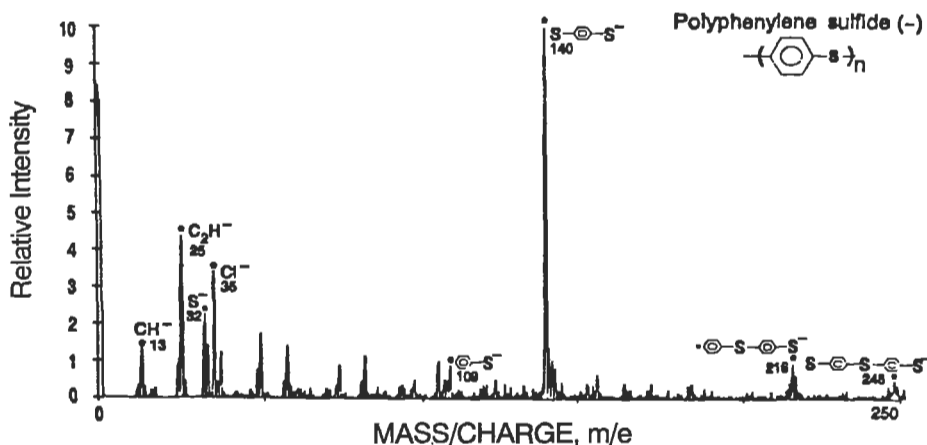
Figure 4   **Negative mass spectrum from polyphenylene sulfide, 0–250 amu.**

Figure 5 Plot of positive CF_3 secondary ion intensity versus ellipsometric thickness from a set of perfluoropolyether standards.

Quantitative Analysis

As with any analytical method, the ability to extract semiquantitative or quantitative information is the ultimate challenge. Generally, static SIMS is not used in this mode, but one application where static SIMS has been used successfully to provide quantitative data is in the accurate determination of the coverage of fluropolymer lubricants.[2] These compounds 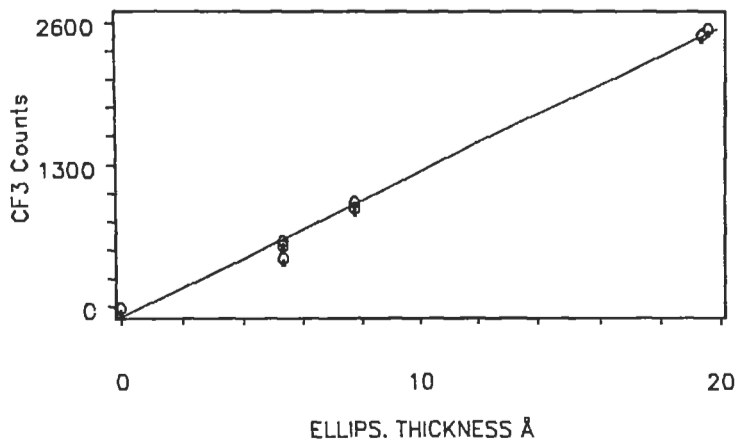provide the lubrication for Winchester-type hard disks and are directly related to ultimate performance. If the lubricant is either too thick or too thin, catastrophic head crashes can occur.

Initially, a set of lubricant film standards of various thicknesses were prepared and their thickness measured by Fourier transform infrared spectroscopy and ellipsometry. Once good correlation between these two techniques was achieved, the same samples were analyzed using static SIMS. The CF_3 peak in the positive SIMS spectrum, which is characteristic of the fluoropolymer lubricant, was measured and its intensity plotted versus the thickness determined by ellipsometry. These results are presented in Figure 5, and show excellent correlation. It must be understood that since static SIMS analyzes the outer few monolayers, this measurement actually follows the coverage of the lubricant film. As more lubricant is put down, the coverage across the sample becomes more uniform, giving a higher secondary ion yield for the CF_3 fragment. Because of the excellent correlation between SIMS and other methods, one can conclude that all these techniques are actually measuring the effect of increasing lubricant coverage. However, static SIMS has been found to be more accurate for film thicknesses below 10 Å, owing to its extreme surface sensitivity. In addition, one also obtains an analysis of any contamination from the complete SIMS spectrum.

Another example of static SIMS used in a more quantitative role is in the analysis of extruded polymer blends. The morphology of blended polymers processed by extrusion or molding can be affected by the melt temperature, and pressure, etc. The surface morphology can have an effect on the properties of the molded polymer. Adhesion, mechanical properties, and physical appearance are just a few properties affected by processing conditions.

In a molded polymer blend, the surface morphology results from variations in composition between the surface and the bulk. Static SIMS was used to semiquantitatively provide information on the surface chemistry on a polycarbonate (PC)/polybutylene terephthalate (PBT) blend.[3] Samples of pure PC, pure PBT, and PC/PBT blends of known composition were prepared and analyzed using static SIMS. Fragment peaks characteristic of the PC and PBT materials were identified. By measuring the SIMS intensities of these characteristic peaks from the PC/PBT blends, a typical working curve between secondary ion intensity and polymer blend composition was determined. A static SIMS analysis of the extruded surface of a blended polymer was performed. The peak intensities could then be compared with the known samples in the working curve to provide information about the relative amounts of PC and PBT on the actual surface.

Chemical Mapping

In addition to data obtained using the spectral mode of analysis, it is often important to know the location of a particular chemical group or compound on the sample surface. Such information is achieved by static SIMS chemical mapping—a procedure in which a specific chemical functionality on the material is imaged, providing information as to its lateral distribution on the surface.

The use of chemical mapping is demonstrated in the following example involving the delamination of a silicone primer and polytetrafluoroethylene (PTFE) material. The positive mass spectrum acquired from the delaminated interface contains peaks known to be uniquely characteristic of PTFE (CF_3 at mass 69) and the silicone primer ($Si(CH_3)_3$ at mass 73). Figures 6 and 7 are secondary ion images of the CF_3 and $(Si(CH_3)_3$ fragments taken from a 1-mm^2 area of the delaminated interface. These maps clearly indicate that the PTFE and the silicone primer exist in well-defined and complementary areas.

Conclusions

Static SIMS has been demonstrated to be a valuable tool in the chemical characterization of surfaces. It is unique in its ability to provide chemical information with high surface sensitivity. The technique is capable of providing mass spectral data (both positive and negative spectrometry), as well as chemical mapping, thereby giving a complete microchemical analysis. The type of information provided by

Figure 6 Positive ion image of CF_3 taken from a 1-mm² area.
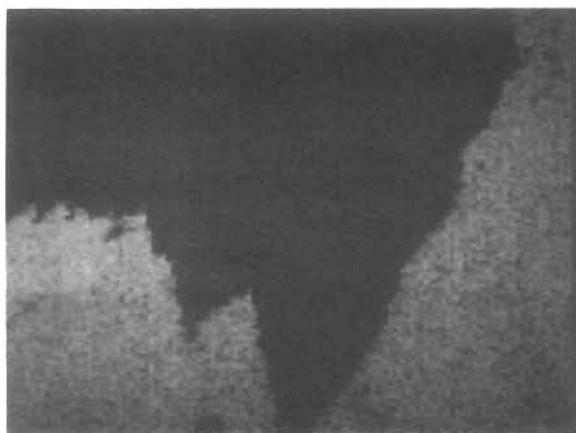
Figure 7 Positive ion image of $Si(CH_3)_3$ taken from a 1-mm² area.

static SIMS has been used to solve problems in a wide range of applications, including impurity analysis, the comparison of surface and bulk compositions, failure analysis, and the determination of adhesion or delamination mechanisms.[4–10]

With the increasing availability of TOF instruments, the field will see more applications involving the analysis of higher molecular weight fragments. This, coupled with the higher mass resolving power of TOF systems, will open up research in such fields as biomedical and pharmaceutical applications, in addition to all areas in high-technology materials where the identification of contaminants

of high amu in trace amounts at surfaces is important. Residues from previous processing steps are prime examples, both in semiconductors and other thin-film technologies.

Related Articles in the Encyclopedia

Dynamic SIMS and SALI

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10.3 SALI

Surface Analysis by Laser Ionization

SUSAN G. MACKAY AND CHRISTOPHER H. BECKER

Contents

- Introduction
- Basic Principles
- Common Modes of Analysis and Examples
- Instrumentation
- Conclusions

Introduction

In other articles in this section, a method of analysis is described called Secondary Ion Mass Spectrometry (SIMS), in which material is sputtered from a surface using an ion beam and the minor components that are ejected as positive or negative ions are analyzed by a mass spectrometer. Over the past few years, methods that *post-ion-ize* the major *neutral* components ejected from surfaces under ion-beam or laser bombardment have been introduced because of the improved quantitative aspects obtainable by analyzing the major ejected channel. These techniques include SALI, Sputter-Initiated Resonance Ionization Spectroscopy (SIRIS), and Sputtered Neu-tral Mass Spectrometry (SNMS) or electron-gas post-ionization. Post-ionization techniques for surface analysis have received widespread interest because of their increased sensitivity, compared to more traditional surface analysis techniques, such as X-Ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES), and their more reliable quantitation, compared to SIMS.

The advantages of SALI are seen most clearly when analyzing trace (ppm to ppb) amounts of material on surfaces or at interfaces. Typically, SALI analyzes the same samples as SIMS, with the added advantage of providing easily quantifiable data.

Technique	SALI	SIMS	XPS	AES	RBS
Analysis modes	Surface, depth-profiling, imaging	Surface, depth-profiling, imaging	Surface, depth-profiling, imaging	Surface, depth-profiling, imaging	Surface, depth-profiling
Common detection limit	ppm–ppb	ppm–ppb	0.05% at.	0.1% at.	2% at. –10 ppm
Probing depth	2–5 Å	2–5 Å	2–30 Å	2–30 Å	30–100 Å
Ultimate spatial resolution	60 nm	60 nm	10 μm	100 Å	1 mm
Quantitative?	Yes	Semi, with rigorous standards	Yes	Yes	Yes

Table 1   Comparison of SALI to other surface spectroscopic techniques.

Whereas SIMS provides highly matrix-dependent data, SALI can resolve problems associated with SIMS ion-yield transients. SALI has been applied to two basic groups of samples: inorganic and organic solid materials. For inorganic analysis or elemental analysis (e.g., semiconductors and metal alloys), ionization by absorption of more than one photon (multiphoton ionization) is generally used as the post-ionization source, while for organic analysis (e.g., polymers and biomaterials), a less destructive single-photon ionization probe is employed. In order to provide lateral and depth information, SALI can be operated in both mapping and depth profiling modes.

SALI compares favorably with other major surface analytical techniques in terms of sensitivity and spatial resolution. Its major advantage is the combination of analytical versatility, ease of quantification, and sensitivity. Table 1 compares the analytical characteristics of SALI to four major surface spectroscopic techniques. These techniques can also be categorized by the chemical information they provide. Both SALI and SIMS (static mode only) can provide molecular fingerprint information via mass spectra that give mass peaks corresponding to structural units of the molecule, while XPS provides only short-range chemical information. XPS and static SIMS are often used to complement each other since XPS chemical speciation information is semiquantitative; however, SALI molecular information can potentially be quantified directly without correlation with another surface spectroscopic technique. AES and Rutherford Backscattering (RBS) provide primarily elemental information, and therefore yield little structural information. The common detection limit refers to the sensitivity for nearly all elements that these techniques enjoy.

SALI, XPS, and AES have a nearly uniform sensitivity for all detectable elements with respect to the chemical composition of the sample matrix. SIMS and RBS, however, have sensitivities that vary greatly due to matrix effects. For RBS the matrix dependence is well understood, with the best sensitivities (10 ppm) found for heavy elements in light matrices while the worst sensitivities (3% at. to undetectable) are seen for light elements in heavy matrices. SIMS sensitivity varies for elements depending on both the chemical composition of the sample and the composition of the primary ion beam. Common primary ion beams are for SIMS O_2^+ and Cs^+ each of which enhances secondary ion yields. Again, an advantage of SALI is its relative insensitivity to the effects of changing matrix composition. Two drawbacks of SALI are that its maximum sensitivity is usually less than optimum case SIMS and, like all sputtering techniques, it is destructive.

A somewhat related technique is that of laser ionization mass spectrometry (LIMS), also known as LIMA and LAMMA, where a single pulsed laser beam ablates material and simultaneously causes some ionization, analogous to samples beyond the outer surface and therefore is more of a bulk analysis technique; it also has severe quantifiaction problems, often even more extreme than for SIMS.

Basic Principles

Figure 1 is a schematic of the SALI process. An energetic probe beam (ions, electrons, or light) is used to desorb material from the sample's surface. The neutral component is then intersected and ionized by a high-power, focused laser beam. The laser beam is passed parallel and close to the surface so that it intersects a large solid angle of the sputtered neutral species, thus improving the sensitivity. The positive ions created by the laser light (photoions) are then extracted by a high-voltage field (>3 kV) and pass into the mass analyzer. A time-of-flight tube is used to mass analyze the photoions created by each pulse of the laser. Lighter ions have a shorter flight time than heavier ions and therefore arrive at the ion detector (channel plate assembly) sooner. A typical SALI analysis looks at a mass range per laser pulse of approximately $m/z = 12$–300 amu (mass spectral fingerprint region) with a total acquisition time of 5 seconds (1000 pulses with a 200-Hz laser).

Analysis of Neutrals

Previous studies of the interaction of energetic particles with surfaces have made it clear that under nearly all conditions the majority of atoms or molecules removed from a surface are neutral, rather than charged. This means that the charged component can have large relative fluctuations (orders of magnitude) depending on the local chemical matrix. Calibration with standards for surfaces is difficult and for interfaces is nearly impossible. Therefore, for quantification ease, the majority neutral component of the departing flux must be sampled, and this requires some type of ionization above the sample, often referred to as post-ionization. SALI uses effi-
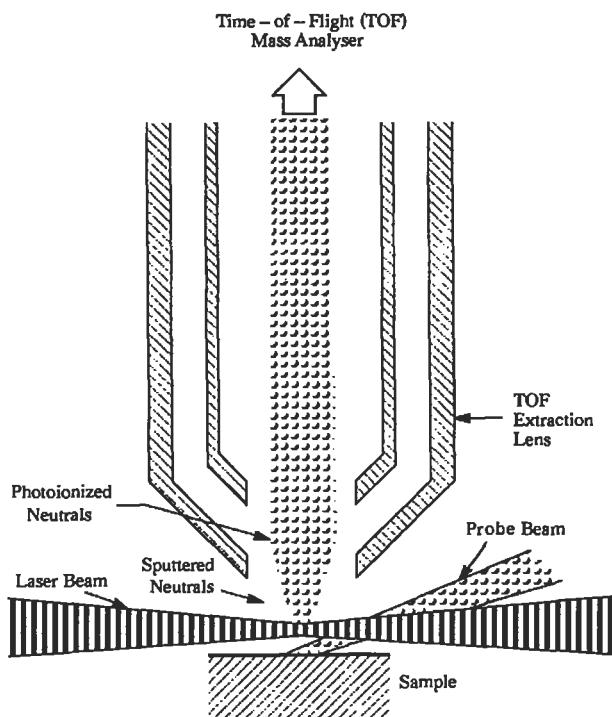
Figure 1   Schematic representation of the fundamental SALI process.

cient, nonresonant (not tuned to a specific energy level), and therefore nonselective photoionization by pulsed untuned laser radiation to accomplish this ionization and thus make this detection scheme a reality. The mass spectrometer, not the laser, performs the chemical differentiation. The commercial availability of intense laser radiation with high brightness makes this technique viable.

Photoionization

Two forms of nonselective photoionization have been used for SALI, one primarily for elemental analysis and the other primarily for molecular analysis. For elemental analysis, a powerful pulsed laser delivering focused power densities greater than 10^{10} W/cm^2 is used for multiphoton ionization (MPI). This typically ionizes all the species within the laser focus volume without the need for wavelength tuning and regardless of chemical type. This nonresonant photoionization yields the desired uniformity of detection probability essential for quantification. For molecular analysis, a soft (i.e., nonfragmenting) photoionization is needed so that the mass peaks in the mass spectrum correspond to larger chemical units. This is supplied by vacuum ultraviolet light with wavelengths in the range 115–120 nm (10–11 eV). Photoionization of this type is achieved by single-photon ionization (SPI).

Relative photoionization cross sections for molecules do not vary greatly between each other in this wavelength region, and therefore the peak intensities in the raw data approximately correspond to the relative abundances of the molecular species. Improvement in quantification for both photoionization methods is straightforward with calibration. Sampling the majority neutral channel means much less stringent requirements for calibrants than that for direct ion production from surfaces by energetic particles; this is especially important for the analysis of surfaces, interfaces, and unknown bulk materials.

Time-of-Flight Mass Spectrometry (TOFMS)

The advantage in using pulsed lasers is that they provide an excellent time marker for TOFMS. With TOFMS, a high mass resolution of several thousand can be achieved by energy focusing using a simple reflecting device, the instrument transmission is exceptional; and there is a multiplex advantage in mass. With the multiplex advantage, all masses are detected (parallel detection) within an extremely high mass range (up to 10,000 atomic mass units or more). The mass multiplex advantage has a dramatic impact on the instrument's sensitivity when numerous elemental or molecular species are present—a very common occurrence.

Surface Removal for Sampling

Surface removal for sampling involves removing atoms and molecules from the top surface layer into the vapor phase. The fact that the ionization step is decoupled from the surface removal step implies a great deal of flexibility and control in the types and conditions of the energetic beam of particles chosen to stimulate desorption. For elemental analysis of inorganic materials, typically a 50-μm Ar^+, or sub-μm diameter Ga^+ beam at several keV is used. Argon is used as an intense, high fluence ion beam that provides minimal chemical modification to the sample. Gallium is used as a liquid metal ion source that provides a highly focused, bright source for small area analysis (60–200 nm). Submonolayer or static analysis can be obtained by pulsing the beam and keeping the total dose extremely low ($< 10^{13}$ ions/cm^2). Depth profiling is accomplished by dc ion-beam milling and gating the pulsed photoionization to sample from the center of the sputter crater, which maintains state-of-the-art depth resolution. Ion-beam erosion is used to reveal buried interfaces during depth profiling, achieving a depth resolution often on the order of 20 Å after sputtering 1 μm in depth. The small-spot Ga^+ beam is well suited for quantitative chemical mapping with sub-μm spatial resolution. For other material types, such as bulk polymers, using energetic electrons, or another laser beam sometimes results in superior mass spectra; these sources often can remove clusters with less fragmentation, than pulsed ion beam sputtering and thus yield more characteristic mass peaks. For thermally sensitive samples, even thermal desorption can be used to investigate their temperature dependence.

Common Modes of Analysis and Examples

SALI applies two methods of post-ionization, MPI and SPI, each of which can be used in one of the three modes of analysis: survey analysis, depth profiling, and mapping:

1 Survey spectra using the MPI method are used primarily for quantification of surface components in inorganic materials, with a detection limit of ppm to ppb. The same mode coupled with SPI can be used for molecular characterization of polymer films.

2 Depth profiling by SALI provides quantitative information through interfaces and for extremely thin films, in the form of reliable chemical concentrations.

3 SALI mapping is a sensitive and quantitative method to characterize the spatial distribution of elements in both insulating and conductive materials.

Survey Mode

Surveys using MPI reveal the elemental composition of solid materials. Therefore this mode is employed most often in the analysis of inorganic materials like semiconductor devices and catalysts. Quantification can be achieved by using loosely matched standards and is accurate to within 10–20%. SPI has two advantages over MPI for the analysis of organic materials. First, it is a soft ionization method, so there is less fragmentation in addition to that of the primary beam, and second, the photoionization cross sections are nearly identical for molecules of similar size but different chemical type. This second characteristic enables SPI to provide semiquantitative raw data for all classes of organic materials without rigorous standards. Figure 2 is an example of a SALI mass spectrum of polyethylene glycol using SPI. The dominance of the monomer peak is an example of the simple molecular identification using this technique.

Depth Profiling Mode

As stated above, SALI depth profiling is performed by gating the post-ionization beam by firing the laser only when the center of the crater is being sampled. This minimizes the contribution from the crater edge to the total signal at a specific depth, which increases the achievable depth resolution. Therefore, the depth resolution achieved by SALI easily equals that of SIMS which also employs gating. The major difference between these two depth profile techniques is that for SALI the sensitivity is nearly uniform for all elements, while for SIMS the sensitivity varies greatly. In selected cases this is an advantage for SIMS because the secondary ion yield for certain elements can be chemically enhanced, for example, by using a primary ion-beam composed of O_2^+ or Cs^+. However, it also severely limits the ability to quantify SIMS data because secondary ion yields can vary by orders of magnitude depending on the chemical composition of the matrix or probe beam. This is
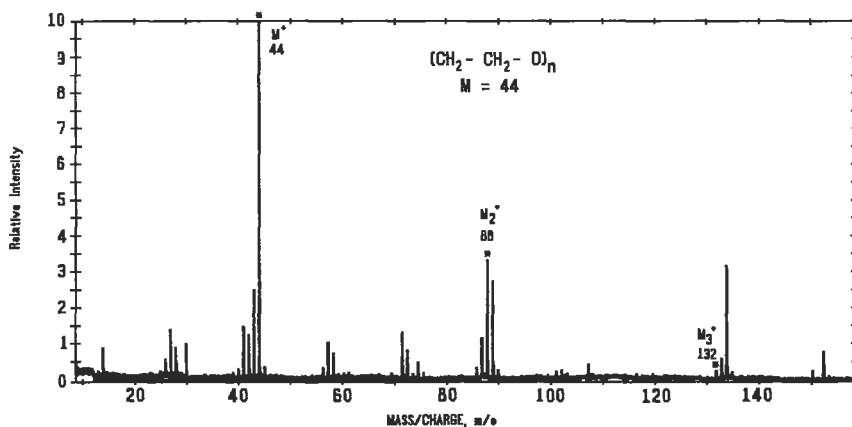
Figure 2 SPI-SALI mass spectrum of a thin film of polyethylene glycol. The major peaks are identified on the spectrum. Analytical conditions: 7-keV Ar⁺, 5-μs pulse length; 118-nm radiation.

a problem when analyzing thin films and elemental distributions across chemically dissimilar interfaces because the changing ion yield causes changes in the ion signal intensity. In these cases SIMS ion yield transients can severely distort a depth profile and can be resolved only by using rigorous standards. An example[1] is a depth profile of a F implant (10^{15} F atoms/cm² at 93 keV) in a 2000 Å-thick polycrystalline Si sample on a thin SiO_2 layer on crystalline Si. Figure 3 is of an unannealed sample, where a smooth F distribution is expected. The SALI depth profile in Figure 3a shows the expected smooth distribution of the F implant. The SIMS data shown in Figure 3b, however, shows the common influence of matrix effects at an interface where the F positive ion yield is enhanced by the oxygen in the SiO_2 layer. The relative insensitivity of SALI to matrix effects is a tremendous advantage over SIMS in terms of quantitative depth profiling. Also, the useful yield (a measure of sensitivity) for the majority of elements falls into the 10^{-3} range when using SALI compared to the 10^{-2} to $< 10^{-7}$ range when using SIMS. Useful yield is defined as the number of ions detected versus the total material removed during analysis, and the efficiency of SALI can be equal to SIMS and orders of magnitude better than other nonselective post-ionization techniques (electron impact and radiofrequency low-pressure plasma).

Mapping Mode

The determination of the lateral distributions of chemical species on surfaces is of constantly increasing technological importance in many applications, such as integrated circuit manufacturing. The two major tools that have been available are
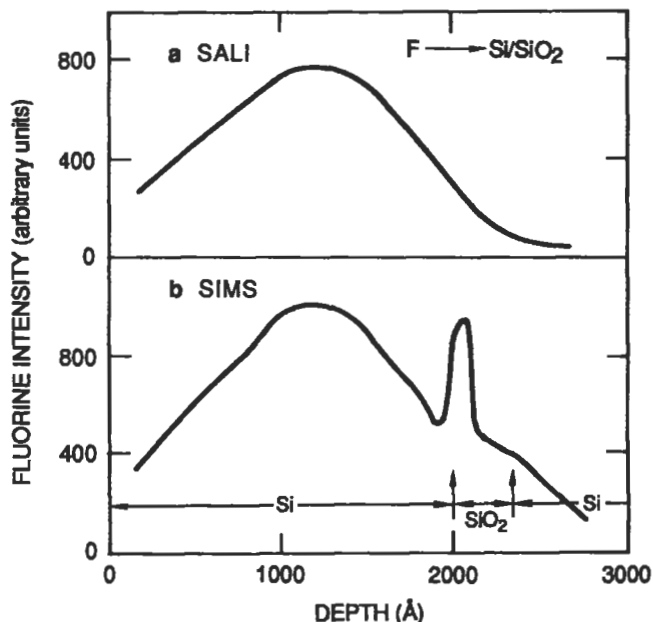
Figure 3   Depth profiles of F implanted into 2000 Å Si on SiO$_2$: (a) SALI profile with Ar$^+$ sputtering and 248-nm photoionization; and (b) positive SIMS profile with O$_2^+$ sputtering. Analytical conditions: (SALI, SiF profile) 7-keV Ar$^+$, 248 nm; (SIMS, F profile) 7-keV O$_2^+$.

Scanning Auger Electron Spectroscopy (SAM) and SIMS (in microprobe or microscope modes). SAM is the most widespread technique, but generally is considered to be of lesser sensitivity than SIMS, at least for spatial resolutions (defined by primary beam diameter d) of approximately ≥ 0.1 μm. However, with a field emission electron source, SAM can achieve sensitivities ranging from 0.3% at. to 3% at. for d ranging from 1000 Å to 300 Å, respectively, which is competitive with the best ion microprobes. Even with competitive sensitivity, though, SAM can be very problematic for insulators and electron-sensitive materials.

The sensitivities for SIMS are extremely variable, depending both on the species of interest and the local chemical matrix (so-called matrix effects). Quantification is very problematic for SIMS imaging because of matrix effects; on the very small scale associated with chemical imaging (sub-μm), it is not possible to generate closely matched reference materials because compositions change quickly and in an uncontrollable way. In the microscope mode, SIMS spatial resolutions are generally limited to about 1 μm. In the scanning mode, liquid-metal ion guns (notably Ga$^+$) have been used with better spatial resolution (sub-μm) but are somewhat unsatisfactory because Ga$^+$ is not effective for increasing secondary ion yields, unlike O$_2^+$

58Ni 68% Isotope   60Ni 26% Isotope

61Ni 1.2% Isotope   62Ni 3.7% Isotope
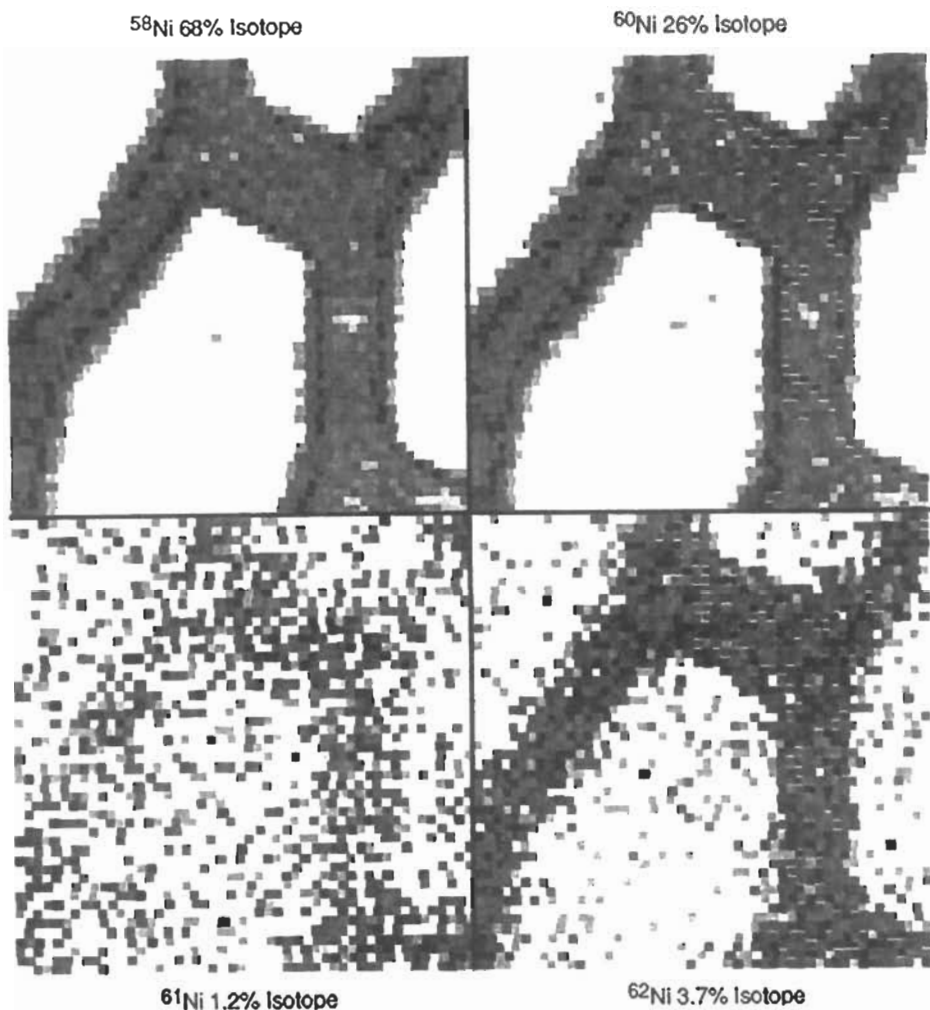
Figure 4   **Chemical images of a nickel TEM grid. Field of view is approximately 25 × 15 μm, 50 × 50 pixels. Analytical conditions: Ga⁺ sputtering, spot size about 0.2 μm, 248-nm radiation, acquisition time 33 minutes.**

or Cs⁺. The sensitivity for scanning SIMS can range, for example, from 0.01–10% at $d = 1$ μm (using O_2^+ or Cs⁺ for ionization enhancement), to 1% to undetectable at $d = 0.1$ μm (using Ga⁺).

By examining the sputtered neutral particles (the majority channel) using nonselective photoionization and TOFMS, SALI generates a relatively uniform sensitivity with semiquantitative raw data and overcomes many of the problems associated with SIMS. Estimates for sensitivities vary depending on the lateral spatial resolution for a commercial liquid-metal (Ga⁺) ion gun. Calculated values[2] for SALI

mapping show the sensitivity ranging from 0.2% to 3% at d = 1 to 0.1 μm. These sensitivities range as shown in Figure 4, which is a SALI image of a nickel TEM grid using Ga^+ sputtering and photoionization of the emitted neutrals at 248 nm (MPI, using KrF radiation). The pixel resolution achieved is < 0.5 μm, while the spot size d of the Ga^+ beam was 0.2 μm. As work in this area progresses and state-of-the-art liquid metal ion guns are used, the lateral resolutions achieved should approach the expected values. While the acquisition time for the sample image was somewhat long (33 minutes) this represents initial work. The acquisition time can be decreased readily by a factor of 10 with improvements in the computer system (factor of 2), and in off-the-shelf laser repetition rates (factor of 5). Since there exists a trade-off between analysis time an sensitivity, any decrease in acquisition time will make the application of SALI mapping more practical.

Instrumentation

A state-of-the-art SALI system combines both MPI and SPI capabilities. One commercial system[3] includes two laser sources: a Nd–YAG laser with a gas tube assembly used for frequency tripling to produce the coherent 118-nm light for SPI; and an excimer laser that produces both 248-nm (KrF) and 193-nm (ArF) wavelengths used for MPI. The system also includes two ion-beam sources: a duoplasmatron (Ar^+) or Cs^+ ion source, and a single or double lens liquid metal ion (Ga^+) source for SALI or TOF-SIMS mapping applications. Secondary Electron Detection (SED) images also can be obtained on this system, since it is equipped with an electron gun and the two ion guns. Each of these sources is compatible with the SED imaging system on the SALI instrument. The electron gun can also be used as an electron-stimulated desorption source. The instrument includes a TOF reflecting mass analyzer, a low-energy electron flood source for charge neutralization, a sample introduction system, a sample manipulator and a UHV chamber.

Conclusions

SALI is a relatively new surface technique that delivers a quantitative and sensitive measure of the chemical composition of solid surfaces. Its major advantage, compared to its "parent" technique SIMS, is that quantitative elemental and molecular information can be obtained. SPI offers exciting possibilities for the analytical characterization of the surfaces of polymers and biomaterials in which chemical differentiation could be based solely on the characteristic SALI spectra.

MPI is especially valuable for elemental analyses with typical useful yield of 10^{-3}. Because SALI is laser-based, expected improvements over the next few years, in particular for vacuum-ultraviolet laser technology, should have a significant impact. High repetition rate Nd–YAG systems with sufficient pulse energy are already available to 50 Hz, and probably can be extended to a few hundred Hz.

Ever brighter vacuum-ultraviolet sources are being developed that would further boost SPI sensitivity, which already is typically 10^{-5} useful yield; general, sensitive elemental analysis would then also be available using SPI, making possible a single laser arrangement for both elemental and molecular SALI.

Related Articles in the Encyclopedia

Static SIMS and SNMS

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   A comparison of the various post-ionization techniques: electron-gas bombardment, resonant and nonresonant laser ionization, etc. While some of the numbers are outdated, the relative capabilities of these methods have remained the same. This is a well-written review article that reiterates the specific areas where post-ionization has advantages over SIMS.

2 J. B. Pallix, C. H. Becker, and N. Newman, *MRS Bulletin*, **12**, no. 6, 52 (1987).

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   This article discusses why one would choose nonresonant multiphoton ionization for mass spectrometry of solid surfaces. Examples are given for depth profiling by this method along with thermal desorption studies.

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An applications oriented discussion of using MPI-SALI for depth profiling, interface analysis in inorganic material systems. Examples of SALI depth profiles are given of a B implant in Si and the fluorine implanted electronic test device which was referenced in this encyclopedia article.

5 J. B. Pallix, U. Schühle, C. H. Becker, and D. L. Huestis, *Anal. Chem.*, **61**, 805 (1989).

An introduction to the principles behind SPI-SALI, this article presents a theoretical discussion of why SPI-SALI is much less fragmenting than MPI-SALI. Examples are shown which describe the additional fragmentation induced by the desorption beam—in this case ESD is compared to ion sputtering. The main focus of the article is the advantages of SPI-SALI for surface analysis of bulk organic polymers.

10.4   SNMS

Sputtered Neutral Mass Spectrometry

JOHN C. HUNEKE

Contents

- Introduction
- Basic Principles
- SNMS Modes and Instrumentation
- Analysis and Quantitation
- Relative Sensitivity Factors
- Applications
- Conclusions

Introduction

The atom flux sputtered from a solid surface under energetic ion bombardment provides a representative sampling of the solid. Sputtered neutral mass spectrometry has been developed as method to quantitatively measure the composition of this atom flux and thus the composition of the sputtered material. The measurement of ionized sputtered neutrals has been a significant improvement over the use of sputtered ions as a measure of flux composition (the process called SIMS), since sputtered ion yields are seriously affected by matrix composition. Neutral particles are ionized by a separate process after sputter atomization, and SNMS quantitation is thus independent of the matrix. Also, since the sputtering and ionization processes are separate, an ionization process can be selected that provides relatively uniform yields for essentially all elements.

SNMS ANALYSIS

$(S^0)^+$

POST SPUTTER IONIZING

M^*
$h\nu$
e

S^0 (NEUTRAL PARTICLES) $\gg S^\pm$

PRIMARY (SPUTTERING) PARTICLES
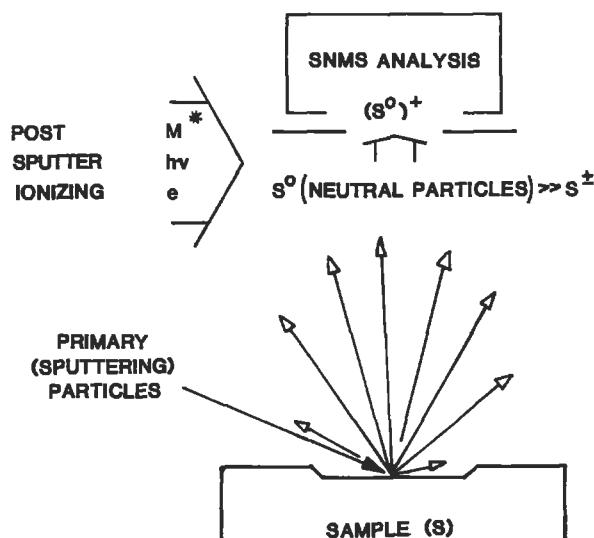
SAMPLE (S)

Figure 1   Schematic of SNMS analysis. Neutral atoms and molecules sputtered from the sample surface by energetic ion bombardment are subsequently ionized for mass spectrometric analysis.

The erosion of the surface by sputtering also provides a means to sample progressively deeper layers to determine concentration depth profiles. SNMS combines the features of sputter erosion, representative sampling, uniform ionization and matrix independence to provide a quantitative sputtering depth profile measurement with comparable sensitivity for all elements in complex thin-film structures comprising a variety of matrix compositions. This capability is used to good advantage, for example, in the compositional analysis of thin-film structures used for magnetic recording heads, optoelectronics, and semiconductor metallizations. The detection limits obtained in depth profiling by SNMS range from 100 to 1000 ppm, which are not as low as can be generally obtained using SIMS, but which are a significant improvement over the detection limits obtained using AES and ESCA.

Useful overviews of all SNMS modes have been provided by Oeschner[1] and Pallix and Becker,[2] and thorough reviews of electron impact SNMS in particular have been provided recently both by Ganschow[3] and by Jede.[4]

Basic Principles

The essentials of SNMS are illustrated in Figure 1. The surface of the solid sample is sputtered by energetic ion bombardment. Generally, at energies above a few hundred eV, several particles are ejected from the surface for each incident particle. A very small fraction of the particles are sputtered as ions, the so-called secondary ions

measured by SIMS. By far the larger number of sputtered particles are neutral atoms and molecules, with atoms dominating. Coupling the nonselective sputter atomization with some method for nonselective ionization for mass spectrometric analysis, as illustrated in Figure 1, SNMS provides a technique in which the analytical signals directly reflect the sample's composition, unlike SIMS where the ionization can be very selective.

If the secondary ion component is indeed negligible, the measured SNMS ion currents will depend only on the ionizing mode, on the atomic properties of the sputtered atoms, and on the composition of the sputtered sample. Matrix characteristics will have no effect on the relative ion currents. SNMS analysis also provides essentially complete coverage, with almost all elements measured with equal facility. All elements in a chemically complex sample or thin-film structure will be measured, with no incompleteness due to insensitivity to an important constituent element. Properly implemented SNMS promises to be a near-universal analytical method for solids analysis.

The SIMS analytical ion signal of a specific element or isotope also can be enhanced by selective ionization of particular atoms, and the detection limit for that element thereby improved. This mode of SNMS is important to specific applications, but it lacks the generality inherent in nonselective SNMS methods. The focus of this article will be on the methods for obtaining complete, accurate, and matrix-independent compositions of chemically complex thin-film structures and materials.

SNMS Modes and Instrumentation

Three post-ionization (i.e., post-sputtering) mechanisms having relatively uniform ion yields appropriate for SNMS have been used to date (cf. Figure 1), and the combination of each of these with an appropriate mass spectrometer provides the basis for all present SNMS instruments. The postionization methods are: electron impact ionization, ionization by multiple photon interactions, and ionization by collision with metastable atoms in a plasma. The SNMS methods incorporating the latter two modes are nonresonant multiphoton ionization mass spectrometry, which is also referred to as Surface Analysis by Laser Ionization (SALI), and Glow-Discharge Mass Spectrometry (GDMS). Both are the subject of other articles in this encyclopedia but are mentioned here because of analytical affinities. This article will concentrate on the first mode, SNMS by electron impact ionization.

The various SNMS instruments using electron impact postionization differ both in the way that the sample surface is sputtered for analysis and in the way the ionizing electrons are generated (Figure 2). In all instruments, an ionizer of the electron-gun or electron-gas types is inserted between the sample surface and the mass spectrometer. In the case of an electron-gun ionizer, the sputtered neutrals are bombarded by electrons from a heated filament that have been accelerated to 80–
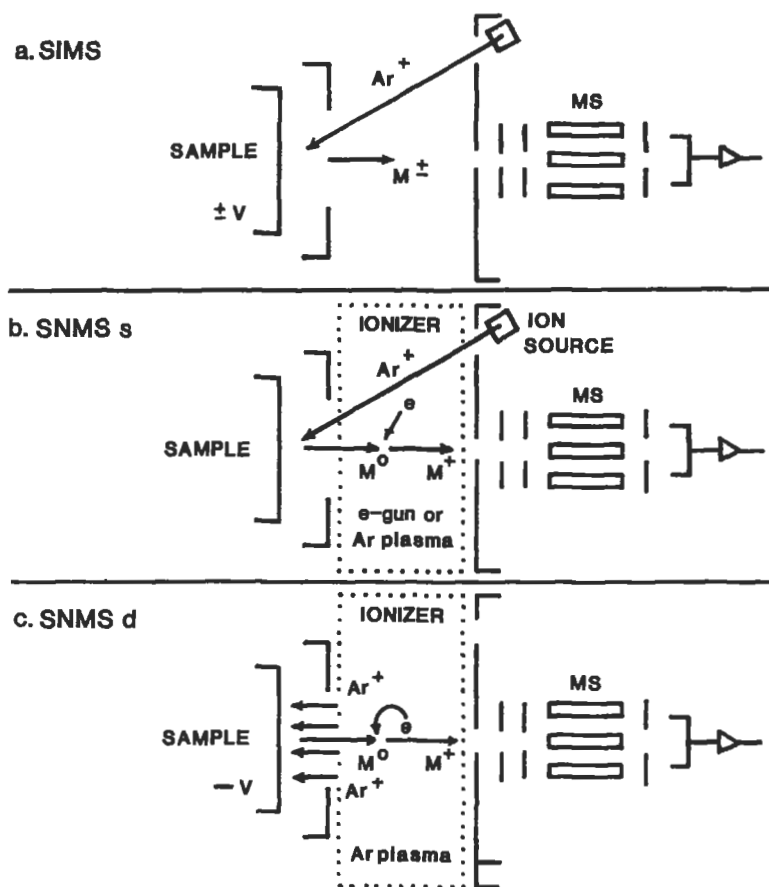
Figure 2 Relationship of SIMS, separate bombardment SNMSs and direct bombardment SNMSd. (a) Materials for SIMS analysis are those ions formed in the sputtering with a focused primary ion beam. The largest fraction of the particles sputtered from the surface are neutral atoms. (b) Ions for SNMS analysis are formed by ionization of the sputtered neutrals. (c) When the plasma is used as an ionizer, plasma ions can also be used to sputter the sample surface at low energies.

100 eV energy in the ionizer volume. Sputtering of the sample surface in electron-gun SNMS is accomplished by a focused ion beam, as provided for the SIMS instrumentation (Figures 2a and 2b). An electron-gun ionizer is commonly used to modify existing SIMS instrumentation to provide supplementary SNMS capability, and SNMS measurements using the separate ion-gun sputtering provided for SIMS will have the same imaging and thin-film depth resolution capabilities as for SIMS. In contrast to SIMS, a noble gas (e.g., Ar) or less reactive element (such as Ga) is most commonly used for ion-beam sputtering in SNMS to minimize

enhancement of secondary ion yields and thus improve quantitative accuracy. Following the initial development and use of electron-gun SNMS in the academic research environment, two such SNMS modules have been made commercially available.

In two other implementations of electron impact SNMS, a plasma is generated in the ionizer volume to provide an electron gas sufficiently dense and energetic for efficient postionization (Figure 2c). In one instrument, the electrons are a component of a low-pressure radiofrequency (RF) plasma in Ar, and in the second, the plasma is an electron beam excited plasma, also in Ar. The latter type of electron-gas SNMS is still in the developmental stages, while the former has been incorporated into commercial instrumentation.

The plasma electron-gas ionizer offers a distinct advantage for low-energy sputtering of the sample surface, since Ar ions are available in the overlying plasma and can be accelerated onto the surface by application of a sample bias voltage (Figure 2c). In neither of the electron-gas SNMS modes does the sample play an integral part in maintaining the plasma. Thus the bias voltage can be made arbitrarily small, enabling plasma-ion sputtering with minimal energy, ion-beam mixing, and thus optimal depth resolution (see below). The surface areas analyzed in the plasma mode of surface sputtering are large compared to SIMS or SNMS profiling by separate focused ion-beam bombardment, and lateral resolution is sacrificed.

The SNMS instrumentation that has been most extensively applied and evaluated has been of the electron-gas type, combining ion bombardment by a separate ion beam and by direct plasma-ion bombardment, coupled with postionization by a low-pressure RF plasma. The direct bombardment electron-gas SNMS (or SNMSd) adds a distinctly different capability to the arsenal of thin-film analytical techniques, providing not only matrix-independent quantitation, but also the excellent depth resolution available from low-energy sputtering. It is from the application of SNMSd that most of the illustrations below are selected. Little is lost in this restriction, since applications of SNMS using the separate bombardment option have been very limited to date.

Analysis and Quantitation

In the process of SNMS analysis, sputtered atoms are ionized while passing through the ionizer and are accelerated into the mass spectrometer for mass analysis. The ion currents of the analyzed ions are measured and recorded as a function of mass while stepping the mass spectrometer through the desired mass or element sequence. If the purpose of the analysis is to develop a depth profile to characterize the surface and subsurface regions of the sample, the selected sequence is repeated a number of times to record the variation in ion current of a selected elemental isotope as the sample surface is sputtered away.

Only the knowledge of relative useful ion yields and isotopic abundances is required to calculate elemental composition from the relative ion current measurements. The useful ion yield D_x is the number of ions x^+ detected relative to the number of atoms of element x sputtered. The measured relative ion current of two isotopes is

$$\frac{I_x}{I_s} = \left(\frac{i_x}{i_s}\right)\left(\frac{c_x}{c_s}\right)\left(\frac{D_x}{D_s}\right) \tag{1}$$

where c_x is the concentration and i_x is the isotopic fraction of the measured isotope of element x. Pragmatically, quantitation is accomplished by multiplying the ratios of the total ion currents for each element (summing over all isotopes of the element) by a multiplicative factor defined as the relative sensitivity factor or RSF.

$$\frac{c_x}{c_s} = \left(\frac{I_x}{I_s}\right)\mathrm{RSF}\left(\frac{x}{s}\right) \tag{2}$$

The fraction of each element present in the material is then equal to the ratio of the RSF-corrected ion current for that element to the sum of the RSF-corrected ion currents for all elements.

It is important for quantitative SNMS that the fractions of element x forming molecules and sputtered ions be negligible, but such is not always the case.

Relative Sensitivity Factors

The relative sensitivity factors for most elements are comparable to within a factor of 25 for ionization with an energetic electron gas.[5] The RSFs for a number of elements determined from the analysis of NIST alloy samples vary by less than an order of magnitude for sputtering energies of 1250 V and more. The RSFs determined are reasonably independent of matrix. Nevertheless, there are differences of up to factors of 1.5 in RSFs of the same element determined from the analysis of several standards. Also, RSFs do change significantly with sputtering voltage. As a consequence, separate calibration is required when sputtering at the lower energies typical of depth profiling.

Similar detailed studies of RSFs have been carried out for GDMS, but not for electron-gun electron impact ionization or for SALI. The spread in elemental RSFs for electron-gas SNMS is comparable to that observed for Ar glow-discharge ionization of sputtered neutrals.[6]

Since elemental RSFs are reasonably similar for electron-gas SNMSd, a standardless analysis will result in compositions accurate to within a factor of 5 for matrices with major element RSFs close to the average, and to within a factor of 25 for matrices with major element RSFs at the extreme values. More importantly,
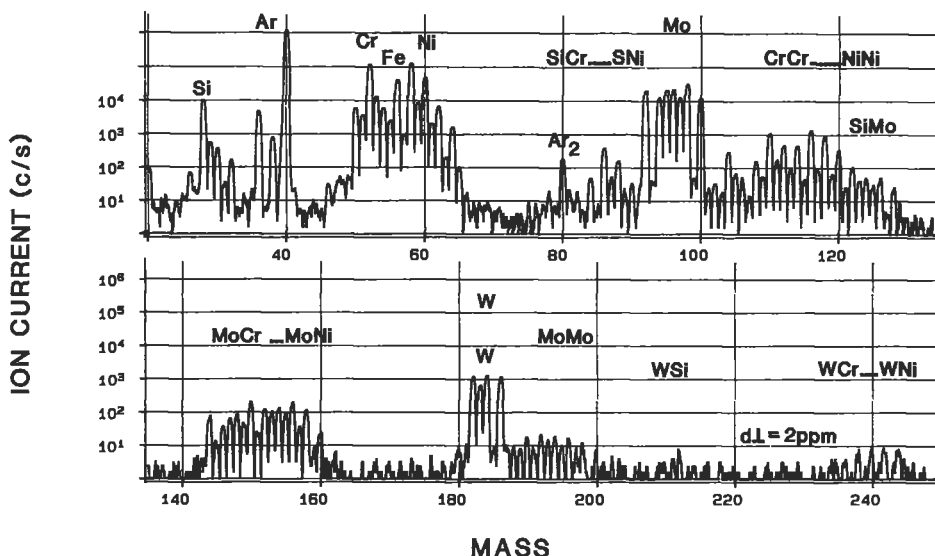
Figure 3   Mass spectrum obtained from the NIST Hasteloy Ni-based standard alloy, using electron-gas SNMSd (Leybold INA-3). The sputtering energy was 1250 V, increasing the sputtered atom flux at the expense of depth resolution. Matrix ion currents were about 10^5 cps, yielding background limited detection at about 2 ppm.

however, there will be no glaring gaps in the analytical results due to extreme insensitivity for a particular element. Every element present will be detected at roughly the same sensitivity. This characteristic of SNMS enables thorough materials characterization of complex samples in a single analysis and by one instrument.

Applications

Bulk Analysis

Independent of depth profiling considerations, SNMS provides a powerful bulk analysis method that is sensitive and accurate for all elements, from major to trace element levels. Since SNMS is universally sensitive, it offers obvious advantages over elementally selective optical methods.

As an example of a standardless bulk analysis by SNMS, a measurement of the complex Ni-based Hasteloy metal (NIST SRM 2402) is presented in Figure 3 and Table 1, in which the "composition" determined from ion-current ratios (not RSF corrected) is compared to the certified chemical composition.

It is very evident in Figure 3 that the chemical complexity of Hasteloy presents special problems for mass spectrometric analysis using a quadrupole mass spectrometer with low mass resolution. Molecular ions comprised of combinations of matrix and plasma atoms are formed in abundance and will obscure many elements

Element	Ion current ratio (%)	Certified content (% at.)
C		0.05
Si		1.90
P	0.005	0.014
S	0.02	0.035
V	0.6	0.27
Cr	26	19.5
Mn	0.6	0.73
Fe	9	8.2
Co	2	1.6
Ni	37	55
Cu	0.07	0.19
Mo	25	11.2
W	0.9	1.46

Table 1 **Semiquantitative bulk analysis by SNMSd of the NIST SRM 2402 Hasteloy metal standard.**

present at low concentrations. This is obviously a clear limitation to many applications, and the use of a high resolving power mass spectrometer is to be preferred in these instances.

Molecular ion mass interferences are not as prevalent for the simpler matrices, as is clear from the mass spectrum obtained for the Pechiney 11630 Al standard sample by electron-gas SNMSd (Figure 4). For metals like high-purity Al, the use of the quadrupole mass spectrometer can be quite satisfactory. The dopant elements are present in this standard at the level of several tens of ppm and are quite evident in the mass spectrum. While the detection limit on the order of one ppm is comparable to that obtained from optical techniques, the elemental coverage by SNMS is much more comprehensive.

Quantitative Depth Profiling

In addition to comprehensive elemental coverage, SNMS also provides for high-resolution depth profile measurements with the same quantitation capability
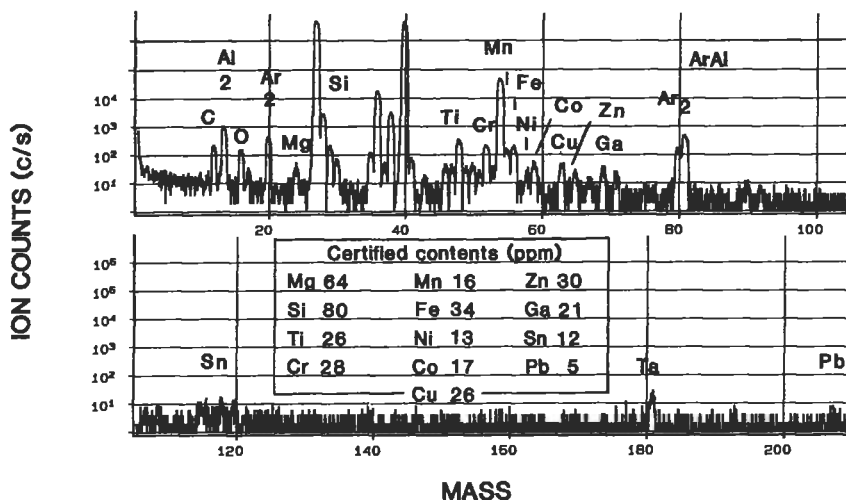
Figure 4 Mass spectrum obtained from the Aluminium Pechiney standard Al 11630, using electron-gas SNMSd with a sputtering energy of 1250 V. The ^{27}Al matrix ion current was significantly greater than 10^6 cps, yielding a background count rate limit less than 1 ppm.

throughout the depth profile regardless of film composition. This feature of SNMS is particularly useful for the measurement of elements located in and near interfaces, which are difficult regions for measurement by other thin-film analytical methods.

The advantage of SNMSd for high-resolution profiling derives from the sputtering of the sample surface at arbitrarily low energies, so that ion-beam mixing can be reduced and depth resolution enhanced. Excellent depth resolution by SNMSd depth profiling is well illustrated by the SNMSd depth profile of a laser diode test structure shown in Figure 5. Structures of this type are important in the manufacture of optoelectronics devices. The test structure is comprised of a GaAs cap overlying a sandwiched sequence of $Al_xGa_{1-x}As$ layers, where the intermediate Al-poor layer is on the order of 100 Å thick. The nominal compositions from growth parameters are noted in Figure 5. The layers are very well resolved to about a 30-Å depth resolution, with accurate composition measurement of each individual layer.

Every material sputters at a characteristic rate, which can lead to significant ambiguity in the presentation of depth profile measurements by sputtering. Before an accurate profile can be provided, the relative sputtering rates of the components of a material must be independently known and included, even though the total depth of the profile is normally determined (e.g., by stylus profilometer). To first order, SNMS offers a solution to this ambiguity, since a measure of the total number of atoms being sputtered from the surface is provided by summing all RSF- and

X ⟦0⟧ 0.8 ⟦0.4⟧ 0 ⟦0.4⟧ 0.8

CONCENTRATION (%)

Al

Ga

40

35

30

Al

25

20 ⊣ ⊢ 100 Å

15

Ga

10

Ga

5

Al

50   100   150   200   250

TIME (s)
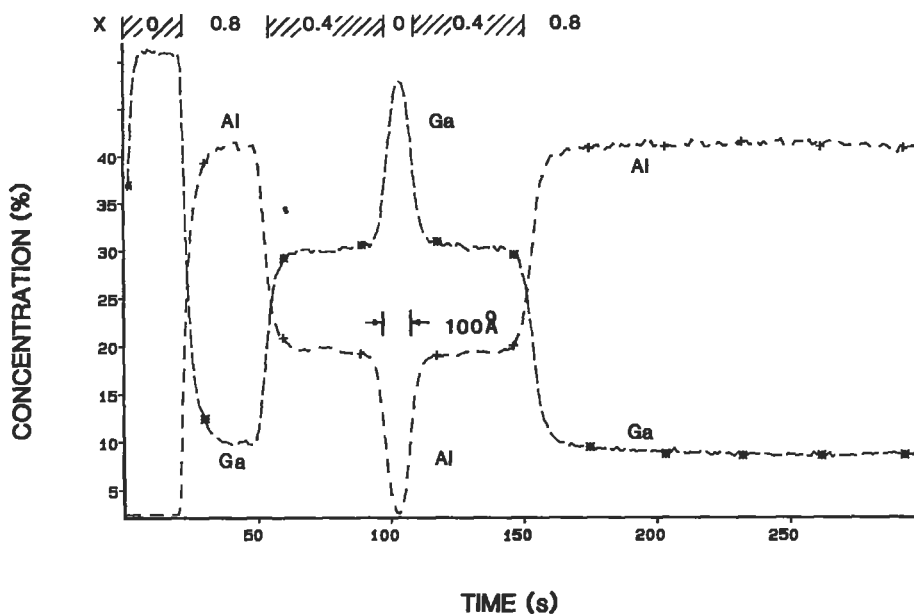
Figure 5   Quantitative high depth resolution profile of a complex $Al_xGa_{1-x}As$ laser diode test structure obtained using electron-gas SNMS in the direct bombardment mode, with 600-V sputtering energy. The data have been corrected for relative ion yield variations and summed to Al + Ga = 50%. The 100-Å thick GaAs layer is very well resolved.

isotope-corrected ion currents (assuming all major species have been identified and included in the measurements.) It is necessary only to scale the time required to profile through a layer by the total sputtered neutral current (allowing for atomic density variations) to have a measure of the relative layer thickness. The profiles illustrated in Figure 5 have not been corrected for this effect.

Al Metallization

The measurement of the concentration depth profiles of the minor alloying elements Si and Al in Al metallizations is also very important to semiconductor device manufacturing. The inclusion of Si prevents unwanted alloying of underlying Si into the Al. The Cu is included to prevent electromigration. These alloying elements are typically present at levels of 1% or less in the film, and the required accuracy of the measurement is several percent. Of the techniques that can be applied to this analysis, SNMS offers the combined advantages of sensitivity to both Si and Cu, good detection limits in the depth profiling (0.01–0.1%), and accuracy of analysis, as well as requiring measuring times on the order of only one-half hour.
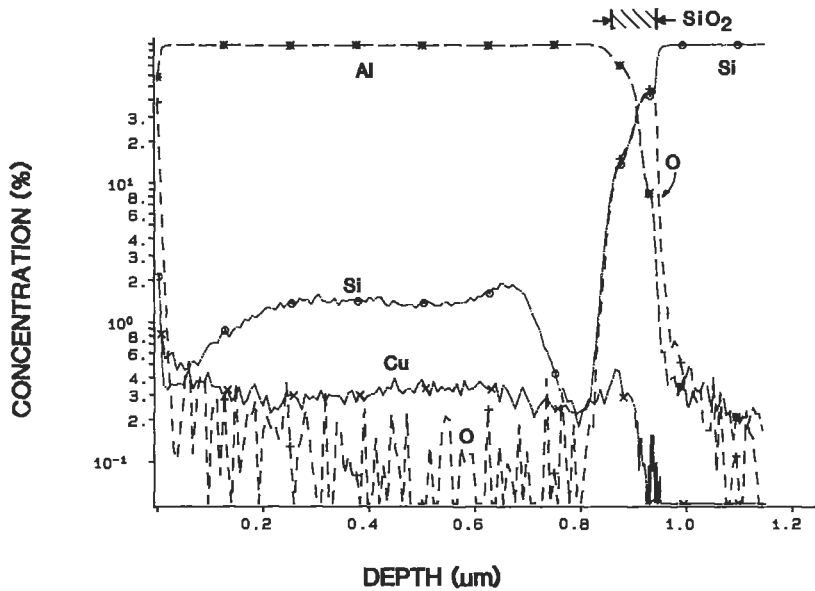
Figure 6   Quantitative depth profile of the minor alloying elements Cu and Si in Al metallization on SiO_2/Si, using electron-gas SNMSd.

A typical SNMSd profile of Al (1% Si, 0.5% Cu) metallization on SiO_2 is shown in Figure 6. The O signal is included as a marker for the Al/SiO_2 interface. The Al matrix signal is some 10^5 cps, yielding an ion count rate detection limit of 10 ppm for elements with similar RSF. The detection limit is degraded from this value by a general mass-independent background of 5 cps and by contamination by O and Si in the plasma. It does not help that in this instance the product (ion yield) × (isotopic abundance) for Cu is an order of magnitude lower than for Al. Nonetheless, the signals of both Si and Cu are quite adequate to the measurement. The Si exhibits a strongly varying composition with depth into the film, in contrast to the Cu distribution.

Diffusion Barriers

An important component of the complex metallizations for both semiconductor devices and magnetic media is the diffusion barrier, which is included to prevent interdiffusion between layers or diffusion from overlying layers into the substrate. A good example is placement of a TiN barrier under an Al metallization. Figure 7a illustrates the results of an SNMSd high-resolution depth profile measurement of a TiN diffusion barrier inserted between the Al metallization and the Si substrate. The profile clearly exhibits an uneven distribution of Si in the Al metallization and has provided a clear, accurate measurement of the composition of the underlying TiN layer. Both measurements are difficult to accomplish by other means and dem-
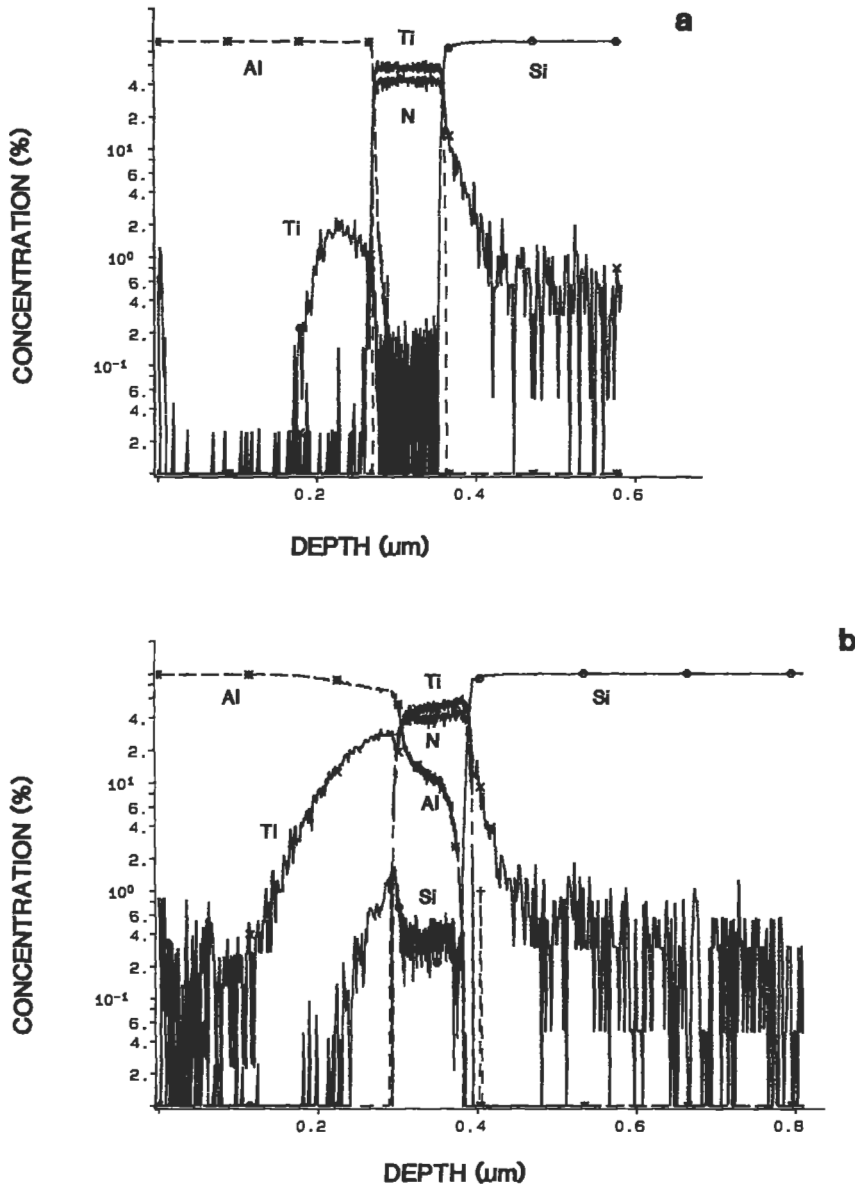
Figure 7 Quantitative high depth resolution profile of the major elements in the thin-film structure of Al/TiN/Si, comparing the annealed and unannealed structures to determine the extent of interdiffusion of the layers. The depth profile of the unannealed sample shows excellent depth resolution (a). The small amount of Si in the Al is segregated toward the Al/TiN interface. After annealing, significant Ti has diffused into the Al layer and Al into the TiN layer, but essentially no Al has diffused into the Si (b). The Si has become very strongly localized at the Al/TiN interface.
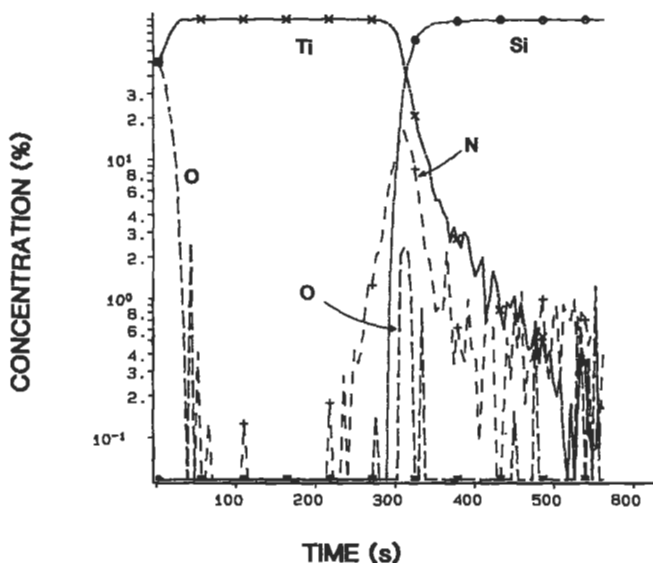
Figure 8   Quantitative high depth resolution profile of O and N in a Ti metal film on Si, using electron-gas SNMS in the direct bombardment mode. Both O and N are measured with reasonably good sensitivity and with good accuracy both at the heavily oxidized surface and at the Ti/Si interface.

onstrate the strength of SNMS for providing quantitative measurements in all components of a complex thin-film structure. The results of processing this structure of Al:Si/TiN/Si are shown in Figure 7b. The measurement identifies the redistribution of the Si to the interfaces, the diffusion of Al and Si into the TiN, and a strong diffusion out of Ti from the TiN into the overlying Al. However, no Al has diffused into the Si nor Si from the substrate into the Al, demonstrating the effectiveness of the TiN barrier.

Yet another strength of SNMS is the ability to measure elemental concentrations accurately at interfaces, as illustrated in Figure 8, which shows the results of the measurement of N and O in a Ti thin film on Si. A substantial oxide film has formed on the exposed Ti surface. The interior of the Ti film is free of N and O, but significant amounts of both are observed at the Ti/Si interface. SNMS is as sensitive to O as to N, and both the O and N contents are quantitatively measured in all regions of the structure, including the interface regions. Quantitation at the interface transition between two matrix types is difficult for SIMS due to the matrix dependence of ion yields.

Conclusions

The combination of sputter sampling and postsputtering ionization allows the atomization and ionization processes to be separated, eliminating matrix effects on elemental sensitivity and allowing the independent selection of an ionization process with uniform yields for essentially all elements. The coupling of such a uniform ionization method with the representative sampling by sputtering thus gives a "universal" method for solids analysis.

Electron impact SNMS has been combined most usefully with controlled surface sputtering to obtain accurate compositional depth profiles into surfaces and through thin-film structures, as for SIMS. In contrast to SIMS, however, SNMS provides accurate quantitation throughout the analyzed structure regardless of the chemical complexity, since elemental sensitivity is matrix independent. When sputtering with a separate focused ion beam, both image and depth resolutions obtained are similar to the those obtained by SIMS. However, using electron-gas SNMS, in which the surface can be sputtered by plasma ions at arbitrarily low bombarding energies, depth resolutions as low as 2 nm can be achieved, although lateral image resolution is sacrificed.

In summary, the forte of SNMS is the measurement of accurate compositional depth profiles with high depth resolution through chemically complex thin-film structures. Current examples of systems amenable to SNMS are complex III-IV laser diode structures, semiconductor device metallizations, and magnetic read–write devices, as well as storage media.

SNMS is still gaining industrial acceptance as an analytical tool, as more instruments become available and an appreciation of the unique analytical capabilities is developed. To date, SNMS has not become established as a routine analytical tool providing essential measurements to a significant segment of industry. The technique still remains largely in the domain of academic and research laboratories, where the full range of application is still being explored. The present stage of SNMS development is appropriate to this environment, and refinements in hardware and software can be expected, given a unique niche and the pressure of commercial or industrial use.

In addition to the analysis of complex thin-film structures typical of the semiconductor industry, for which several excellent examples have been provided, an application area that offers further promise for increased SNMS utilization is the accurate characterization of surfaces chemically modified in the outer several hundred-Å layers. Examples are surfaces altered in some way by ambient environments—a sheet steel surface intentionally altered to enhance paint bonding, or phosphor particles with surfaces altered to enhance fluorescence. A strength of SNMS that will also become more appreciated with time is its ability to provide, with good depth resolution, quantitative measurements of material trapped at interfaces, for example, contaminants underlying deposited thin films or migrating to interfacial regions during subsequent processing. As these and other application

areas are explored more fully, the place of SNMS will become more evident and secure, and the evolution of SNMS instrumentation even more rapid.

Related Articles in the Encyclopedia

SIMS, SALI, and LIMS

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10.5 LIMS

Laser Ionization Mass Spectrometry

FILIPPO RADICATI DI BROZOLO

Contents

- Introduction
- Basic Principles
- Instrumentation
- Applications
- Sample Requirements
- Conclusions

Introduction

Laser ionization mass spectrometry or laser microprobing (LIMS) is a microanalytical technique used to rapidly characterize the elemental and, sometimes, molecular composition of materials. It is based on the ability of short high-power laser pulses (~10 ns) to produce ions from solids. The ions formed in these brief pulses are analyzed using a time-of-flight mass spectrometer. The quasi-simultaneous collection of all ion masses allows the survey analysis of unknown materials. The main applications of LIMS are in failure analysis, where chemical differences between a contaminated sample and a control need to be rapidly assessed. The ability to focus the laser beam to a diameter of approximately 1 mm permits the application of this technique to the characterization of small features, for example, in integrated circuits. The LIMS detection limits for many elements are close to 10^{16} at/cm^3, which makes this technique considerably more sensitive than other survey microanalytical techniques, such as Auger Electron Spectroscopy (AES) or Electron Probe Microanalysis (EPMA). Additionally, LIMS can be used to analyze insulating sam-

ples, as well as samples of complex geometry. Another advantage of this technique is its ability sometimes to provide basic molecular information about inorganic as well as organic surface contaminants. A growing field of application is the characterization of organic polymers, and computerized pattern recognition techniques have been successfully applied to the classification of various types of mass spectra acquired from organic polymers.

The LIMS technique is rarely used for quantitative elemental analysis, since other techniques such as EPMA, AES or SIMS are usually more accurate. The limitations of LIMS in this respect can be ascribed to the lack of a generally valid model to describe ion production from solids under very brief laser irradiation. Dynamic range limitations in the LIMS detection systems are also present, and will be discussed below.

Basic Principles

LIMS uses a finely focused ultraviolet (UV) laser pulse (~10 ns) to vaporize and ionize a microvolume of material. The ions produced by the laser pulse are accelerated into a time-of-flight mass spectrometer, where they are analyzed according to mass and signal intensity. Each laser shot produces a complete mass spectrum, typically covering the range 0–250 amu. The interaction of laser radiation with solid matter depends significantly upon the duration of the pulse and the power density levels achieved during the pulse.[1] When the energy radiated into the material significantly exceeds its heat of vaporization, a plasma (ionized vapor) cloud forms above the region of impact. The interaction of the laser light with the plasma cloud further enhances the transfer of energy to the sample material. As a consequence, various types of ions are formed from the irradiated area, mainly through a process called nonresonant multiphoton ionization (NRMPI). The relative abundances of the ions are a function of the laser's power density and the optical properties and chemical state of the material. Typically, the ion species observed in LIMS include singly charged elemental ions, elemental cluster ions (for example, the abundant C_x^- negative ions observed in the analysis of organic substances), and organic fragment ions. Multiply charged ions are rarely observed, which sets an approximate upper limit on the energy that is effectively transferred to the material.[1, 5]

The material evaporated by the laser pulse is representative of the composition of the solid,[1] however the ion signals that are actually measured by the mass spectrometer must be interpreted in the light of different ionization efficiencies. A comprehensive model for ion formation from solids under typical LIMS conditions does not exist, but we are able to estimate that under high laser irradiance conditions ($>10^{10}$ W/cm^2) the detection limits vary from approximately 1 ppm atomic for easily ionized elements (such as the alkalis, in positive-ion spectroscopy, or the halogens, in negative-ion spectroscopy) to 100–200 ppm atomic for elements with poor ion yields (for example, Zn or As).
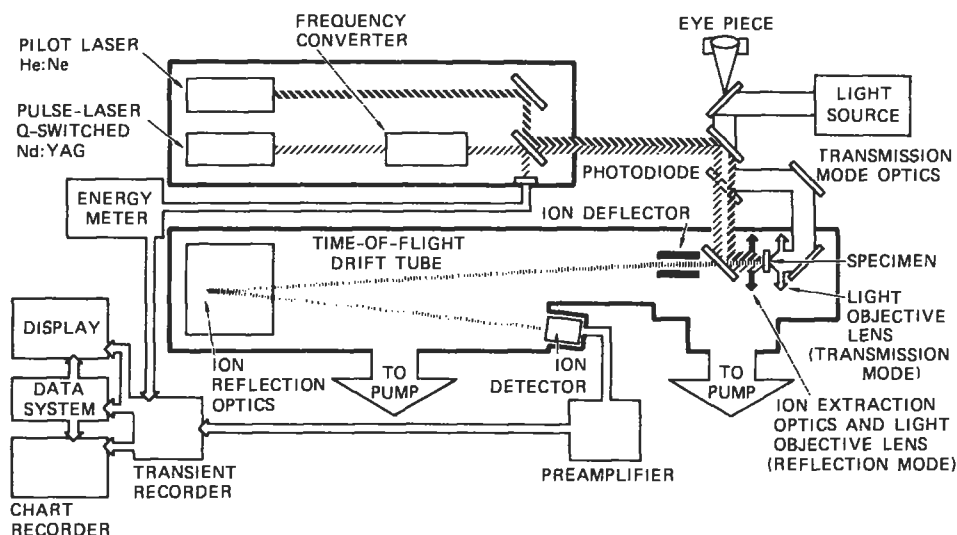
Figure 1 Schematic diagram of a LIMS instrument, the LIMA 2A (Cambridge Mass Spectrometry, Ltd., Kratos Analytical, UK).

The large variability in elemental ion yields which is typical of the single-laser LIMS technique, has motivated the development of alternative techniques, that are collectively labeled post-ablation ionization (PAI) techniques. These variants of LIMS are characterized by the use of a second laser to ionize the neutral species removed (ablated) from the sample surface by the primary (ablating) laser. One PAI technique uses a high-power, frequency-quadrupled Nd–YAG laser (λ = 266 nm) to produce elemental ions from the ablated neutrals, through nonresonant multiphoton ionization (NRMPI). Because of the high photon flux available, 100% ionization efficiency can be achieved for most elements, and this reduces the differences in elemental ion yields that are typical of single-laser LIMS. A typical analytical application is discussed below.

Instrumentation

The schematic diagram of a LIMS instrument is shown in Figure 1. The instrument's basic components include:

1 A Q-switched, frequency-quadrupled Nd–YAG laser (λ = 266 nm) and its accompanying optical components produce and focus the laser pulse onto the sample surface. The typical laser spot size in this instrument is approximately 2 μm. A He–Ne pilot laser, coaxial with the UV laser, enables the desired area to be located. A calibrated photodiode for the measurement of laser energy levels is also present
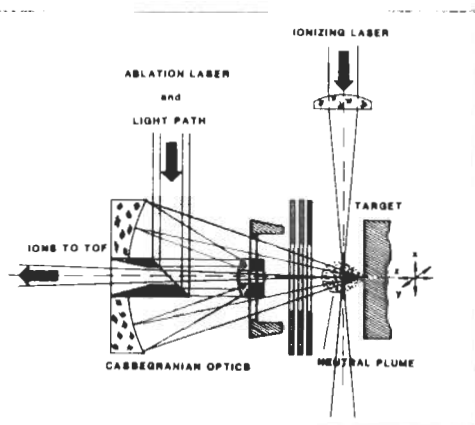
Figure 2   Schematic view of the ion source region of the LIMS instrument in the PAI configuration.

2   The time-of-flight mass spectrometer (under high vacuum) consists of a sample stage equipped with *xyz* motion, the ion extraction region, and the ion flight tube (approximately 2 m in length) with energy focusing capabilities

3   The ion detection system consists of a high-gain electron multiplier and the signal digitizing system, along with a computer for data acquisition and manipulation.

Figure 2 presents a schematic view of the ion source region in the PAI configuration. A second high-irradiance, frequency quadrupled pulsed Nd–YAG laser is focused parallel to and above the sample surface, where it intercepts the plume of neutral species that are produced by the ablating laser. Appropriate focusing optics and pulse time-delay circuitry are used in this configuration.

A typical LIMS analysis is performed by positioning the region of interest of the sample by means of the He–Ne laser beam, after which the Nd–YAG laser is fired. The UV laser pulse produces a burst of ions of different masses from the analytical crater. These ions are accelerated to almost constant kinetic energy and are injected into the spectrometer flight tube. As the ions travel through the flight tube and through the energy-focusing region, small differences in kinetic energy among ions of the same mass are compensated. Discrete packets of ions arrive at the detector and give rise to amplified voltage signals that are input to the transient recorder. The function of the transient recorder is to digitize the analog signal from the electron multiplier, providing a record of both the arrival time and the intensity of the signals associated with each mass. The data are then transferred to the computer for further manipulation, the transient recorder is cleared and rearmed, and the instrument is ready for the acquisition of another spectrum.

This sequence of events is quite rapid. If we take typical instrumental conditions of the LIMA 2A, where the UV laser pulse duration is 5–10 ns, the fight path is ~2 m, and the accelerating potential is 3 kV, then an H^+ ion arrives at the detector i n approximately 3 μs, and a U^+ ion arrives at the detector in approximately 40 μs. Since the time width of an individual signal can be as short as several tens of nano-seconds, a high speed detection and digitizing system must be employed.

Typical mass resolution values measured on the LIMA 2A range from 250 to 750 at a mass-to-charge ratio $M/Z = 100$. The parameter that appears to have the most influence on the measured mass resolving power is the duration of the ioniza-tion event, which may be longer than the duration of the laser pulse (5–10 ns), along with probable time broadening effects associated with the 16-ns time resolu-tion of the transient recorder.[3]

The intensity of an ion signal recorded by the transient recorder is proportional to the number of detected ions. There are two limiting factors to this proportional-ity, one due to the nonlinear output of the electron multiplier at high-input ion sig-nals, and the other due to the dynamic range of the digitizer. The dynamic range of typical venetian blind-type electron multipliers for linear response to fast transients is less than four orders of magnitude. Electron multipliers characterized by other geometries (mesh type) are currently being evaluated, and may provide a larger inherent dynamic range.[3]

The second limiting factor in the quantitative measurement of the ion signal intensity is associated with the digitization of the electron multiplier output signal by the transient recorder. For example, the Sony-Tektronix 390 AD transient recorder in the LIMA 2A is a 10-bit digitizer with an effective dynamic range of 6.5 bits for 10-MHz signals. This device provides approximately 90 discrete voltage output levels at input frequencies of typical ion signals.[4]

Limitations in the digitizer's dynamic range can be overcome by using multiple transient recorders operating at different sensitivities, or by adding logarithmic preamplifiers in the detection system. From the preceding discussion it appears, however, that quantitative analysis is not the primary area of application of LIMS. Semiquantitative and qualitative applications of LIMS have been developed and are discussed in the remainder of this article.

Applications

Most applications of LIMS are in failure analysis. A typical microanalytical failure analysis problem, for example, may involve determinating the cause of corrosion in a metallization line of an integrated circuit. One can achieve this by performing an elemental survey analysis of the corroded region. Since it is not always known which elements are normal constituents of the material in question and which are truly contaminants, the vast majority of these analyses are performed by comparing the elemental make-up of the defective region to that of a control region. The com-
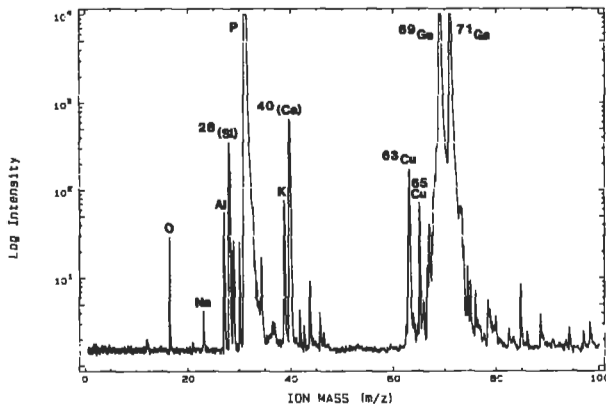
Figure 3 Positive-ion mass spectrum acquired from defective sample. Intense copper ion signals are observed (M/Z = 63 and 65).

parison of mass spectra of the two regions may reveal the presence of additional elements in the defective region. Those elements are often the cause or byproducts of the corrosion. In this type of analysis, the selection of a relevant control sample is obviously critical.[2]

LIMS analytical applications may be classified as elemental or molecular survey analyses. The former can be further subdivided into surface or bulk analyses, while molecular analyses are generally applicable only to surface contamination. In the following descriptions of applications, a comparison with other analytical techniques is presented, along with a discussion of their relative merits.

Bulk Analysis

One example of the application of LIMS to bulk contamination microanalysis is the analysis of low level contamination in GaP light emitting diodes (LEDs). The light emission characteristics of GaP LEDs can be severely affected by the presence of relatively low levels of transition elements. Although the nature of the poisoning species may be suspected or inferred from intentional contamination experiments, the determination of elemental contaminants in actual failures is a difficult analytical problem, in particular because of the small size and complex geometry of the parts. Figures 3 and 4 illustrate two positive-ion mass spectra that were acquired from cross sections of a defective and a nondefective GaP LED, respectively. The laser power density employed in this analysis was high to maximize the detection of low-level contaminants. The depth of sampling is estimated to be 1000–1500 Å. The two mass spectra exhibit intense signals for Ga⁺, along with moderately intense signals for P⁺. The defective LED also exhibits readily recognizable signals at M/Z = 63 and 65, matching in relative intensity the two Cu isotopes. The presence of Cu in the defective LED can explain its anomalous optical behavior. This
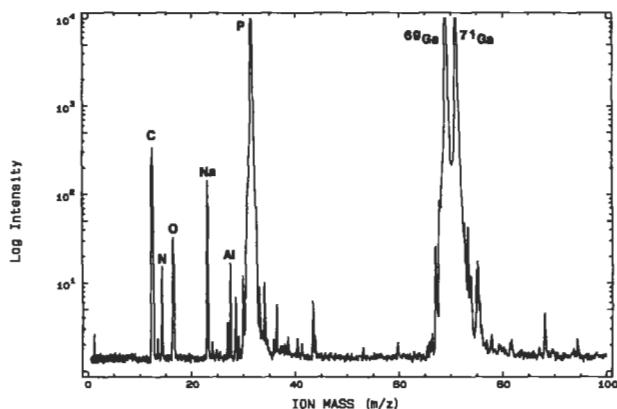
Figure 4   Positive-ion mass spectrum acquired from the contact region of a control sample. Copper ion signals are absent.

example is a good illustration of the unique advantages of LIMS over other analytical techniques. These include the ability to perform rapid survey analysis to detect unknown contaminants. Two other advantages of LIMS illustrated by this example are its ability to analyze a small sample having nonplanar geometry, without time-consuming sample preparation, and its sensitivity, which is superior to that of most electron beam techniques.

Surface Analysis

An example of elemental contamination surface microanalysis is shown inFigure 5. This is a negative-ion mass spectrum acquired from a small window (~4 μm) etched through a photoresist layer deposited onto a HgCdTe substrate. An Al film is then deposited in these windows to provide electrical contact with the substrate. Windows were found to be defective because of poor adhesion of the metallic layer. The spectrum shown in Figure 5 was acquired from a defective window, and reveals the presence of intense signals of Cl^- and Br^-, neither of which is observed in similar regions with good adhesion characteristics. In this case, the photoresist had been etched with solutions containing Cl and Br. The laser power density employed in this analysis was low, and the sampling depth was estimated to be < 500 Å. This analysis indicates that poor adhesion on the contaminated windows is due to incomplete rinsing of etching solutions. The ability of LIMS to operate on nonconductive materials is a major advantage in this case, since both the HgCdTe substrate and the surrounding photoresist are insulating. Techniques that use charged-particle beams (electrons, AES or EPMA; ions, SIMS) could probably not be applied in this case.
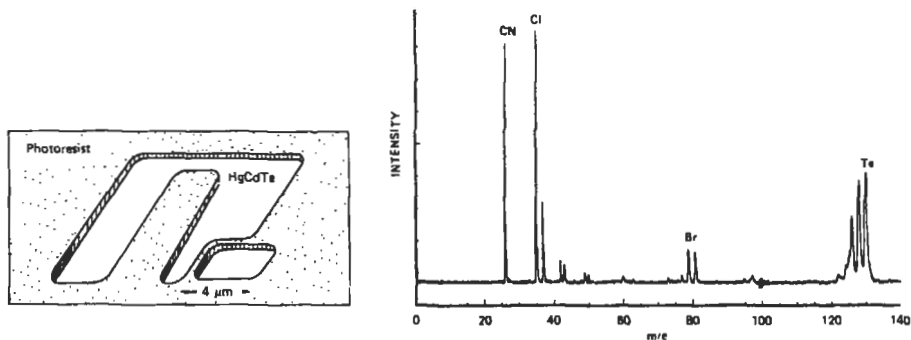
Figure 5 Diagram of the windows cut in the photoresist on an HgCdTe substrate (top). Spectrum acquired from a defective window, and reveals the presence of intense signals of Cl⁻ and Br⁻ (bottom).

Organic Surface Microanalysis

The laser irradiation of a material can produce molecular ions, in addition to elemental ions, if the power density of each pulse is sufficiently low. The analysis of such molecular species includes the study of organic materials ranging from polymers to biological specimens, as well as the analysis of known or suspected organic surface contaminants. LIMS organic spectroscopy is primarily a qualitative technique, which is used to identify a number of fragment ions in a spectrum that are diagnostic for a given class of organic species.

Organic contamination in the microelectronics industry is often related to the presence of organic polymer residues, for example, photoresist. These organic residues are a serious problem for surface adhesion, for example in the case of bond pads. Examples of LIMS organic surface analysis are shown in Figures 6 and 7: mass spectra acquired from a commercial photoresist, using positive- and negative-ion detection, respectively. The positive-ion mass spectrum in Figure 6 exhibits intense signals for alkalis (Na and K) along with a series of signals that are C-based fragment ion peaks. Some of these are undoubtedly aromatic fragment ions ($M/Z =$ 77, 91, and 115, among others), and are diagnostic of this particular photoresist. Similarly, the negative-ion mass spectrum in Figure 7 exhibits an intense signal at $M/Z = 107$, which arises from Novolak resin, one of the constituents of the photoresist. Other, less intense signals of this spectrum include the species SO_2, SO_3, and HSO_3, which are also known to be present in the photoresist.

Laser Post-Ionization of Ablated Neutrals

A ZnSe-on-GaAs epitaxial layer required a sensitive survey of near-surface contamination. PAI was selected for ZnSe analysis because its major constituents and many of the expected impurities are elements that have poor ion yields in conventional LIMS. Figures 8 and 9 are two mass spectra acquired from the ZnSe epitaxial layer,
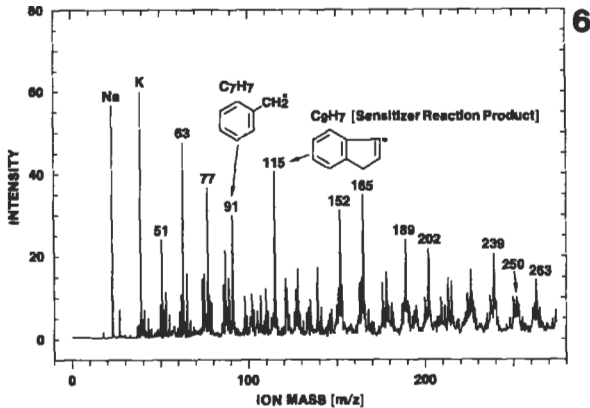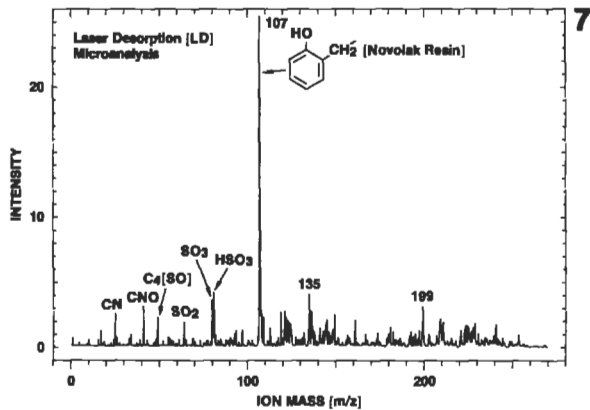
Figures 6 and 7 Mass spectra acquired from a commercial photoresist, using positive- and negative-ion detection, respectively.

using conventional single-laser LIMS and the PAI configuration, respectively. The single-laser spectrum in Figure 8 exhibits primarily the Zn^+ and Se^+ signals, and weak signals for Cr^+ and Fe^+. The high background signal level following the intense Se signal is related to detector saturation. The ablator laser irradiance for this spectrum was estimated to be $> 10^{10}$ W/cm^2, hence the high background signal.

In contrast, the PAI mass spectrum in Figure 9 exhibits readily observable signals for Cd^+ and Te^+ in addition to the Zn and Se signals. Note also the low background in the region that follows the Se signal. The ablator laser irradiance in the PAI spectrum was approximately 10^9 W/cm^2, a factor of 10 lower than in the single-laser analysis. The lower ablator laser irradiance samples the top 100 Å of the sample, compared to 1000 Å or more in single-laser analysis, and hence provides better sur-
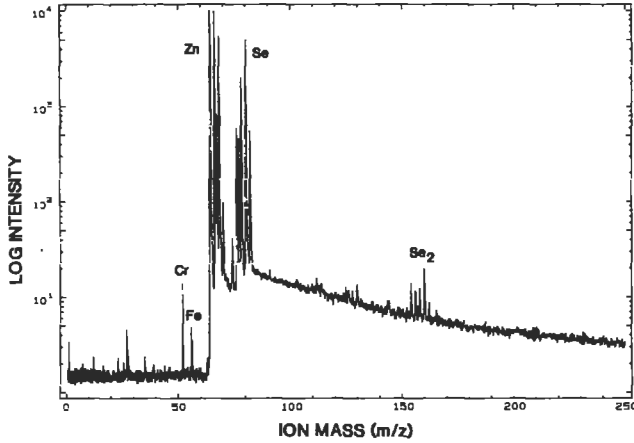
Figure 8 Conventional, single-laser mass spectrum of ZnSe.
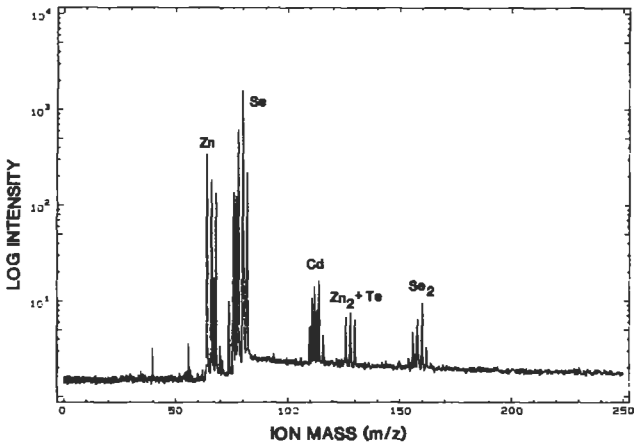
Figure 9 Spectrum of ZnSe using the two-laser (PAI) instrumental configuration.

face sensitivity. In conclusion, the PAI variant of LIMS is especially useful when the elements present have high ionization potentials that preclude efficient ion detection via conventional LIMS analysis, and in those cases when a higher surface sensitivity is desired.

Sample Requirements

A general requirement for LIMS analysis is that the material must be vacuum compatible and able to absorb UV laser radiation. With regard to the latter require-

ment, the absorption characteristics of UV-transparent materials can be improved with the use of thin UV-opaque coatings, such as Au or C. Care must be exercised, however, that the coating does not introduce excessive contamination, and practice is needed to determine the best coating for each sample.

A typical LIMS instrument accepts specimens up to 19 mm (0.75 in) in diameter and up to 6 mm in thickness. Custom designed instruments exist, with sample manipulation systems that accept much larger samples, up to a 6-in wafer. Although a flat sample is preferable and is easier to observe with the instrument's optical system, irregular samples are often analyzed. This is possible because ions are produced and extracted from μm-sized regions of the sample, without much influence from nearby topography. However, excessive sample relief is likely to result in reduced ion signal intensity.

The electrical conductivity of the sample is, to a first approximation, much less critical than in the case of charged-particle beam techniques (e.g., AES or SIMS), because the laser beam does not carry an electric charge, and is pulsed with a very low duty cycle. However, charging effects are sometimes observed in the negative-ion analysis of insulating samples, such as ceramics or silicon oxide. Charging probably arises from the acceleration of large numbers of electrons from the sample surface, along with the negative ions, which leaves behind a positively charged sample surface. Effects of this type may be alleviated with the use of conductive masks over the sample surface.

Conclusions

LIMS is primarily used in failure microanalysis applications, which make use of its survey capability, and its high sensitivity toward essentially all elements in the periodic table. The ability to provide organic molecular information on a microanalytical scale is another distinctive feature of LIMS, one that is likely to become more important in the future, with improved knowledge of laser desorption and ionization mechanisms.

Future trends for LIMS are likely to include hardware improvements, theoretical advances in the understanding of the basic mechanisms of laser–solid interactions, and improved methods for data handling and statistical analysis. Among the hardware improvements, one can count the advent of post-ionization techniques, which are briefly presented in this article and are discussed elsewhere in the Encyclopedia, and improvements in detection system dynamic ranges, through the use of different types of electron multipliers and improved transient recorders. These innovations are expected to result in improved quantification of the results. The introduction of faster pulsed lasers may also prove a significant improvement in mass resolution for LIMS, thus making it more suitable for organic analysis. Improvements in software may include compilations of computerized databases of LIMS organic mass spectra, the development of pattern recognition techniques, and the introduction of expert systems in the analysis of large bodies of LIMS data.[6]

Related Articles in the Encyclopedia

SALI, SIMS, SNMS, GDMS, and AES

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10.6 S S M S

Spark Source Mass Spectrometry

WILLIAM L. HARRINGTON

Contents

- Introduction
- Basic Principles
- Comparison With Other Techniques
- Conclusions

Introduction

No single trace elemental technique can provide a complete analysis of the many materials used in today's high technology applications. In the 30 years since its commercial introduction, SSMS has proven to be a versatile technique that can be applied to a wide variety of material types. The high-voltage radiofrequency (RF) spark source, which is used to volatilize and ionize the sample elements, has been shown to do so with relatively uniform probability across the entire periodic table. Although far from perfect in this respect, sensitivities for most elements in most matrices are therefore uniform and are constant within about a factor of 3, even at trace levels of less than 1 part per million atomic (ppma). Like most mass spectrometric techniques, SSMS is linear with respect to concentration over a wide range, achieving 8–9 orders of magnitude in cases where the signals are interference free. This relatively uniform, high sensitivity, combined with the ability to examine materials in a wide variety of forms, makes SSMS an excellent choice for trace elemental surveys of bulk and some thin-film specimens. The three most-used trace element techniques for survey analysis are Emission Spectrometry (ES), Glow Discharge Mass Spectrometry (GDMS), and SSMS. After a detailed discussion of SSMS, a comparison with these and other techniques will be made.

Bulk solids
Silicon (boules and wafers)
GaAs
Evaporation sources (e.g., Al, Au, and Ti)
Precious metals (Pt, Au, Rh wire, and melts)
Steel
Alloys (Ni-Co-Cr, Al-Si, Cu-Ni, and Inconel)
Ga metal (cooled to solid phase using liquid nitrogen)

Powders
Graphite
Rare earth oxides and phosphors
Ceramics (Al_2O_3) and glasses
Mining ores and rocks
Superconductors and precursor materials

Thin films
Silicon wafers and SiO_2 films
Si / sapphire (SOS), Si / insulators (SOI)
Epitaxial GaAs
Buried oxides (SIMOX)
Plated, sputtered, or evaporated metals

Table 1   **Typical materials analyzed.**

Table 1 lists some of the materials typically analyzed by SSMS and some of the forms in which these materials may exist. The basic requirement is that two conducting electrodes be formed of the material to be analyzed. Details of the analysis of each type of sample will be discussed in a later section.

Although a number of studies have been made concerning the basic properties of the RF vacuum spark used for excitation,[1-4] the discharge is typically erratic, producing a widely fluctuating signal for mass analysis. For this reason, the most widely used form of this instrumentation consists of a mass spectrometer of the

The figure shows a schematic. Labels include:

PULSED DISCHARGE CIRCUIT 100KV MAX.

SAMPLE ELECTRODE

BEAM SUPPRESSOR ELECTRODE +1.5kV

SAMPLE ATOMS VAPORIZED A(m) A(x)

SAMPLE ELECTRODE

IONS

+1.0kV

+20kV

-1.0kV

MATRIX – m
IMPURITY – x

TOTAL IONS COLLECTED BY MONITOR I_M^+

IONS COLLECTED BY DETECTOR

$I_D^+(x)$ $I_D^{2+}(m)$ $I_D^+(m)$

ION PATHS

MAGNET

$$I_M^+ \approx I_D^+(m) + I_D^{2+}(m) + \ldots$$
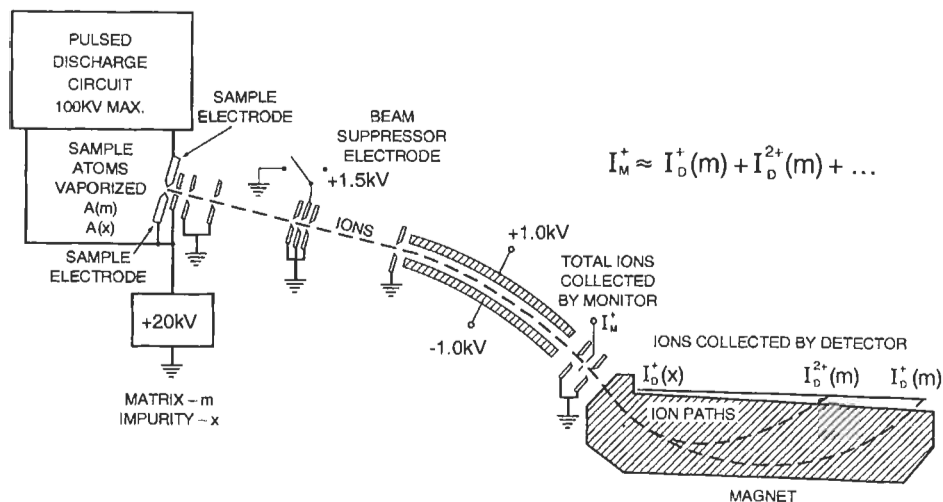
Figure 1   Schematic diagram of a Mattauch-Herzog geometry spark source mass spectrometer using an ion-sensitive plate detector.

Mattauch-Herzog geometry,[5] which simultaneously focuses all resolved masses onto one plane, allowing the integrating properties of an ion-sensitive emulsion to be used as the detector. Although electrical detection with an electron multiplier can be applied,[6] the ion-sensitive emulsion-coated glass "photographic" plate is the most common method of detection and will be described in this article.

Basic Principles

General Technique Description

A schematic diagram of a spark source mass spectrometer is shown in Figure 1. The material to be analyzed forms the two electrodes separated by a spark gap. A pulsed 500-kHz high-voltage discharge across the gap volatilizes and ionizes the electrode material. The positive ions released are accelerated to 20–30 kV and passed into the mass spectrometer for energy and direction focusing. The electrostatic analyzer passes ions with an energy spread of about 600 eV, and focuses the beam onto a slit monitor that intercepts a constant fraction of the ions. This allows an accurate measurement of the number of ions (as Coulombic charge) entering the magnetic sector to be separated according to their mass-to-charge ratios and subsequently refocused and collected on the ion-sensitive plate detector. Figure 2 shows an example of SSMS data recorded on such a detector. The position of the collected ions (in the form of a line image of the source slit) provides qualitative identification of the isotopic masses (note the mass scale added to the plate to aid identification), and
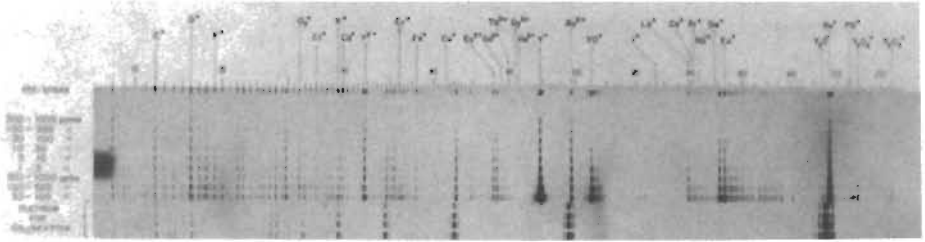
Figure 2 Ion-sensitive plate detector showing the species produced by the SSMS analysis of a $Y_2O_3:Eu_2O_3$ mixture compacted with gold powder.

the blackness of the lines can be related to the number of ions striking a position (i.e., the concentration).

Because the beam monitor allows accurate measurement of the total number of ions that are analyzed, a graded series of exposures (i.e., with varying numbers of ions impinging on the plate) is collected, resulting in the detection of a wide range of concentrations, from matrix elements to trace levels of impurities. In Figure 2, the values of the individual exposures have been replaced with the concentration range that can be expected for a mono-isotopic species just visible on that exposure. In this example, exposures from a known Pt sample have been added to determine the response curve of the emulsion.

Sample Requirements and Examples

For *bulk conductors* and *semiconductors,* sample preparation consists of breaking, cutting, or sawing the solid approximately into the dimensions 1/16 in. × 1/16 in. × 1/2 in. Large, irregular sample electrodes can be accommodated; however, they often shield the path of ions into the mass spectrometer, thereby reducing the beam current and increasing the analysis time. If the preparation, handling, or packaging contaminates the sample electrodes with elements that are not of interest, they can be degreased in high purity methanol, etched in an appropriate semiconductor-grade acid, and washed in several portions of methanol before analysis.

The final, and most critical cleaning is performed by presparking all electrode surfaces that will be consumed, before collecting the actual exposures for analysis. The presparking removes in vacuum the outer layers of the sample, which may contain trace levels of contamination due to handling or atmospheric exposure. This step also coats the surfaces in the analysis chamber to minimize memory effects, i.e., to minimize the chances of detecting elements from a previously analyzed sample. Cryosorption pumping[7] using an Al_2O_3 or charcoal-coated plate filled with liquid nitrogen is also used during presparking and analysis to maintain reproducible source pressures and to reduce hydrocarbon interferences.
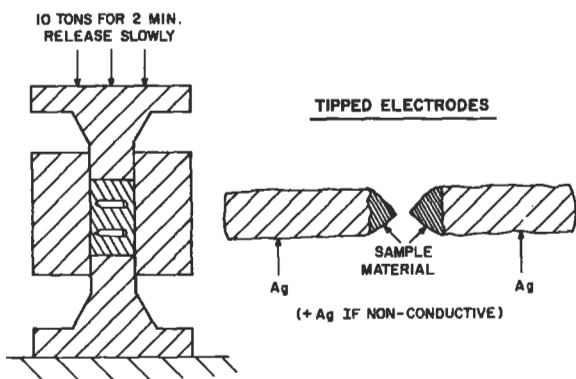
Figure 3   Schematic of a polyethylene slug die used to compact powder samples. When the amount of material available for analysis is small, tipped electrodes can be formed.

Table 2 is a typical example of SSMS analysis of a high-purity Pt wire that was simply broken in two and presparked. The elements from Be to U were determined in a single analysis requiring a total time of 1–2 hours. Hydrogen and Li must be measured in a separate set of exposures using a lower magnetic field and therefore generally are not included in a standard SSMS analysis. Because detection limits vary with plate sensitivity, background, isotopic abundance, and elemental mass, individual limits are listed for those elements not detected and are noted as less than (<). For practical reasons, a factor of about 3 better detection limits (3× longer analysis time) is generally the limit for this technique.

Powders or nonconductors represent important forms of materials that are well suited for SSMS analysis. Powders of conductive material generally can be prepared without a binder, but insulators first must be ground to a powder with a mortar and pestle, such as boron carbide and agate, then mixed with a high-purity conductive binder, such as Ag powder or graphite powder, and pressed to form solid, conductive electrodes. To prevent contamination from the metal die, a polyethylene cylinder is drilled to hold the powder such that the tips and sides of the electrodes touch only the polyethylene and not the steel parts of the die. If the sample material is limited in quantity, small portions (1–10 mg) can be tipped onto the end of high purity Ag.A die and tipped electrodes are shown diagrammatically in Figure 3.

Of course, this procedure for nonconducting powders dilutes the sample, causing poorer detection limits and limiting the purity that can be specified to that of the binder.

Although SSMS cannot be considered a surface technique due to the 1–5 μm penetration of the spark in most materials, few other techniques can provide a trace elemental survey analysis of surfaces consisting of films or having depths of interest

Element	Concentration (ppma)	Element	Concentration (ppma)
		Rh	3
		Pd	4
Be	≤ 0.003	Ag	0.1
B	0.003	Cd	< 0.04
C*	6	In	0.2
N*	0.1	Sn	< 0.04
O*	3	Sb	< 0.02
F	0.004	Te	< 0.04
Na	0.02	I	< 0.02
Mg	0.4	Cs	< 0.02
Al	0.2	Ba	< 0.02
Si	2	La	< 0.02
P	0.04	Ce	< 0.02
S	0.04	Pr	< 0.02
Cl	0.03	Nd	< 0.07
K	< 0.02	Sm	< 0.06
Ca	5	Eu	< 0.04
Sc	≤ 0.03	Gd	< 0.07
Ti	0.4	Tb	< 0.02
V	0.02	Dy	< 0.07
Cr	≤ 0.3	Ho	< 0.02
Mn	0.07	Er	< 0.06
Fe	4	Tm	< 0.03
Co	0.02	Yb	< 0.07
Ni	0.6	Lu	< 0.03
Cu	3	Hf	< 0.06
Zn	0.03	Ta**	4
Ga	0.02	W	< 0.08
Ge	< 0.02	Re	< 0.04
As	0.02	Os	< 0.2
Se	< 0.02	Ir	< 0.3
Br	< 0.02	Pt	Major
Rb	< 0.01	Au	≤ 3
Sr	≤ 0.02	Hg	< 0.2
Y	< 0.008	Tl	< 0.08
Zr	3	Pb	< 0.7
Nb	< 0.009	Bi	< 0.2
Mo	≤ 0.2	Th	< 0.04
Ru	0.2	U	< 0.04

* Upper limits; source not baked to reduce background.

Table 2   SSMS analysis of high-purity Pt metal.

of ~5 μm. Although the penetration depth can be somewhat controlled by the spark gap voltage, the electrode separation, and the speed of sample scanning, 1–5 μm is the typical range of penetration depths that can be achieved without punching through to deeper layers. Figure 3 shows a method for surface analysis using a high-purity metal probe (Au) as a counter electrode to spark an area of a sample's surface. The tip of the probe is positioned on the axis of the mass spectrometer, and the sample is scanned over the probe tip to erode tracks across the surface. By scanning over areas of about 1 cm², detection limits on the order of 1 ppma can be achieved. By combining this survey surface analysis with depth profiling techniques, such as Secondary-Ion Mass Spectrometry (SIMS) or Auger Electron Spectroscopy (AES), elements of interest can be identified by SSMS and then profiled in detail by the other methods.

The SSMS point-to-plane surface technique has been shown to be particularly useful in the survey analysis of epitaxial films, heavy metal implant contamination, diffusion furnace contamination, and deposited metal layers.

Data Evaluation

Qualitatively, the spark source mass spectrum is relatively simple and easy to interpret. Most instrumentation has been designed to operate with a mass resolution M/dM of about 1500. For example, at mass $M = 60$ a difference of 0.04 amu can be resolved. This is sufficient for the separation of most hydrocarbons from metals of the same nominal mass and for precise mass determinations to identify most species. Each exposure, as described earlier and shown in Figure 2, covers the mass range from Be to U, with the elemental isotopic patterns clearly resolved for positive identification.

The spark source is an energetic ionization process, producing a rich spectrum of multiply charged species ($M/2$, $M/3$, $M/4$, etc.). These masses, falling at halves, thirds, and fourths of the unit mass separation can aid in the positive identification of elements. In Figure 2, species like Au^{+2} and Y^{+2} are labeled. The most abundant species (matrix elements and major impurities) also form dimers and trimers (and so forth) at two and three times (and so forth) the mass of the monomer. Although these species can cause interference with certain trace elements, they also can aid in positively identifying a particular element. Finally, the spectrum generally contains mixed polyatomic species, such as MO^+, MO_2^+, MC^+ (in graphite), and MAg^+ (in silver). All such possibilities must be considered in the qualitative interpretation of a spark source mass spectrum.

Of course, the most reliable and accurate method of quantitative analysis is to calibrate each element with standards prepared in matrices similar to the unknown being analyzed. For a survey technique that is used to examine such a wide variety of materials, however, standards are not available in many cases. When the technique is used mainly in one application (typing steels, specifying the purity of alloys for a selected group of elements, or identifying impurities in silicon boules and

wafers), such standards can be developed and should be applied. Because of the erratic nature of the spark (in terms of time) and variability in the response of the ion-sensitive emulsion detector, accuracy using standards to generate relative sensitivity factors is generally within 20–50%.

Due to the relative uniformity of ion formation by the RF spark (although its timing is erratic), the most widely used method of quantitation in SSMS is to assume equal sensitivity for all elements and to compare the signal for an individual element with that of the total number of ions recorded on the beam monitor. By empirically calibrating the number of ions necessary to produce a certain blackness on the plate detector, one can estimate the concentration. The signal detected must be corrected for isotopic abundance and the known mass response of the ion-sensitive plate. By this procedure to accuracies within a factor of 3 of the true value can be obtained without standards.

The optical density (blackness) of the lines recorded can be measured most accurately using a microdensitometer to scan each line and measure the transmission of light through it. A set of known relative exposures (from charge accumulated by the mass spectrometer beam monitor and known isotopic ratios) is used to establish the emulsion response curve relating transmission to exposure. The absolute position of this response curve on the exposure axis can be determined using standards or from isotopes of a pure element. For concentration determinations requiring the highest precision, the microdensitometer approach is recommended. This method, however, is time consuming; it can be considerably shortened by a well-established "visual" method.

If a graded series of exposures is made in relative steps of 1, 2, 5, 10, 20, 50, etc. (see the graded series of exposures in Figure 2), the exposure necessary to produce a barely detectable line for a particular isotope can be determined by simply observing a well-lighted plate with a 3–5× eyepiece. By determining the average exposures for which barely detectable lines appear for known concentrations of some elements in various matrices, a particular instrument can be calibrated to provide estimates of concentration without further analysis of standards, except to occasionally check the relationship between the beam monitor and the emulsion response. This visual method is surprisingly consistent when care is taken to provide accurate relative exposures, and it produces values that are generally accurate within a factor of 3. Several elements, such as Na, K, Ca, and Al, are best estimated using a multiply charged species (+2 in most cases). For the alkaline and alkaline earth elements in particular, the number of singly charged ions can be greatly enhanced by thermal excitation; a more accurate assessment is made by measuring the +2 species and applying an empirically determined correction factor. The accuracy for elemental concentrations determined in this manner is generally within a factor of 10.

Characteristic	ES	GDMS	SSMS
Detection limits	1–10 ppm	0.00001–0.01 ppm	0.003–0.03 ppm
Concentration	Minor, trace	Major, minor, Ultra-trace	Minor, trace
Elemental coverage	Metals	All elements	All elements
Accuracy without standards with standards	± 10× ± 20%	± 3× ± 10–20%	± 3× ± 20–50%
Matrix effects	Strong	Weak	Weak/ medium
Bulk/ surface	Bulk	Bulk	Bulk and surface
Conductivity	Conductor or insulator	Conductor: run as is Insulator: + Ag	Conductor: run as is Insulator: + Ag or C
Sample Form	Solid/ powder	1 Conducting pin (shape important)	2 Conducting pins (can be irregular)

Table 3   SSMS—comparison with other techniques.

Comparison With Other Techniques

Although numerous analytical techniques have been developed for the quantitative determination of specific elements at trace levels in solids, the three most-used techniques providing multi-element surveys are Emission Spectroscopy (ES), Glow Discharge Mass Spectrometry (GDMS), and SSMS. GDMS is covered in detail elsewhere in this volume, but it is instructive to compare these techniques in tabular form. Table 3 provides this comparison for a number of characteristics that should be considered when choosing a technique. In most situations the required detection limits clearly define one's choice. Elemental coverage is important when nonmetals, such as As, P, Cl, F, C, and O, play a role as trace elements, making the mass spectrometric techniques a clear choice. Sample shape and form are also issues that must be considered. The versatility of SSMS in accommodating a wide variety of materials while maintaining high sensitivity for all elements is one of its prime features.

Inductively Coupled Plasma-Optical (ICP-optical) methods and ICPMS are extremely sensitive elemental survey techniques that also are described in this volume. ICP methods, however, require a solution for analysis, so that the direct
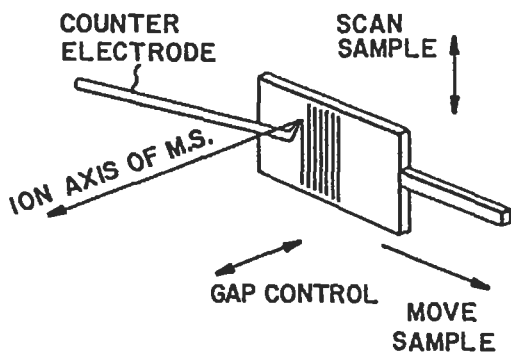
Figure 4   **SSMS surface analysis. The point-to-plane technique allows ppma elemental surveys over a depth of 1–5 μm.**

examination of solids is not possible. Because solution techniques offer relative ease of preparing standards, ICP-optical methods and ICPMS might be chosen in cases where accuracy is most important and the solids can be dissolved without contamination.

Conclusions

SSMS can provide a complete elemental survey with detection limits in the 10–50 ppba range and can deal with a wide variety of sample types and forms. Although GDMS offers higher sensitivity and accuracy of 20%, SSMS is still the technique of choice in many situations. Materials, such as carbon, that do not sputter rapidly enough for good GSMS detection limits, and insulators that cause erratic sputtering when combined with a conductive powder, are excellent candidates for SSMS analysis. In addition, the point-to-plane surface method is one of the few techniques available that can provide a complete elemental survey of 1–5 μm thick films with detection limits on the order of 1 ppma (see Figure 4).

Having described SSMS in some detail as a very useful technique for trace elemental survey analysis, one must note that the lack of manufacture of new instruments and the rising development of GDMS limit its future use. Industrial and service laboratories having SSMS instruments and experienced personnel will continue to use SSMS very effectively. Where there is the need for increased sensitivity, reaching detection limits of less than 1 ppba, and where there is sufficient justification to warrant the cost of GDMS ($600,000–$700,000 for magnetic sector instruments, and about $250,000 for quadrupole instruments), it is anticipated that SSMS gradually will be replaced. With progress being made in the instrumentation and methodology of GDMS, there are currently very few instances where

GDMS cannot be used instead of SSMS. As GDMS source designs are developed to allow clean, thin-film analyses, and some limitations are accepted for the analysis of insulators, GDMS instrumentation will replace more and more of the older SSMS installations. For the present, however, there are excellent laboratories having SSMS instrumentation and services, and SSMS should be used when it proves to be the technique of choice.

Related Articles in the Encyclopedia

GDMS, ICPMS, and ICP-Optical

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10.7 GDMS

Glow-Discharge Mass Spectrometry

JOHN C. HUNEKE AND WOJCIECH VIETH

Contents

- Introduction
- Basic Principles
- Sample Preparation and Analytical Protocol
- GDMS Quantitation
- Applications
- Conclusions

Introduction

Glow-Discharge Mass Spectrometry (GDMS) is a mass spectrometric analytical technique primarily used to measure trace level impurities in conducting or semi-conducting solids. It can also be used, but less commonly, for elemental depth profile analyses. The primary advantages of GDMS are its sensitivity (ppt detection limits in some cases); its quantitative accuracy (20% on average), achieved without complicated standardization procedures; and its ability to detect essentially all elements in the periodic table from lithium to uranium at approximately the same sensitivity.

Because GDMS can provide ultratrace analysis with total elemental coverage, the technique fills a unique analytical niche, supplanting Spark-Source Mass Spectrometry (SSMS) by supplying the same analysis with an order-of-magnitude better accuracy and orders-of-magnitude improvement in detection limits. GDMS analy-

sis has matured rapidly and has become more widely available since the recent introduction of commercial GDMS instrumentation.

Basic Principles

Ion Sources

In general, all GDMS ion sources use a noble gas glow-discharge plasma sustained at about 1 Torr pressure and a few Watts of discharge power. A conducting solid sample for GDMS analysis forms the cathode for a DC glow discharge (Figure 1). Atoms are sputtered nonselectively from the sample surface by ions accelerated from the plasma onto the surface by the cathode voltage. The sputtered atoms diffuse into the plasma and are mostly ionized by collision with metastable discharge gas atoms (so-called Penning ionization) but also in small part by electron impact. Penning ionization, more so than electron impact ionization, provides similar ion-production efficiencies for the majority of the elements. Plasma ions extracted through the exit aperture, including the analyte ions, are electrostatically accelerated into a mass analyzer for measurement.

Ion sources for GDMS have undergone significant evolution, ultimately resulting in discharge cells exposing only the sample (cathode) surface and the metal interior of the Ta discharge cell (anode) to the plasma, a design that minimizes contamination and enhances reliability. The glow-discharge cells accept a variety of shapes and surface conditions, requiring only sufficient length or diameter of the sample. Typically, pin- or wafer-shaped samples are required. It is very helpful to include cryocooling into the design of the discharge cell to enable the analysis of materials having low melting point and to reduce the density of molecular ions created from "atmospheric" gas related contaminants in the glow-discharge plasma.

At the current time, analytical glow-discharge sources incorporate a DC glow discharge. Efforts have been underway to develop glow-discharge sources appropriate for the analysis of electrically insulating materials (e.g., glass and ceramic), which comprise a very important class of materials for which few methods are currently available for complete, full-coverage analysis to trace levels. Two alternatives have been suggested as appropriate: RF-powered glow-discharge plasmas; and electron beam-assisted plasmas. While efforts are being made in both directions, no analytically viable sources have yet been made available.

The sputter sampling of the exposed surface also provides concentration depth profiling capability for GDMS. Depth resolution of some 0.1 μm has been demonstrated, with 1–2 orders of magnitude dynamic range due to geometric limitations and the high operating pressure of the glow-discharge source. With a rapid sputtering rate of about 1 μm/min, GDMS is particularly useful for thick-film (10–100 μm) depth profiling. GDMS can provide accurate, sensitive, and matrix inde-
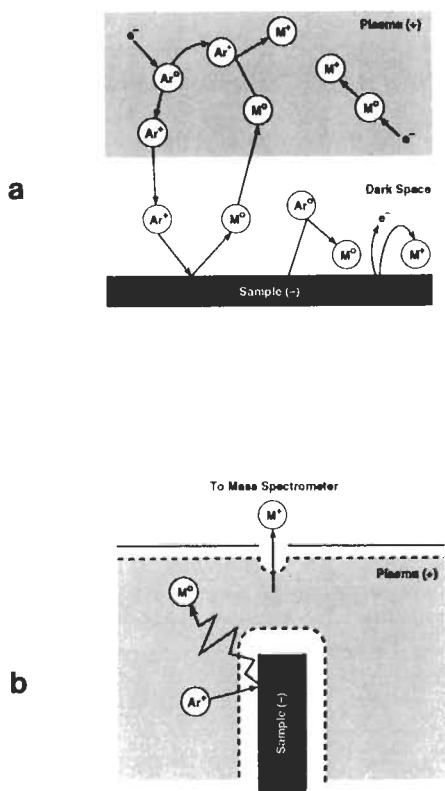
Figure 1   Schematic of DC glow-discharge atomization and ionization processes. The sample is the cathode for a DC discharge in 1 Torr Ar. Ions accelerated across the cathode dark space onto the sample sputter surface atoms into the plasma (a). Atoms are ionized in collisions with metastable plasma atoms and with energetic plasma electrons. Atoms sputtered from the sample (cathode) diffuse through the plasma (b). Atoms ionized in the region of the cell exit aperture and passing through are taken into the mass spectrometer for analysis. The largest fraction condenses on the discharge cell (anode) wall.

pendent concentration depth profiles throughout a complex film structure, including interfaces.

Mass Spectrometers

Demonstration of GDMS feasibility and research into glow-discharge processes has been carried out almost exclusively using the combination of a glow-discharge ion source with a quadrupole mass spectrometer (GDQMS). The combination is inexpensive, readily available and suitable for such purposes. In addition, the quadru-

pole provides the advantage of rapid mass spectrum scanning for data acquisition. Because ion transmission is limited and significant molecular ion mass interferences are unresolvable with the low mass resolution capabilities of the quadrupole, elemental detection limits by GDQMS are only slightly better than those provided by Optical Emission Spectroscopy (OES) methods, and the analytical usefulness of the GDQMS overlaps that of OES techniques (cf. Jakubowski, et al.[1]). Even so, the full elemental response of GDMS provides a substantial enhancement in analytical capability compared to the more selective OES. The introduction of GDMS instrumentation using high mass resolution, high-transmission magnetic-sector mass spectrometers has circumvented the major limitations of the quadrupole, providing an instrument with sub-ppb detection limits, albeit at the expense of analytical time. GDMS instrument and source descriptions have recently been the subject of an extensive review by Harrison and Bentz.[2]

The optimal analytical GDMS instrument for bulk trace element analysis is the one providing the largest analytical signal with the lowest background signal, the fewest problems with isobaric interferences in the mass spectrum (e.g., the interference of $^{40}Ar^{16}O^+$ with $^{56}Fe^+$), and the least contamination from instrument components or back contamination from preceding sample analyses. The first commercial GDMS instrument incorporated a high mass resolution magnetic-sector mass spectrometer to enable interfering isobaric masses to be eliminated, while at the same time providing high useful ion yields. The ion detection system of this instrument combined a Faraday cup collector, for the direct current measurement of the large ion beam associated with the matrix element, with a single-ion counting capability to measure the occasional trace element ion. The resulting ion current measuring system provides the necessary large dynamic range for matrix to ultratrace level measurements.

Instrument configurations other than a magnetic-sector mass spectrometer with a pin sample source are also suitable for analytical GDMS, but with some compromise in analytical performance. If analysis to ultratrace levels is not required, but only measurements to levels well above the background of isobaric mass spectral interferences, low-resolution quadrupole mass spectrometer based instruments can be configured. Such instruments have recently been made available by several instrument manufacturers. In these cases, the unique advantage of GDMS lies not with the ultratrace capability but with the full elemental coverage from matrix concentrations to levels of 0.01–0.1 ppm. Also, quadrupole MS mass spectral analysis requires significantly less time, enabling the more rapid analysis suitable for depth profiling of films.

Sample Preparation and Analytical Protocol

Accurate GDMS analysis has required the development of analytical procedures appropriate to the accuracy and detection limits required and specific to the mate-

rial under analysis. Protocol particulars will differ from laboratory to laboratory. To use GDMS to advantage (i.e., to improve measurements to the ppb level) the surface exposed to the sampling plasma must be very clean. Common methods for surface cleaning are chemical etching and electropolishing using high-purity solutions. If such cleaning is not feasible (e.g., for pressed powders), presputtering of the surface in the glow-discharge source or with a separate sputtering unit to remove contaminants prior to analysis is generally required. (This procedure could not, of course, be used prior to concentration depth profiling measurements.) The risk of recontamination to ppb levels is high, and care must be taken in rinsing, handling, and transporting the cleaned sample.

The composition of the sample measured by GDMS reflects the surface composition, and the argument must be made that the measurement is representative of the bulk. This requires thorough sputter cleaning of residual contaminants and sputter equilibrium of the phases exposed at the surface. The pragmatic (and reasonably conservative) criterion that both goals have been accomplished is that the same composition has been obtained in consecutive measurements during the analysis (i.e., a "confirmed" analysis). Other than these requirements, the analysis protocol must be suitable for the instrument and the detection limits required, since in many instances the detection limit arises from lack of signal and not from backgrounds or interferences.

Accurate final results from GDMS are available very quickly. Samples for GDMS analysis requires little preparation other than shaping and cleaning, although the cutting of a pin or wafer from extremely hard materials can be time consuming. The actual GDMS analysis takes only on the order of one to two hours, depending on elemental coverage and detection limits required. Data reduction is on-line and essentially immediate.

GDMS Quantitation

Pragmatically, the relative concentrations of elements are determined from the measured ion beam ratios by the application of relative sensitivity factors, which are determined experimentally from standard samples:

$$\frac{M}{N} = \frac{I(M)}{I(N)} \, \mathrm{RSF}_N(M)$$

where M and N are the elements of concern, I is the measured ion current (including all isotopes of the element), and $\mathrm{RSF}_N(M)$ is the relative sensitivity factor for M relative to N.

Vieth and Huneke[3] have recently presented a thorough discussion of GDMS quantitation, including the measurement of relative GDMS sensitivity factors and a modeling of glow-discharge source processes to enable semiempirical estimates of
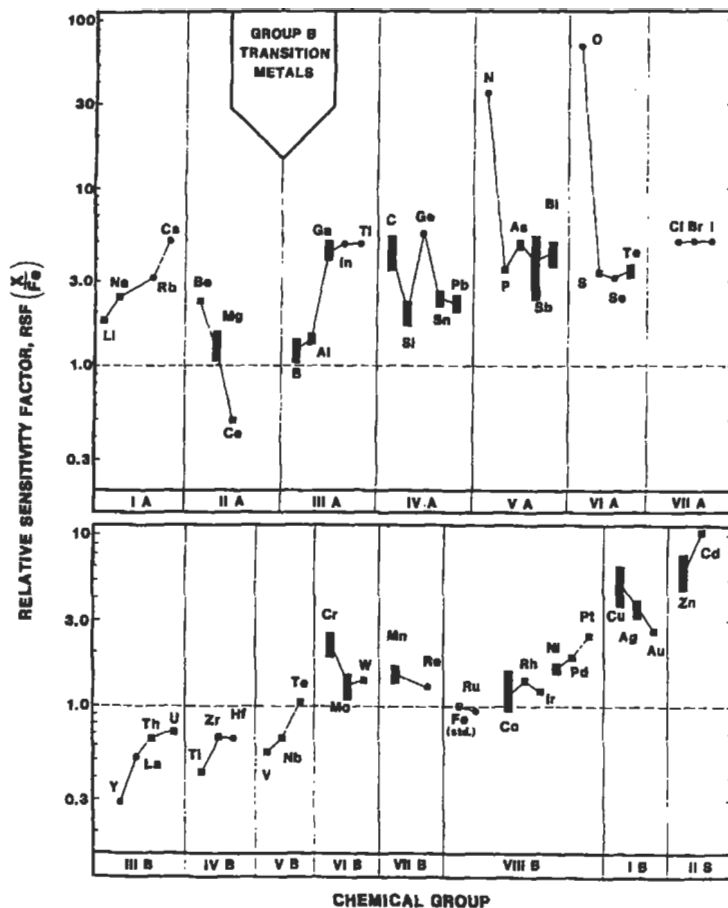
Figure 2   Elemental relative sensitivity factors as a function of chemical grouping in the periodic table. The factors are determined from the measurement of 30 standard samples representing 6 different matrix elements. The factors are matrix-independent and similar within a factor of 10, except for C and O. There is a pronounced trend across the group-B elements, with a similar but separate trend across the group-A elements.

RSFs. Figure 2 exhibits the average RSFs determined from analyses of 30 different standard samples of seven different matrices. The RSFs are matrix independent, with the spread in RSF determinations being due primarily to standard alloy inhomogeneities. It is remarkable that for all but N and O the factors range over only a decade.

The sensitivity factors summarized in Figure 2 are appropriate for analyses using a particular instrument (the VG 9000 GDMS) under specific glow-discharge conditions (3 mA and 1000 V in Ar, with cryocooling of the ion source) and with a well-controlled sample configuration in the source. RSFs depend on the sample–source configuration. In particular, they vary significantly with the spacing between the sample and the ion exit aperture from the cell. Use of the factors shown in Figure 2 under closely similar conditions will result in measurements with 20% accuracy. These factors can also be used to reduce the data obtained on other instruments, but the accuracy of the results will be reduced. In particular, the factors shown can be only approximately valid for results obtained using a quadrupole mass spectrometer, since ion-transmission characteristics differ significantly between the quadrupole mass spectrometer and the magnetic-sector spectrometer used to obtain the results of Figure 2.

It is clear from the RSF data shown in Figure 2 that even without the use of RSFs, a semiquantitative analysis accurate to within an order of magnitude is quite possible, and GDMS indeed will provide full coverage of the periodic table. The analysis of a material of unknown composition will be elementally complete to trace levels, with no glaring omissions that may eventually return to haunt the end user of the material.

Applications

The application of GDMS is strongest in the areas of:

1 Qualification of 5N–7N pure metals, since GDMS provides full elemental coverage to ultratrace levels

2 The analysis of specific elements for which GDMS is particularly well suited compared to other methods (e.g., measurement to ppb levels of S, Se, Te, Pb, Bi, Tl, in high-performance alloys; and measurement of U and Th in sputter targets)

3 The analysis of a material known to be impure, but with unspecified impurity elements

4 The analysis of a material in limited supply, and when too little is available for analysis by alternative methods.

A number of examples of the application of GDMS to various metals and alloys are exhibited below. All measurements were performed using the VG 9000 GDMS instrument with standard glow-discharge conditions of 3-mA discharge current and 1000-V discharge voltage except as noted. The standard pin dimensions were a diameter of 1.5–2.0 mm and a length of 18–22 mm.

Indium and Gallium Metal

Table 1 summarizes the results of an analysis to the 6N–7N total impurity level of very high purity In and Ga metals, such as would be used in the manufacture of III–

Element	Concentration (ppmw) In	Ga	Element	Concentration (ppmw) In	Ga
Li	<0.00006		Y	<0.00001	<0.00008
Be	<0.0001	<0.0005	Zr	<0.00006	<0.0003
B	0.002	<0.0003	Nb	<0.00009	<0.0001
C	(<20.)	(<0.9)	Mo	0.001	<0.001
N	(<200.)	(<20.)	Ru	<0.0002	<0.0006
O	(<60.)	(<8.)	Rh	<0.00006	<0.0003
F	(<0.2)	(<0.04)	Pd	<0.0003	<0.06
Na	0.005	0.05	Ag	0.001	<0.3
Mg	<0.00009	0.002	Cd	<0.004	<0.01
Al	0.002	0.005	In	Matrix	3.3
Si	0.005	0.03	Sn	<0.003	0.28
P	<0.0001	<0.0006	Sb	<0.002	<0.001
S	<0.0002	<0.0008	Te	<0.003	0.006
Cl	(<2.)	(<0.9)	I	0.001	<0.001
K	<0.001	<0.005	Cs	<0.02	<0.0005
Ca	<0.002	0.02	Ba	<0.0003	<0.04
Sc	<0.00001	<0.0005	La	<0.0002	<0.0003
Ti	0.001	0.001	Ce	0.00004	<0.005
V	<0.00002	<0.0001	Nd	<0.0001	<0.01
Cr	<0.0001	<0.0005	Hf	<0.0001	<0.0005
Mn	<0.00007	<0.0003	Ta	(<3.)	(<0.3)
Fe	0.0003	<0.0004	W	<0.0002	<0.0009
Co	<0.00004	<0.0002	Re	<0.00007	<0.0004
Ni	0.07	<0.001	Os	<0.0001	<0.0009
Cu	0.0007	0.04	Ir	<0.0001	<0.003
Zn	0.006	<0.003	Pt	<0.0003	<0.001
Ga	<0.0004	Matrix	Au	<0.002	<0.01
Ge	<0.002	<0.03	Hg	<0.0005	<0.005
As	<0.0009	<0.001	Tl	0.064	<0.001
Se	<0.02	<0.007	Pb	0.18	0.16
Br	<0.001	<0.04	Bi	0.004	0.008
Rb	<0.00005	<0.007	Th	<0.00003	<0.0001
Sr	<0.00002	<0.0001	U	<0.00003	<0.0001

Table 1 Analysis of very high purity In and Ga metal by GDMS (VG 9000). Only three lanthanide elements have been measured as characteristic of all of the lanthanides. Concentrations preceded by a limit sign were not detected above the instrument background. The detection of elements included in parentheses were limited by instrumental or atmospheric contamination.

V semiconductor material (e.g. InGaAs semiconductor). Very high purity Ga and In are required for the manufacture of semiconductor grade GaAs substrate material and in the deposition of the III–V alloy epilayer structures on these substrates, for example for the manufacture of laser diodes.

The analysis of Ga requires careful sample preparation to avoid altering the composition during solidification of the sample pin and preparation for analysis. The Ga pin was formed by drawing molten Ga into Teflon tubing and quickly freezing the Ga with liquid nitrogen. The low melting points of both metals requires analysis using low power and cryocooling of the discharge cell.

Some 70 elements are surveyed for their presence as impurities, and the detection limits must be on the order of 0.001–0.01 ppmw to qualify the material at the 6N–7N level. (The designation 6N is equivalent to specifying a total impurity content less than 1 ppmw; the metal is thus at least 99.9999% pure). The table shows mainly detection-limited values. The strict limit sign denotes the absence of an identifiable signal above the noise limit. Better limits result for elements with higher useful ion yields. Lower useful ion yields, or the need to measure a minor isotope (cf., Sn) results in a degradation of the detection limit. The detection of several elements is limited by contamination in the ion source. The gaseous atmospheric species are present at low, but not insignificant levels in the plasma gas. Ta and Au are obscured by Ta and TaO sputtered from source components. If all source components are not rigorously cleaned of material sputtered in previous analyses, residual material from these analyses will be observed at 0.1–10 ppm levels in the present analysis.

It is important to emphasize that GDMS provides an essentially complete elemental impurity survey to very low detection limits in a timely, cost effective manner. Although this level of analysis requires long signal integration times, the Ga measurement requires only a few hours to obtain an accurate, confirmed analysis to 7N levels. Except for the presence of rather high In in the Ga, the remaining impurities are at sub ppmw levels. Detection limits in the Ga are clearly adequate for 7N qualification.

The results of the analysis of 3N5 and 6N pure In metals for selected elements are summarized in Table 2. These measurements illustrate the precision possible when the impurity signals are given additional signal integration time at the cost of elemental coverage. The precision of GDMS elemental analysis for the homogeneously distributed impurities is much better than 5% to ppbw concentration levels. At lower levels the standard deviation increases due to detector noise and ion counting statistics, but the precision is still acceptable even at ppt levels. This data illustrate the trade-off between elemental coverage and improved detection limits. Very good detection limits can be obtained for almost all elements, but the time investment to achieve sub-ppb detection limits over the full elemental survey is substantial and not normally cost effective.

Element	Concentration (ppmw)	Standard deviation (%)	Element	Concentration (ppmw)	Standard deviation (%)
	3N5 (99.95%)			6N (99.9999%)	
Fe	0.038	4.7	Al	0.00056	33.
Ni	0.366	1.5	Fe	0.00025	25.
Cu	0.683	4.1	Ni	0.072	3.7
Cd	0.453	1.7	Cu	0.0069	9.6
Sn	20.5	0.6	Sn	0.0019	23.
Tl	0.698	1.9	Sb	0.0021	14.
Pb	61.3	1.3	Tl	0.044	5.4
Bi	0.202	1.7	Pb	0.066	3.4

Table 2 Precision of trace elemental analysis of 3N5 (99.95%) and 6N (99.9999%) pure In metals by GDMS (VG 9000). The data are the average of five measurements. The integration time per isotope per measurement was 500 ms (3N5 In) and 1500 ms (6N In), respectively.

Semiconductors

The results of GDMS analysis of several types of semiconductor substrates is shown in Table 3. Silicon is the most commonly used of these semiconductors. Gallium phosphide and ZnTe provide examples of III–V and II–VI semiconductors, respectively. The absence of the transition metals in particular is very important to the proper functioning of devices built on these substrates. Consequently, the detection limits for the full range of metals must be very good. GDMS provides detection limits at the ppb and lower levels. The detection limits in Si are significantly worse than the detection limits in the other two semiconductors, reflecting the fact that the sputter sampling rate, and thus the analytical signal of the Si, is significantly lower than for the other material. The Si results also provide an example for which the detection limit has been determined by a matrix-specific mass spectral interference (e.g., the $SiAr^{++}$ ions interfere with the measurement of the S^+ ions and are not mass resolvable.) While such interferences may limit the measurement of a particular impurity in a particular matrix, they are not the general rule.

TiW Sputtering Target and W Metal Powder

The results of a GDMS analysis of high-purity TiW are summarized in Table 4. High-purity TiW is very commonly used as the metallization to provide the conducting links in the construction of semiconductor devices. The metallization is commonly deposited by sputtering from a high-purity alloy target onto the sub-

| | Concentration (ppmw) | | | | Concentration (ppmw) | | |
Element	Si	GaP	ZnTe	Element	Si	GaP	ZnTe
Li	<0.007	<0.0004	0.013	Y	<0.001	<0.00007	<0.00005
Be	<0.003	<0.0005	<0.0001	Zr	<0.003	<0.0003	<0.0003
B	<0.006	75.	0.002	Nb	<0.002	<0.002	<0.0004
C	(<5.)	(<5.)	(<3.)	Mo	<0.01	<0.001	<0.001
N	(<50.)	(<10.)	(<30.)	Ru	<0.009	<0.001	<0.001
O	(<60.)	(<10.)	(<30.)	Rh	<0.005	<0.001	<0.003
F	(<0.04)	(<0.8)	(<0.002)	Pd	<0.01	<0.002	<0.006
Na	<0.01	0.033	<0.019	Ag	<0.01	<0.05	<0.001
Mg	<0.006	<0.0004	0.004	Cd	<0.04	<0.004	<0.005
Al	<0.009	0.006	0.011	In	<0.007	<0.01	<0.1
Si	Matrix	0.008	0.024	Sn	<0.03	<0.004	<0.006
P	<0.01	Matrix	<0.002	Sb	<0.03	<0.002	<0.02
S	<0.1	0.9	<0.006	Te	<0.01	<0.007	Matrix
Cl	(<3.)	(<1.)	(<0.7)	I	<0.01	<0.0008	<0.04
K	<0.01	0.008	0.004	Cs	<0.003	<0.0002	<0.002
Ca	<0.03	<0.007	<0.04	Ba	<0.002	<0.0008	<0.003
Sc	<0.001	<0.00007	<0.0003	La	<0.001	<0.00009	<0.007
Ti	<0.002	0.0006	<0.0008	Ce	<0.009	<0.0006	<0.002
V	<0.002	<0.0002	<0.0001	Nd	<0.002	<0.0005	<0.01
Cr	<0.005	<0.0006	<0.002	Hf	<0.008	<0.0005	<0.0003
Mn	<0.005	0.002	<0.0007	Ta	(<7.)	(<7.)	(<3.)
Fe	<0.02	0.01	0.04	W	<0.008	<0.001	<0.0005
Co	<0.003	<0.0002	<0.0002	Re	<0.006	<0.0003	<0.0002
Ni	<0.01	<0.0005	0.003	Os	<0.005	<0.0007	<0.002
Cu	<0.015	<0.004	0.12	Ir	<0.01	<0.0007	<0.001
Zn	<0.03	<0.002	Matrix	Pt	<0.01	<0.002	<0.02
Ga	<0.02	Matrix	0.019	Au	<0.03	<0.009	<0.01
Ge	<0.06	<0.03	<0.02	Hg	<0.02	<0.003	<0.001
As	0.075	1.2	<0.0007	Tl	<0.01	<0.002	<0.0005
Se	<0.06	<0.007	0.4	Pb	<0.01	<0.001	<0.001
Br	<0.04	<0.005	<0.002	Bi	<0.008	<0.0006	<0.0002
Rb	<0.005	<0.0003	<0.0002	Th	<0.002	<0.0002	<0.00007
Sr	<0.002	<0.0001	<0.0001	U	<0.003	<0.0002	<0.00008

Table 3 **Results of GDMS analyses for impurities in three high-purity semiconductor substrates. Lower detection limits are achieved for materials with higher sputtering rates.**

Element	Concentration (ppmw)		Element	Concentration (ppmw)	
	TiW	W		TiW	W
Li	<0.0006	<0.005	Y	<2.	<0.00007
Be	<0.0007	<0.005	Zr	<0.04	≤0.005
B	0.03	0.014	Nb	<0.01	<0.003
C	(<12.)	(<9.)	Mo	0.68	0.47
N	(<14.)	(2.)	Ru	<0.0007	<0.0007
O	(<170.)	(50.)	Rh	<0.0003	<0.0003
F	(<0.2)	(<0.1)	Pd	<0.002	<0.002
Na	<0.01	0.02	Ag	<0.002	<0.004
Mg	<0.001	0.17	Cd	<0.008	<0.007
Al	0.27	≤0.08	In	<0.001	0.005
Si	1.2	0.34	Sn	0.04	0.07
P	2.5	1.0	Sb	<0.002	<0.002
S	0.3	0.01	Te	<0.01	<0.003
Cl	(<8.)	(<0.5)	I	<0.001	<0.001
K	<0.02	<0.06	Cs	<0.0006	<0.0006
Ca	<0.03	0.33	Ba	0.002	0.005
Sc	<0.005	0.00006	La	<0.0001	<0.0001
Ti	Matrix	0.35	Ce	<0.0001	<0.0001
V	0.19	0.004	Nd	<0.0006	<0.0006
Cr	3.7	0.03	Hf	0.004	<0.008
Mn	0.92	0.026	Ta	(<90.)	(<20.)
Fe	6.	0.26	W	Matrix	Matrix
Co	0.02	0.001	Re	<0.2	<0.06
Ni	0.87	0.11	Os	<0.009	<0.01
Cu	0.3	<0.01	Ir	<0.0008	<0.004
Zn	≤0.06	<0.01	Pt	<0.002	<0.05
Ga	<0.003	0.02	Au	<0.05	<0.02
Ge	<0.003	<0.003	Hg	<0.08	<0.07
As	0.40	0.14	Ti	<0.001	<0.002
Se	<0.005	<0.04	Pb	<0.001	≤0.005
Br	<0.01	<0.01	Bi	<0.0009	<0.001
Rb	<0.01	<0.0008	Th	<0.00004	0.0003
Sr	<40.	<0.001	U	<0.00003	0.00008

Table 4   **Results of GDMS analyses for impurities at the 4N–5N level in a TiW sputter target and a W metal powder. The W analysis required a pressed pin sample (1 mm × 1 mm x 10 mm). The dependence of RSFs on pin–aperture spacing require a different RSF suite for proper quantitation. Detection limits for U and Th have been improved using longer integration times.**

strate; the sputter target alloy must typically be at least 4N–5N pure. The impurity content of the transition metals in particular must be kept low. It is also a common requirement that the U and Th in these metallizations must be below 1 ppb total (U + Th). GDMS is particularly adept at combining measurements for total impurity qualification with the measurement of selected elements at ultratrace levels. In this instance it is also the case that the detection limits for the gaseous species, which are relatively high because of instrument background, are nonetheless adequate for the qualification of the metal for low C, N, O, F, and Cl contents. The accuracy of the elemental concentration determination is independent of the amount present, and GDMS can provide the contents of alloying elements as well as of impurity elements. The accuracy of GDMS analysis (better than 20%) is generally suitable for confirming alloy type.

The results of GDMS analysis for the qualification of W metal powder as incorporated, for example, into such TiW sputter targets is also presented in Table 4. The powder must be formed into a self-supporting pin, which can be done using an appropriate polypropylene die and suitably high pressures. The pressing procedure must be clean, so as to not compromise the analysis. As a further complication, the surface of the pressed pin cannot be cleaned in the "normal" way, by etching the surface. Instead, the surface must be presputtered in the GDMS source for some time to reduce surface contaminants to acceptable levels. Many impurity elements are present in the W powder at 0.1–1 ppmw levels. GDMS is capable of accurate measurement to much lower levels, as indicated by the ppbw detection limits of many of the elements. Very low detection limits are required if qualification analysis to 6N and lower impurity levels is to include essentially all elements. For many elements, detection limits depend on the specific matrix being analyzed. For example, the presence of ions of $TiAr^{++}$ interferes with the measurement of the Ca^+ ions, and the corresponding detection limit on Ca is relatively high.

If the critical impurities are known, then only a selected list of elements need to be examined, with some improvement in the cost effectiveness of the analysis. However, the list of elements to be included in the qualification analysis is often historical and related to the limitations of the analytical methods previously used for qualification rather than for technological reasons related to the end use of the metal. As a result, problems in application can arise for no obvious reason. The time and cost of extending the impurity list for GDMS analysis to include essentially all elements is minimal, considering the additional information gained.

The analysis of nonconducting material using a DC glow-discharge source can be carried out in a manner similar to the analysis of the W powder. The sample must be ground to a fine powder, with care taken to minimize contamination, and then mixed with a high-purity, electrically conducting powder, such as Ag, to obtain an electrically conducting pin. The analysis of the nonconducting material by this method is limited mainly by the presence of corresponding impurities in the binding metal.

Conclusions

GDMS has now become a well-established analytical technique for direct multielemental analysis of conducting solids. Glow-discharge instruments incorporating high mass resolution magnetic mass spectrometers as well as quadrupole mass spectrometers are now commercially available. With high mass resolution GDMS, the quantitative measurement of essentially all elements in a single analysis with detection limits in the sub-ppbw concentration range is possible. With appropriate analytical protocol the time required for an elemental survey analysis to ppb limits is 1–2 hours, with an average accuracy not worse than 20%. Direct determinations in the pptw concentration range for single elements are also routinely possible for many elements, the primary consideration being analysis time and cost of analysis. GDMS has become a viable, and in many cases, preferable mode of analysis largely through the analytical capabilities brought by high mass resolution. With similar accuracy, glow-discharge quadrupole mass spectrometry with low mass resolving power provides a more rapid analysis compatible with thick-film depth profiling requirements. With nominal detection limits of 10–100 ppb and full elemental coverage, GDQMS offers a significant improvement on optical analytical methods.

Comparable mass spectrometric methods for solids analysis are spark-source (SSMS), Inductively Coupled Plasma (ICP-MS), and Secondary Ion Mass Spectrometry (SIMS). Of these, GDMS and SSMS are most similar in capability, but GDMS provides a 1–2 orders-of-magnitude better detection limit and an order-of-magnitude improvement in measurement accuracy. SIMS is generally hampered by extremely variable and matrix-dependent elemental sensitivities, and very limited sampling volume. However, SIMS does offer sub-ppb detection limits for selected elements, as well as microanalytical capability. ICP-MS was developed primarily for the accurate ppt level analysis of liquid samples, but can be used for solids analysis by sample dissolution or by laser-ablation sampling, yielding ppb detection limits. The advantage of ICP-MS lies in the sample homogenization resulting from dissolution.

Analytical GDMS instrumentation will continue to develop in response to market demands and as application areas are explored more thoroughly. GDMS is in a time of rapidly expanding industrial acceptance in the area of high-purity metals characterization, and the analytical niche for GDMS seems well assured. Serious efforts are underway to expand this niche to include ppb-level measurements on insulating solids. While the use of GDMS for the chemical characterization of steels and similar alloys has been limited, GDQMS may play a useful role in this area as well as providing unique capabilities for the accurate quantitative analysis of thick-film structures.

Related Articles in the Encyclopedia

SSMS, ICPMS, ICP-Optical, and SIMS

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10.8   ICPMS

Inductively Coupled Plasma Mass Spectrometry

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Contents

- Introduction
- Basic Principles and Instrumentation
- Sampling
- Quantification
- Interferences
- Novel Sampling Techniques
- Conclusions

Introduction

The importance of the electrical and physical properties of materials has strained the limits of characterization techniques in general, and elemental analysis techniques in particular. This includes not only the analysis of surfaces, films, and bulk materials, but also of the chemicals, gases, and equipment used to form them. Often properties of a material are affected by doping levels in the 10^{14} range, which means characterization at the parts-per-billion (ppb) to sub-ppb levels. Inductively Coupled Plasma Mass Spectrometry (ICPMS) is capable of this degree of sensitivity and has developed in the same time frame that high-purity materials have developed. These materials probably have played a large part in pushing instrument development quickly from a research stage to fairly common usage and wide ranging applications.

ICPMS can be considered a high-sensitivity extension of mass spectrometry, as well as an increased-sensitivity detector replacing optical ICP (ICP-OES) analysis. In fact, both viewpoints are accurate, and the wide application of ICPMS analysis

in the world of materials science is evidence of that. ICPMS is an extremely sensitive technique. In high-purity water, for example, detection limits for many elements are under 100 parts per trillion (ppt). In higher sensitivity instruments, the limits are under 10 ppt.

The information derived from ICPMS analysis is, simply, a mass spectrum of the sample. This includes a wealth of information, however. In one sampling, which can take less than one minute, information on almost all elements in the periodic table can be derived to at least low ppb levels. This *multiplexing* advantage is extraordinarily valuable in materials analysis as it can give one a good look at a sample quickly and with surprisingly good quantitation results. (Semiquantitative analysis will be discussed later.) The mass spectrum contains not only elemental information but also isotopic information for each element. This is useful for giving a positive identification of most elements, for identifying interferences, and for providing alternative masses for characterization.

Other techniques that give elemental analysis information include the more established optical methods such as Atomic Absorption (AA), Graphite Furnace Atomic Absorption (GFAA), emission spectroscopy, Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES), and X-Ray Fluorescence (XRF). Newer mass spectrometry based techniques include Spark Source Mass Spectrometry (SSMS), Glow Discharge Mass Spectrometry (GDMS), and Secondary Ion Mass Spectrometry (SIMS). Elemental information may also be gained from other techniques such as Auger electron spectroscopy and X-Ray Photoelectron Spectroscopy (XPS). Of course there are other methods and new ones are being developed continually. Each of these techniques is useful for the purposes they were intended. Some, such as AA, have advantages of cost; others, such as XRF, can handle samples with minimal sample handling. ICPMS offers the detection limits of the most sensitive techniques (in many cases greater sensitivity) and easy sample handling for most samples.

Basic Principles and Instrumentation

An ICPMS spectrometer consists of:
1 An inductively coupled plasma for sample ionization
2 A mass spectrometer for detecting the ions
3 A sample introduction system.

All of these components are critical to the high sensitivity found in ICPMS instruments. Figure 1 shows their arrangement.

Mass Spectrometer

The mass spectrometer usually found on ICPMS instruments is a quadrupole mass spectrometer. This gives high throughput of ions and resolutions of 1 amu. Only a
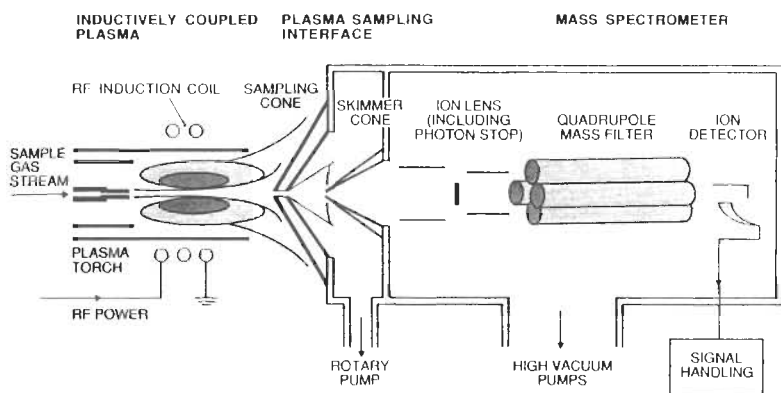
Figure 1   Schematic of an ICPMS.

relatively small mass range is required for analysis of materials broken down into their elemental composition as all atomic masses are below 300 amu.

A quadrupole mass spectrometer allows ions of a specific charge-to-mass ratio to pass through on a trajectory to reach the detector. This is accomplished by applying dc and rf potentials to four rods (hence the name quadrupole) that can be tuned to achieve different mass conductances through the spectrometer. The detector only counts ions, it is the quadrupole tuning that determines which ions are counted. The quadrupole can be tuned through a wide mass range quickly; a scan from 1 amu to 240 amu can take less than a second. An increased signal-to-noise ratio is accomplished by time averaging many scans.

Detectors used in ICPMS are usually electron multipliers operating in a pulse-counting mode. This gives a useful linear detector range of 10^6 (6 orders of magnitude). Some instruments can also use these detectors in an analog mode that is less sensitive. A combination of these modes allows an increase of operating range to over 10^8. This means that one can measure concentrations from 10 ppt to over a ppm in one sample. Another method of increasing the range is by using a Faraday detector in combination with the pulse counting, giving a 10^{10} range.

Two vacuum systems are used to provide both the high vacuum needed for the mass spectrometer and the differential pumping required for the interface region. Rotary pumps are used for the interface region. The high vacuum is obtained using diffusion pumps, cryogenic pumps, or turbo pumps.

Inductively Coupled Plasma

The inductively coupled plasma and the torch used in ICPMS are similar to that used in ICP-OES. In ICPMS, the torch is aimed horizontally at the mass spectrometer, rather than vertically, as in ICP-OES. In ICPMS the ions must be transported physically into the mass spectrometer for analysis, while in ICP-OES light is trans-

mitted to the entrance slits of the monochromator. Most ICPMS instruments operate on 27.15 kHz.

Interface

The part that marries the plasma to the mass spectrometer in ICPMS is the interfacial region. This is where the 6000° C argon plasma couples to the mass spectrometer. The interface must transport ions from the atmospheric pressure of the plasma to the 10^{-6} bar pressures within the mass spectrometer. This is accomplished using an expansion chamber with an intermediate pressure. The expansion chamber consists of two cones, a sample cone upon which the plasma flame impinges and a skimmer cone. The region between these is continuously pumped.

The skimmer has a smaller aperture than the sample cone, which creates a pressure of 10^{-2} atmospheres in the intermediate region. The ions are conducted through the cones and focused into the quadrupole with a set of ion lenses. Much of the instrument's inherent sensitivity is due to good designs of these ion optics.

Sampling

Sample introduction into the ionizing plasma is normally carried out in the same manner as for ICP-OES. An aqueous solution is nebulized and swept into the plasma.

Obtaining the aqueous solution to analyze is often a challenge in materials analysis. Thin films usually can be dissolved by acids without dissolving the underlying substrate, however sometimes this is difficult. A film can also be oxidized and the oxide dissolved. Temperatures involved in this procedure are sometimes quite elevated so care must be taken to maintain sample integrity. The chemistry of the sample must be kept in mind so that the limits of the analysis are known.

By far the most simple acid to work with in ICPMS is nitric acid. This has minimal spectral interferences and in concentrations under 5% does not cause excessive wear to the sample cones. Other acids cause some spectral interferences that often must be minimized by dilution or removal. When HF is used, a resistant sampling system must be installed that does not contain quartz.

Organic polymer materials may be analyzed by ashing at relatively high temperatures. This involves oxidation of the carbon containing matrix, leaving an inorganic residue that is taken up in acid. An alternative in some cases is to dissolve the polymer in solvent and analyze the nonaqueous solution directly. Nonaqueous media will be discussed in a later section.

Solutions may typically be analyzed with up to 0.2% dissolved solids. This means a dilution factor of 1000. For example, an element that will give a 0.1 ppb detection limit in deionized water will give a detection limit of 100 ppb in a film dissolved in acid and diluted to 0.1% solids.

The role of the nebulizer in ICPMS is to transform the liquid sample into an aerosol. This is carried into the plasma by an argon flow after passing through a

cooled spray chamber to remove excess vapor. Types of nebulizers in common use include Meinhard, DeGalen, and cross-flow nebulizers. A more novel nebulizer is the ultrasonic nebulizer.

Detection limits in ICPMS depend on several factors. Dilution of the sample has a large effect. The amount of sample that may be in solution is governed by suppression effects and tolerable levels of dissolved solids. The response curve of the mass spectrometer has a large effect. A typical response curve for an ICPMS instrument shows much greater sensitivity for elements in the middle of the mass range (around 120 amu). Isotopic distribution is an important factor. Elements with more abundant isotopes at useful masses for analysis show lower detection limits. Other factors that affect detection limits include interference (i.e., ambiguity in identification that arises because an elemental isotope has the same mass as a compound molecules that may be present in the system) and ionization potentials. Elements that are not efficiently ionized, such as arsenic, suffer from poorer detection limits.

There are fewer interferences in ICPMS, compared to other techniques. Because most elements have more than one isotope it is unusual to find an element that cannot be analyze: Several isotopes are almost always present. One of the most troublesome examples is the analysis of iron. Iron has three isotopes ^{54}Fe, ^{56}Fe, and ^{57}Fe; the most abundant by far is ^{56}Fe. These are all interfered with by argon molecules: ArN^+ at 54 amu, ArO^+ at 56 amu, and $ArOH^+$ at 57 amu. This gives detection limits of about 6–12 ppb for iron using ^{57}Fe rather than the < 0.1 ppb expected. Other interferences are almost always present, most involve molecular species formed by atmospheric constituents and argon. There are few interferences above 57 amu. The cone material, usually Ni, may also give a background peak. Matrix elements will give other interferences, for example, organic solvents give large interferences for ArC^+ at 52 amu, $Ar^{13}C^+$ st 53 amu, and CO_2^+ at 44 amu. A tungsten matrix will show tungsten isotope patterns for WO^+, WO_2^+, and WO_3^+.

Another type of interference in ICPMS is suppression of the formation of ions from trace constituents when a large amount of analyte is present. This effect depends on the mass of the analyte: The heavier the mass the worse the suppression.[1] This, in addition to orifice blockage from excessive dissolved solids, is usually the limiting factor in the analysis of dissolved materials.

Solvents

ICPMS offers a high-sensitivity method for the direct analysis of organic solvents. The large amount of carbon present introduces some problems unique to ICPMS. The need to transport ions directly from the plasma source into the mass spectrometer, and the small orifice needed to accomplish this, means that plugging is a problem. This is avoided by adding oxygen to the plasma, converting it from a reducing environment to an oxidizing one. Carbon dioxide is formed from the carbon. Other modifications include operating the spray chamber at a lower temperatures

and increasing the RF power to the plasma. New interferences arise in organic solvent matrices.[2]

Solids

Direct sampling of solids may be carried out using laser ablation.[3] In this technique a high-power laser, usually a pulsed Nd–YAG laser, is used to vaporize the solid, which is then swept into the plasma for ionization. Besides not requiring dissolution or other chemistry to be performed on the sample, laser ablation ICPMS (LA-ICPMS) allows spatial resolution of 20–50 µm. Depth resolution is 1–10 µm per pulse. This aspect gives LA-ICPMS unique diagnostic capabilities for geologic samples, surface features, and other inhomogeneous samples. In addition minimal, or no, sample preparation is required.

Laser sampling is more a physical phenomenon than a chemical one. The energy of the laser is used to nonselectively ablate the sample. This insures homogeneous sampling of a physically defined area regardless of the nature of the components: Solubilities are not a factor. This technique shows much promise for ceramics, glasses, and geologic samples.

Another method devised for direct sampling of solids involves direct insertion of the sample into the plasma.[4, 5] In this procedure the sample is delivered through the central tube of the torch. The sample may be premixed with graphite powder.

Gases

Recently the high sensitivity of ICPMS has been applied to gas phase samples. This development has been driven mostly by new generation semiconductor processes, which use chemical vapor deposition techniques rather than the previously more common physical deposition techniques (i.e., sputtering). As geometries in devices shrink, more stringent purity is required for chemical precursors. Many of the gases and vapors are highly reactive, complicating the analysis.

One way to analyze gases is to simply add the gas or vapor to the plasma torch where the nebulized aqueous sample ordinarily would be introduced. This works for some gases but results in a dry plasma. It is difficult to know how the instrument is responding to the sample or how significant suppression effects are. For organometallic vapors the same problems arise as in sampling organic solvents. Carbon build-up on the sampling cone can plug the orifice into the mass spectrometer. Organometallic samples often react violently with oxygen or water and care must be taken when adding oxygen to the system to alleviate carbon deposition.

These problems are overcome through the use of a torch designed for both stable and reactive gases and vapors. The torch, which is shown in Figure 2, has an insertion tube to introduce the gas phase sample immediately preceding the plasma. It is mixed within the torch with an aqueous standard introduced through the nebulizer in the normal manner. The reactive gas or vapor will oxidize in the mixing region of the torch and be swept into the plasma for ionization and analysis. The standard
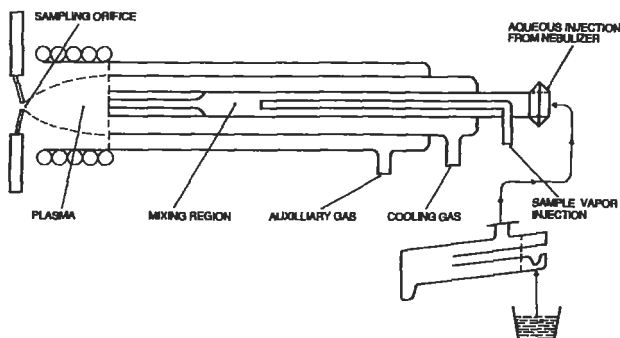
Figure 2   Gas–vapor sampling torch.

acts as an external measure of instrument performance and sensitivity.[6] Another innovation in the analysis of gases involves the use of a ceramic sample cone that maintains a higher temperature than metal cones during operation to minimize plugging, allowing a more concentrated sample to be used.[7]

Quantitation

One of the important advantages of ICPMS in problem solving is the ability to obtain a semiquantitative analysis of most elements in the periodic table in a few minutes. In addition, sub-ppb detection limits may be achieved using only a small amount of sample. This is possible because the response curve of the mass spectrometer over the relatively small mass range required for elemental analysis may be determined easily under a given set of matrix and instrument conditions. This curve can be used in conjunction with an internal or external standard to quantify within the sample. A recent study has found accuracies of 5–20% for this type of analysis.[8] The shape of the response curve is affected by several factors. These include matrix (particularly organic components), voltages within the ion optics, and the temperature of the interface.

Full quantitation is accomplished in the same manner as for most analytical instrumentation. This involves the preparation of standard solutions and matching of the matrix as much as possible. Since matrix interferences are usually minimized in ICPMS (relative to other techniques), the process is usually easier.

ICPMS is uniquely able to borrow a quantitation technique from molecular mass spectrometry. Use of the isotope dilution technique involves the addition of a spike having a different isotope ratio to the sample, which has a known isotope ratio. This is useful for determining the concentration of an element in a sample that must undergo some preparation before analysis, or for measuring an element with high precision and accuracy.[9]

Conclusions

ICPMS is a relatively new technique that became useful and commercially available early in its development. As a result, the field is continually changing and growing. The following is a summary of the directions of ICPMS instrumentation as described by three commercial instrument representatives.[10]

Trends in instrumentation are toward both lower and higher cost. Lower cost instruments may have limited capabilities, including less sensitivity than what is now typical of ICPMS. These instruments are used for the more routine types of analyses. Higher end instrumentation includes attaching the plasma source to a high-resolution magnetic sector mass spectrometer rather than a quadrupole. This avoids many mass-related interferences, such as occur for iron and calcium. Other instrument developments include improved ease of use, hardiness, and application specific software packages. Future improvements will include more extensive calculation software to correct for interferences by taking advantage of the large amount of isotopic information present. Combination instruments that offer a glow discharge source in addition to the ICP source have been introduced.

Like all techniques, ICPMS sampling is moving toward many hyphenated techniques. ICPMS instruments have been combined with flow injection analysis, electrothermal vaporization, ion chromatography, liquid chromatography, and chelation chromatography. Laser ablation-ICPMS has been discussed earlier. New lasers combined with frequency doubling and quadrupling crystals are being developed.

Gases for mixing with argon, such as N_2 and Xe, have been the subject of study for some time. Some new instrumentation will incorporate manifolds for making this process easier. Other plasma developments include microwave-induced plasmas with He to eliminate interferences from argon containing molecular species.

ICPMS, although a young technique, has become a powerful tool for the analysis of a variety of materials. New applications are continually being developed. Advantages include the ability to test for almost all elements in a very short time and the high sensitivity of the technique.

Related Articles in the Encyclopedia

ICP-OES, XRF, SSMS, and GDMS

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10.9 ICP-OES

Inductively Coupled Plasma-Optical Emission Spectroscopy

JOHN W. OLESIK

Contents

- Introduction
- Basic Principles
- Sample Introduction
- Instrumentation—Detection Systems
- Limitations and Potential Errors
- Conclusions

Introduction

The Inductively Coupled Plasma (ICP) has become the most popular source for multielement analysis via optical spectroscopy[1,2] since the introduction of the first commercial instruments in 1974. About 6000 ICP-Optical Emission Spectrometry (ICP-OES) instruments are in operation throughout the world.

Approximately 70 different elements are routinely determined using ICP-OES. Detection limits are typically in the sub-part-per-billion (sub-ppb) to 0.1 part-per-million (ppm) range. ICP-OES is most commonly used for bulk analysis of liquid samples or solids dissolved in liquids. Special sample introduction techniques, such as spark discharge or laser ablation, allow the analysis of surfaces or thin films. Each element emits a characteristic spectrum in the ultraviolet and visible region. The light intensity at one of the characteristic wavelengths is proportional to the concentration of that element in the sample.

The strengths of ICP-OES are its speed, wide linear dynamic range, low detection limits, and relatively small interference effects. Automated instruments with

multiple detectors can determine simultaneously 40 or more elements in a sample in less than one minute. The relationship between emission intensity and concentration is linear over 5–6 orders of magnitude. Therefore, trace and minor elements often can be measured simultaneously without prior separation or preconcentration. Detection limits are similar or better to those provided by Flame Atomic Absorption (FAA) which generally detects one element at a time. Detection limits are typically better for Graphite-Furnace Atomic Absorption (GFAA) or Inductively Coupled Plasma Mass Spectrometry (ICPMS) than for ICP-OES. However, commercial GFAA instruments do not provide the simultaneous multielement capabilities of ICP-OES. ICPMS can provide nearly simultaneously analysis via rapid scanning or hopping between mass-to-charge ratios. Detection limits are generally better for ICP-OES than for X-Ray Fluorescence Spectrometry (XFS), except for S, P, and the halogens.

ICP-OES is a destructive technique that provides only elemental composition. However, ICP-OES is relatively insensitive to sample matrix interference effects. Interference effects in ICP-OES are generally less severe than in GFAA, FAA, or ICPMS. Matrix effects are less severe when using the combination of laser ablation and ICP-OES than when a laser microprobe is used for both ablation and excitation.

The accuracy of ICP-OES ranges from 10% using simple, pure aqueous standards, to 0.5% using more elaborate calibration techniques. Precision is typically 0.2–0.5% for liquid samples or dissolved solids and 1–10% for direct solid analysis using electrothermal or laser vaporization. ICP-OES is used in a wide variety of applications because of its unique speed, multielement analysis capability, and applicability to samples having a wide range of compositions. Trace and minor elements have been determined in a variety of metal alloys. ICP-OES also has been applied to geological samples. Trace metals have been measured in petroleum samples, as have impurities in nuclear materials. ICP-OES has been used for elemental analysis of superconductors, ceramics, and other specialty materials. The technique also has been widely applied to measure impurities in the raw materials and acids used in semiconductor processing.

Basic Principles

An ICP-OES instrument consists of a sample introduction system, a plasma torch, a plasma power supply and impedance matcher, and an optical measurement system (Figure 1). The sample must be introduced into the plasma in a form that can be effectively vaporized and atomized (small droplets of solution, small particles of solid or vapor). The plasma torch confines the plasma to a diameter of about 18 mm. Atoms and ions produced in the plasma are excited and emit light. The intensity of light emitted at wavelengths characteristic of the particular elements of interest is measured and related to the concentration of each element via calibration curves.
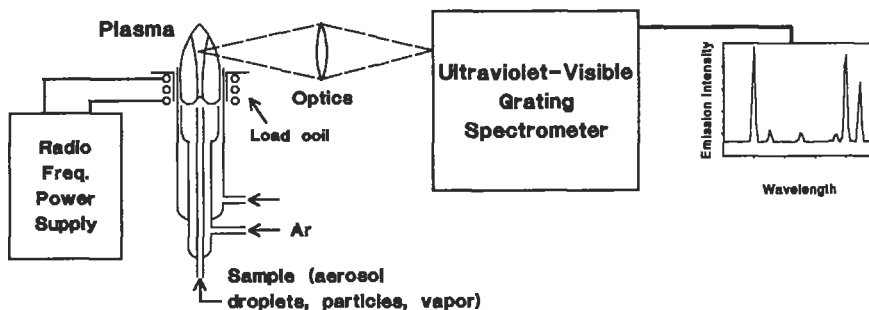
Figure 1   Instrumentation for inductively coupled plasma-optical emission spectrometry.

Plasma Generation and Sample Decomposition

The plasma is a high-temperature, atmospheric pressure, partially ionized gas. Argon is used most commonly as the plasma gas, although helium, nitrogen, oxygen, and mixed gas plasmas (including air) also have been used. The plasma is sustained in a quartz torch consisting of three concentric tubes (Figure 1). The inner diameter of the largest tube is about 18 mm. The outer and intermediate gases (typically, 10–16 L/min and 0–1 L/min Ar, respectively) are directed tangentially, producing a large swirl velocity resulting in efficient cooling of the quartz torch.[1, 2] The sample is carried into the center of the plasma through a third quartz or ceramic tube (with 0.7–1.0 L/min Ar), where it is introduced as a liquid aerosol (droplets less than 10 μm in diameter), fine powder, or vapor and particulates produced by laser or thermal vaporization.

The plasma is generated using a radiofrequency generator, typically at 27 or 40 MHz. Current is carried through a water cooled, three-to-five turn *load coil* surrounding the torch. Electrons in the plasma are accelerated by the resulting oscillating magnetic fields. Energy is transferred to other species, including the sample, through collisions.

In the plasma, the sample is vaporized and chemical bonds are effectively broken resulting in free atoms and ions. Temperatures of 5000–9000 K have been measured in the plasma compared to typical temperatures of 2000–3000 K in flames and graphite furnaces.

Generation of Emission Signals

Atoms and ions are excited via collisions, probably mainly with electrons, and then emit light. Most elements with ionization energies less than 8 eV exist mainly as singly charged ions in the plasma. Therefore, spectral lines from ions are most intense for these elements, whereas elements with high ionization energies (such as B, Si, Se and As), as well as the easily ionized alkalis (Li, Na, K, Rb, and Cs), emit most strongly as atoms.
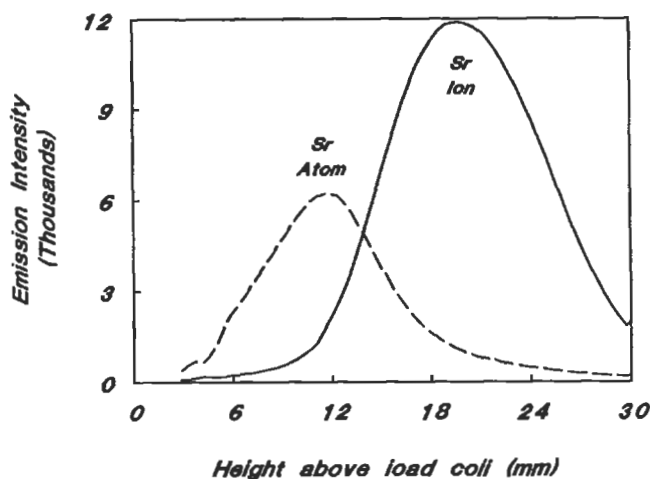
Figure 2   Emission intensity for Sr atom (460 nm) and Sr ion (421 nm) as a function of height about the load coil in a 1-kW Ar plasma.

Emission intensities depend on the observation height within the plasma Figure 2); the detailed behavior varies with the specific nature of the atom or ion. Emission from most ions peaks at nearly the same location, called the *normal analytical zone*, typically 10–20 mm above the top of the current-carrying induction coil. Similarly, atoms with high ionization energies (> 8 eV) or high excitation energies emit most intensely in the normal analytical zone. Emission usually is collected from a 3–5 mm section of the plasma near the peak emission intensity. Emission from atoms with low ionization energies and low excitation energies (Li, Na, K, Cs, and Rb) is most intense lower in the plasma. Unlike ion emission intensities, the atomic emission intensity peak location is a strong function of ionization and excitation energies.

Usually, the ultraviolet and visible regions of the spectrum are recorded. Many of the most intense emission lines lie between 200 nm and 400 nm. Some elements (the halogens, B, C, P, S, Se, As, Sn, N, and O) emit strong lines in the vacuum ultraviolet region (170–200 nm), requiring vacuum or purged spectrometers for optimum detection.

Quantitation

Calibration curves must be made using a series of standards to relate emission intensities to the concentration of each element of interest. Because ICP-OES is relatively insensitive to matrix effects, pure solutions containing the element of interest often are used for calibration. For thin films the amount of sample ablated by spark discharges or laser sources is often a strong function of the sample's composition. Therefore, either standards with a composition similar to the sample's must be used or an internal standard (a known concentration of one element) is needed.

0.1–1 ppb	1–10 ppb		10–50 ppb		50–100 ppb	100–500 ppb
Ba	Ag	Li	Al	Nb	As	Rb
Be	B	Lu	Au	Nd	K	U
Ca	Co	Mo	Bi	Ni	P	
Mn	Cu	Re	C	Pb	Pd	
Mg	Cd	Sc	Ce	Pr	S	
Sr	Cr	Ti	Cs	Pt	Se	
	Eu	V	Dy	Rh	Te	
	Fe	Y	Er	Ru	Tl	
	Ho	Yb	Ga	Sb		
	I	Zn	Ge	Si		
	La	Zr	Gd	Sm		
			Hf	Sn		
			Hg	Ta		
			In	Tb		
			Ir	Th		
			Na	W		

Table 1 Typical detection limits (ppb) for ICP-OES (using a pneumatic nebulizer for sample introduction) of the most sensitive emission line between 175 nm and 850 nm for each element.

Detection Limits

Typical elemental detection limits are listed in Table 1. The detection limit is the concentration that produces the smallest signal that can be distinguished from background emission fluctuations. The continuum background is produced via radiative recombination of electrons and ions ($M^+ + e^- \rightarrow M + h\nu$ or $M^+ + e^- + e^- \rightarrow M + e^- + h\nu$). The structured background is produced by partially or completely overlapping atomic, ionic, or in some cases, molecular emission. To obtain precision better than 10% the concentration of an element must be at least 5 times the detection limit.

Detection limits for a particular sample depend on a number of parameters,[1, 2] including observation height in the plasma, applied power, gas flow rates, spectrometer resolution,[3] integration time, the sample introduction system, and sample-induced background or spectral overlaps.[3]

Sample Introduction

Samples must be introduced into the plasma in an easily vaporized and atomized form. Typically this requires liquid aerosols with droplet diameters less than 10 μm, solid particles 1–5 μm in diameter, or vapors. The sample introduction method strongly influences precision, detection limits, and the sample size required.

Introduction of Liquids and Solutions of Dissolved Solids

Most often samples are introduced into the plasma as a liquid aerosol. Solid samples are dissolved using an appropriate procedure. Pneumatic nebulizers of various designs[1,2] generate aerosols by pumping or aspirating a flow of solution into a region of highly turbulent, high-speed gas flow. Concentric cross-flow nebulizers are used for solutions having less than 1% dissolved solids. V-groove (Babington) nebulizers can be used for highly viscous solutions having a high dissolved solid content. Most of the droplets produced by these nebulizers are too large to be vaporized effectively in the plasma; therefore, a spray chamber is used to remove large droplets via gravity and to cause them to impact onto the walls. The smallest droplets are able to follow the gas flow into the plasma. Typically only 1–2% of the sample reaches the plasma, and liquid sample volumes of 1 mL or more are required.

Flow injection techniques can be used to inject sample volumes as small as 10 μL into a flowing stream of water with little degradation of detection limits. Frit nebulizers[1, 2] have efficiencies as high as 94% and can be operated with as little as 2 μL of sample solution.

Electrothermal vaporization[1, 2] can be used for 5–100 μL sample solution volumes or for small amounts of some solids. A graphite furnace similar to those used for graphite-furnace atomic absorption spectrometry can be used to vaporize the sample. Other devices including boats, ribbons, rods, and filaments, also can be used. The chosen device is heated in a series of steps to temperatures as high as 3000 K to produce a dry vapor and an aerosol, which are transported into the center of the plasma. A transient signal is produced due to matrix and element-dependent volatilization, so the detection system must be capable of time resolution better than 0.25 s. Concentration detection limits are typically 1–2 orders of magnitude better than those obtained via nebulization. Mass detection limits are typically in the range of tens of pg to ng, with a precision of 10% to 15%.

There are advantages to direct solid sampling. Sample preparation is less time consuming and less prone to contamination, and the analysis of microsamples is more straightforward. However, calibration may be more difficult than with solution samples, requiring standards that are matched more closely to the sample. Precision is typically 5% to 10% because of sample inhomogeneity and variations in the sample vaporization step.

In the direct insertion technique,[1, 2, 4] the sample (liquid or powder) is inserted into the plasma in a graphite, tantalum, or tungsten probe. If the sample is a liquid, the probe is raised to a location just below the bottom of the plasma, until it is dry. Then the probe is moved upward into the plasma. Emission intensities must be measured with time resolution because the signal is transient and its time dependence is element dependent, due to selective volatilization of the sample. The intensity–time behavior depends on the sample, probe material, and the shape and location of the probe. The main limitations of this technique are a time-dependent background and sample heterogeneity-limited precision. Currently, no commercial instruments using direct sample insertion are available, although both manual and highly automated systems have been described.[4]

Arc and spark discharges have been used to ablate material from a solid conducting sample surface.[1, 2] The dry aerosol is then transported to the plasma through a tube. Detection limits are typically in the low ppm range. The precision attainable with spark discharges that sample over a relatively large surface area (0.2–1 cm^2) is typically 0.5% to 5.0%. Calibration curves are linear over at least 3 orders of magnitude, and an accuracy of 5% or better is realized. Commercial instruments are available. In some cases it is possible to use pure aqueous standards to produce the calibration curves used for spark ablation ICP-OES. In general, calibration curves for spark or arc ablation followed by ICP-OES are more linear and less sample matrix-dependent than calibration curves in spark or arc emission spectrometry.

A vapor sample and dry aerosol also can be produced from surfaces via laser ablation.[1, 2] Typically, solid state pulsed Nd–YAG, Nd–glass, or ruby lasers have been used. The amount of material removed from the sample surface is a function of the sample matrix and the laser pulse energy, wavelength and focusing, but is usually in the μm range. Part-per-million detection limits are possible, and the technique is amenable to conducting and nonconducting samples. Precision is typically 3% to 15%. Shot-to-shot laser pulse energy reproducibility and sample heterogeneity are the two main sources of imprecision in this technique.

Instrumentation—Detection Systems

Three different types of grating spectrometer detection systems are used (Figure 3): sequential (slew-scan) monochromators, simultaneous direct-reading polychroma-
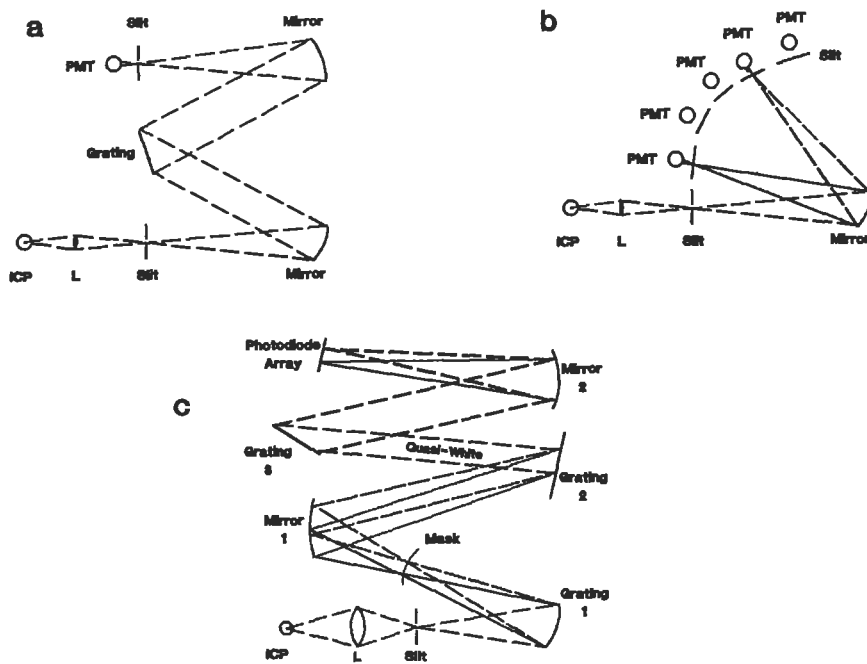
Figure 3   Grating spectrometers commonly used for ICP-OES: (a) monochromator, in which wavelength is scanned by rotating the grating while using a single photomultiplier tube (PMT) detector; (b) polychromator, in which each photomultiplier observes emission from a different wavelength (40 or more exit slits and PMTs can be arranged along the focal plane); and (c) spectrally segmented diode-array spectrometer.

tors, and segmented diode array-based spectrometers. The choice detection system depends on the number of samples to be analyzed per day, the number of elements of interest, whether the analysis will be of similar samples or of a wide range of sample types, and whether the chosen sample-introduction system will produce steady-state or transient signals.

Slew-scan spectrometers (Figure 3a) detect a single wavelength at a time with a single photomultiplier tube detector.[1,2] The grating angle is rapidly slewed to observe a wavelength near an emission line from the element of interest. A spectrum is acquired in a series of 0.01–0.001 nm steps. The peak intensity is determined by a fitting routine. Background emission can be measured near the emission line of interest and subtracted from the peak intensity. The advantage of slew-scan spectrometers is that any emission line can be viewed, so that the best line for a particular sample can be chosen. Their main disadvantage is the sequential nature of the multielement analysis and the time required to slew from one wavelength to another (typically a few seconds).

Direct-reading polychromators[1, 2] (Figure 3b) have a number of exit slits and photomultiplier tube detectors, which allows one to view emission from many lines simultaneously. More than 40 elements can be determined in less than one minute. The choice of emission lines in the polychromator must be made before the instrument is purchased. The polychromator can be used to monitor transient signals (if the appropriate electronics and software are available) because unlike slew-scan systems it can be set stably to the peak emission wavelength. Background emission cannot be measured simultaneously at a wavelength close to the line for each element of interest. For maximum speed and flexibility both a direct-reading polychromator and a slew-scan monochromator can be used to view emission from the plasma simultaneously.

The spectrally segmented diode-array spectrometer[5] uses three gratings to produce a series of high-resolution spectra, each over a short range of wavelengths, at the focal plane (Figure 3c). A 1024-element diode array is used to detect the spectra simultaneously. By placing the appropriate interchangeable mask in the focal plane following the first grating, the short wavelength ranges to be viewed are selected. The light is recombined by a second grating, forming a quasi-white beam of light. A third grating is used to produce high-resolution spectra on the diode array. It is much easier to change masks in this spectrometer than to reposition exit slits in a direct-reading polychromator. The diode array-based system also provides simultaneous detection of the emission peak and nearby background. This capability is particularly advantageous when using a sample-introduction technique that generates a transient signal.

Limitations and Potential Analysis Errors

One of the major problems in ICP-OES can be spectral overlaps.[1, 2, 9] Some elements, particularly rare earth elements, emit light at thousands of different wavelengths between 180 nm and 600 nm. Spectral interferences can be minimized, but not eliminated, by using spectrometers with a resolving power $(\lambda / \Delta\lambda)$ of 150,000 or higher.[1, 3] If a spectral overlap occurs, the operator can choose a different line for analysis; or identify the source of the interfering line, determine its magnitude, and subtract it from the measuring intensity. Tables of potential spectral line overlaps for many different emission lines are available.[6, 7] Some manufacturers provide computer database emission line lists. Most commercial direct-reading polychromators include software to subtract signals due to overlapping lines.[8] This is effective if the interferant line intensity is not large compared to the elemental line of interest and another line for the interferant element can be measured.

Although nonspectral interference effects are generally less severe in ICP-OES than in GFAA, FAA, or ICPMS, they can occur.[1, 2, 9] In most cases the effects produce less than a 20% error when the sample is introduced as a liquid aerosol. High concentrations (500 ppm or greater) of elements that are highly ionized in the
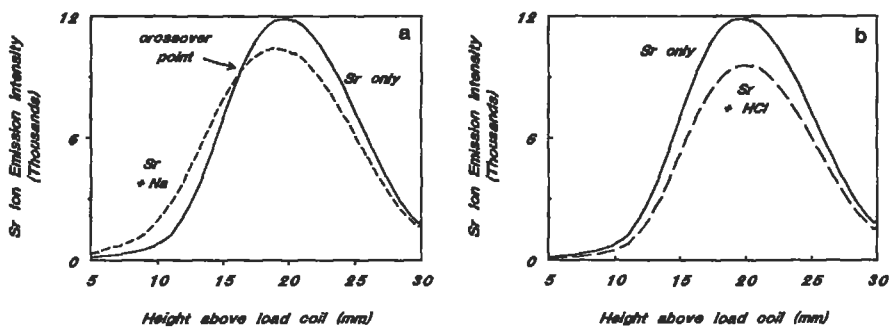
Figure 4 Effect of matrix on Sr ion emission at different heights in the plasma. Samples contained 50 ppm Sr in distilled, deionized water: (a) emission in the presence and absence of NaCl (solid line—no NaCl added; dashed line—0.05 M NaCl added); and (b) effect of the presence and absence of HCl (solid line—no HCl added; dashed line—0.6 M HCl added).

plasma can affect emission intensities. The magnitude and direction of the effect depends on experimental parameters including the observation height in the plasma, gas flow rates, power, and, to a lesser degree, the spectral line used for analysis and the identity of the matrix. A location generally can be found (called the *cross-over* point) where the effect is minimal (Figure 4a). If emission is collected from a region near the cross-over point, errors due to the presence of concomitant species will be small (generally less than 10% or 20%).

The presence of organic solvents (1% by volume or greater) or large differences in the concentration of acids used to dissolve solid samples can also affect the emission intensities (Figure 4b).[1, 2, 9] Direct solid-sampling techniques generally are more susceptible to nonspectral interference effects than techniques using solutions. The accuracy can be improved through internal standardization or by using standards that are as chemically and physically similar to the sample as possible.

Errors due to nonspectral interferences can be reduced via matrix matching, the method of standard additions (and its multivariant extensions), and the use of internal standards.[1, 2, 9]

Applications

ICP-OES has been applied to a wide range of sample types, with no single area or technology dominating. Elemental analysis can be performed on virtually any sample that can be introduced into the plasma as a liquid or dry aerosol. Metals and a wide variety of industrial materials are routinely analyzed. Environmental samples, including water, waste streams, airborne particles, and coal fly ash, are also amenable to ICP-OES. Biological and clinical samples, organic solvents, and acids used in semiconductor processing are widely analyzed.

Laser-ablation ICP-OES has been used to analyze metals, ceramics, and geological samples. This technique is amenable to a wide variety of samples, including surfaces and thin films (μm depths analyzed), similar to those analyzed by laser microprobe emission techniques (LIMS). However, interference effects are less severe using separate sampling and excitation steps, as in laser-ablation ICP-OES. Laser-ablation ICPMS is becoming more widely used than laser-ablation ICP-OES because the former's detection limits are up to 2 orders of magnitude. Spark discharge-ablation ICP-OES is used mainly to analyze conducting samples.

Conclusions

ICP-OES is one of the most successful multielement analysis techniques for materials characterization. While precision and interference effects are generally best when solutions are analyzed, a number of techniques allow the direct analysis of solids. The strengths of ICP-OES include speed, relatively small interference effects, low detection limits, and applicability to a wide variety of materials. Improvements are expected in sample-introduction techniques, spectrometers that detect simultaneously the entire ultraviolet–visible spectrum with high resolution, and in the development of intelligent instruments to further improve analysis reliability. ICPMS vigorously competes with ICP-OES, particularly when low detection limits are required.

Related Articles in the Encyclopedia
ICPMS, GDMS, SSMS, and LIMS

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