CHAPTER 1

Introduction

1.1 MATTER AND THE MASS SPECTROMETER

The world we live in is a highly customized environment tailored to maximize our comfort level. This comfort level (which pertains to our well-being, environment, security, transportation, information access, etc.) is acquired through our capacity to fabricate materials that do not exist in nature. This capacity is aided through our ability to understand what has been fabricated, how this interacts with its environment, and how this can be tailored to our needs. This understanding is provided through the act of analysis.

Our ability to customize our environment is something that can be said for almost every age the human race has progressed through. Indeed, some eras are associated with the material developed. Examples include the Bronze Age (∼3300 BCE to ∼1200 BCE) and the Iron Age (∼1200 BCE to ∼500 CE). Two more recent examples of this customization include the use of Carbon for creating plastics and Silicon for constructing computer chips in what is now referred to as the computer or information age.

Indeed, plastics have become one of the most ubiquitous materials in today’s everyday life. Plastics, fabricated from crude oil, are composed of a Carbon backbone formed from \( n \) repeating units (\( n = \) an integer >1) of some monomer (a molecule that binds to other molecules or atoms), hence the name polymer. For example, Polyethylene is defined as \((\text{C}_2\text{H}_4)_n\), Polypropylene as \((\text{C}_3\text{H}_6)_n\), and Polyvinylchloride (PVC) as \((\text{C}_2\text{H}_3\text{Cl})_n\). Some applications of these three examples are as follows:

1. Polyethylene is used in manufacturing plastic bags, bottles, containers, and so on.
2. Polypropylene is used in packaging/labeling materials, textiles, bottles, and so on.
3. PVC is used in manufacturing specific types of tubing, signs, furniture, and so on.
In addition, there are many more types of plastics and applications.

The element below carbon in the periodic table is that of silicon. When purified from sand (one source), this is the basis of the solid-state semiconductor industry, as we know it today. Indeed, owing to the increasing prevalence of Complementary Metal Oxide Semiconductor (CMOS)-based integrated circuits and the ever-decreasing size of the transistor (over a billion transistors can now be squeezed into a single cm-by-cm-sized chip), more silicon-based transistors have been manufactured than anything else summed over the entire history of mankind.

Interestingly enough, the element below Silicon in the periodic table has played a pivotal role in the continued scaling of transistor dimensions. This stems from the fact that introducing Germanium into substitutional sites within the Silicon lattice induces strain, which, in turn, enhances charge mobilities. Post CMOS-based devices, on the other hand, may be Graphene based. Note: Graphene is an allotrope of Carbon (allotropes are composed of the same elements but have different geometric structures).

Our ability to fabricate a material that exhibits properties specifically tailored to the desired need has arisen from the knowledge attained from the way in which matter interacts with each other and its environment. The common definition of matter is anything that has mass and volume (Barker 1870). According to this definition, all matter is composed of atoms irrespective of the phase (solid, liquid, or gas) it exists in (Note: We do not directly interact with the fourth state of matter, otherwise referred to as plasma).

The physical properties of matter can be defined by the knowledge of the following:

1. the type of atoms present, i.e. which elements are present,
2. the bonds between the atoms,
3. the molecular or crystalline structure.

Atoms are the smallest divisible unit of mass that exists under the conditions we live in. Each element displays a different chemical reactivity (Note: Atoms can only be broken down in high-energy plasmas, energetic sub-atomic particle collisions, etc.). Most atoms, however, do not like to exist as individual entities, rather they prefer to combine with other atoms. Some examples include N₂, O₂, and CO₂ as is present in the air, NaCl in table salt, and more complex combinations present in plastics, semiconductors, and so on.

As first realized in 1909 (Rutherford 1911), atoms are composed of a dense nucleus, which is made up of protons and neutrons around which electrons orbit. The reactivity of an atom is defined by the electrons. The number of electrons in a neutral atom is defined by the number of protons (the number of protons equal the number of electrons in neutral atoms) with the number of protons defining the element (Carbon has six protons). The number of neutrons is generally equal to the number of protons, but it can differ.
Atoms with the same number of protons but with a different number of neutrons are referred to as isotopes, with the mass of the specific atom defined by the sum of the protons and neutrons. For example, Carbon 12 (mass equals 12 u) has six protons and six neutrons. Its chemical symbol is $^{12}$C. Carbon 13 ($^{13}$C), on the other hand, has six protons and seven neutrons. Isotopic mass is covered in Section 2.1.1.1.

Although isotopes of the same element display the same reactivity, their ratio can provide insight into adsorption/diffusion characteristics, past events/environments, and the date at which any such events occurred. The study of the latter is termed Chronology. The ability to derive such information stems from the fact that isotope ratios change in a predictable manner over time owing to what are referred to as fractionation effects. This ability and the ability to date materials are discussed further in Sections 1.2.3.

The existence of naturally occurring isotopes was first reported by J.J. Thomson in 1913 (Thomson 1913) and later confirmed by F.W. Aston in 1919 using Magnetic Sector-based Mass Spectrometry (Aston 1922).

Magnetic Sector-based Mass Spectrometry separates the isotopes of the elements by passing the monoenergetic beam of ions (atoms that have had an electron removed or added such that it has a charge) through a magnetic field placed normal (perpendicular) to the ion beam’s initial direction of travel. This causes the deflection of the beam based on the mass-to-charge ratio ($m/q$) of the ion as illustrated in Figure 1.1. Note: This ratio is also specified as ($m/z$). If all ions have the same charge, as is the case in Figure 1.1, the deflection is then simply dependent on the mass of the ion. As the vast majority of an atom’s mass is defined by the protons and neutrons within the respective nuclei, Mass Spectrometry provides a method for separating the isotopes and hence the elements/molecules of different masses. All forms of Mass Spectrometry can thus be viewed as scales for weighing individual atoms or combinations thereof, i.e. molecules.

Mass Spectrometry has become a highly effective technique for elucidating the type and amount of any isotope, element, or molecule present within unknown samples in the gaseous state or made to be gaseous state (originally liquid). Secondary Ion Mass Spectrometry (SIMS) is a variant of Mass Spectrometry that is used in the

![Cross-sectional image of how the isotopic constituents of a Ti$^+$ ion beam are separated while passing through a Magnetic Sector mass filter. Note: The magnetic field direction is perpendicular to the trajectory plane of the beam, i.e. perpendicular to the page and $q = 1$. The original instruments recorded mass separated images on photographic plates, as is shown.](image-url)
INTRODUCTION

chemical analysis of solid or made to be solid (frozen) materials. SIMS is discussed further in Section 1.2.

1.2 SECONDARY ION MASS SPECTROMETRY

SIMS now represents a fully commercialized technology that is widely used in both industry and academia for defining the isotopic, elemental, or molecular composition over highly localized microscopic regions within the surface and/or near the surface region (just below) of any solid. In specialized cases, frozen liquids can also be examined. As noted in Appendix A.10, an ion spectrometry is one that derives their information by recording ions as opposed to electrons or photons.

The popularity of SIMS stems, in part, from:

1. The ability to detect all of the elements within the periodic table (H–U) and combinations thereof, i.e. those that make up molecules. In many cases, this information can be collected quasi-simultaneously from the same surface/volume.

2. The detection limits provided (the ability to detect small concentrations, which in the case of SIMS can extend down to sub parts per billion levels), along with the associated sensitivity (the ability to detect small concentration differences) and the dynamic range (the ability to measure signals over some range, which in SIMS extends to $\sim 10^9$ when using multiple detectors).

3. The ability to map the distribution of any isotope or collection thereof (this ability can be used to replicate elemental or molecular distributions) on or within any solid to spatial and depth resolution values of $1 \mu m$ or less ($10 nm$ represents the ultimate physical limit in SIMS) and $\sim 1 nm$, respectively.

4. The minimal sample preparation procedures required before analysis (in most cases, no preparation is needed).

The primary disadvantage commonly associated with SIMS lies in the relative difficulty in quantifying the recorded signal/s. This stems from the often unpredictable variations in the intensity of the recorded signal with substrate type and with the analysis conditions used. As a result, quantification requires that matrix-matched reference materials be analyzed in concert with the sample of interest (methodologies are covered in Section 5.4.3). This is in contrast to, for example, X-ray Photoelectron Spectroscopy (XPS) where quantification can be carried out without the aid of matrix-matched reference materials. Note: The use of reference materials in XPS can, however, enhance the accuracy of the measurement.

The information of interest in SIMS is carried within the ions emitted from the surface of a solid following energetic ion impact (a focused beam of between $\sim 0.1$ and $50$ keV is most commonly used) as schematically illustrated in Figure 1.2. The impacting ions are referred to as the primary ions, whereas the emitted ions are
Figure 1.2  Pictorial illustration of the main components found in a SIMS instrument along with the common data output noted in Dynamic SIMS. Note: In Static SIMS, the data output is limited to mass spectra and spatial imaging for reasons discussed in the text.

referred to as the secondary ions. This figure also reveals the typical data formats available to SIMS as a whole, with these being:

1. mass spectra of all ionized species removed from the solid,
2. spatial distribution mapping of any signal of interest,
3. depth distribution mapping of any signal of interest (this is only available in the Dynamic SIMS mode of operation as is discussed later in this section).

Combining depth distribution mapping with spatial distribution mapping allows for three-dimensional volumetric images to be generated.

The mass filter used in commercially available SIMS instruments defines the instrument type, with the respective instruments referred to as

1. magnetic sector SIMS instruments (similar to those used in the original mass spectrometers)
2. quadrupole SIMS instruments (first appeared in the 1970s)
3. Time-of-Flight SIMS instruments (first appeared in the 1980s)

Note: There are other possible mass filter types, all of which are covered in Section 4.2.3.1.

In addition, there are two distinct modes in which SIMS analysis can be carried out. These modes, whose capabilities have been realized for sometime (Benninghoven et al. 1987), are otherwise referred to as Static SIMS and Dynamic SIMS. Static SIMS provides insight into the elemental and/or molecular distributions from the outer undisturbed monolayer, whereas Dynamic SIMS provides the elemental and/or molecular distributions over many atomic layers (in depth). Although the physics underlying signal generation in both modes share many
similarities (see Chapter 3), the analytical requirements along with the data collection procedures differ (see Chapters 4 and 5).

As Static SIMS can be used for probing the chemical composition as well as providing molecular signatures specific to the outermost monolayer of the surface of interest, this has attracted significant interest in fields extending from Materials Sciences to Biosciences (for further details, see Section 1.2.3) whether in academic or industrial settings.

Dynamic SIMS using chemically active atomic or small molecular primary ion beams \((\text{Cs}^+, \text{O}^-, \text{O}_2^+)\) provides the utmost in detection limits in localized elemental analysis. As a result, this is the technique of choice for following dopant distributions as a function of depth in the semiconductor industry (a sector of Materials Sciences) and for mapping isotopic distributions in the Earth Sciences (for further details, see Section 1.2.3). Little in the way of molecular information is accessible under these conditions.

An exception to the above rule (the access to molecular information in Dynamic SIMS) is noted when using large cluster primary ions \((\text{C}_{60}^+, \text{Ar}_n^+, \text{etc., where } n \text{ can equal several thousands})\). This is realized because these ions introduce the possibility of molecular depth profiling and imaging. Cluster ion beams can also be used to examine surface distributions under Static-like conditions. As a result, the use of cluster ion beams in SIMS opens many new fields of application (Mahoney 2013).

Further discussion on the definitions of Dynamic and Static SIMS whether in their conventional forms or otherwise can be found in Sections 4.1.1.1–4.1.1.3.

At this point, it is worth mentioning some acronyms used in this field and its related fields. As the probe beam used in SIMS is often scanned across the solid surface, the term “SIM,” which refers to \textit{Scanning Ion Microscope}, has been used. Likewise, the term “\textit{Imaging Mass Spectrometry}” (IMS) has been used to describe image analysis, which is carried out using some form of mass spectrometric technique. To avoid confusion with \textit{Ion Mobility Spectrometry} (also referred to as IMS), the term “\textit{Mass Spectrometry Imaging}” (MSI) is now more commonly used. Note: The term “\textit{SIMs}” should not be confused with that now most commonly relayed in search engines on the World Wide Web. Here, the vast majority of results concern \textit{multiple SIMulationS} as applies to the virtual gaming industry. The SIMS acronym is also used for \textit{Stereoscopic Imaging and Measurement Systems}. This describes a methodology for relaying depth information during imaging.

### 1.2.1 History

The basis of SIMS can be traced back to the beginning of the twentieth century with the first experimental evidence of secondary ions reported by J.J. Thomson in 1910 (Thomson 1910). As quoted “\textit{the secondary rays \ldots which were on the most part neutral with a small fraction of positively charged particles, were recorded following bombardment of a metal sample by primary kanalstralen (Canal rays).}” These positive ions were noted within a \textit{Crookes tube} when a metal specimen held under vacuum conditions was bombarded by ions. The resulting emissions were
then passed through an electric field and recorded on a photographic plate. The term *kanalstralen* was introduced by Eugen Goldstein in 1886 after he noted the production of rays (later understood to be positive ions) through holes of an anode from a low-pressure electrical discharge tube.

The first positive ion mass spectrograph from a gaseous sample was collected by Aston in 1919 after the discovery by Wilhelm Wien in 1898 that magnetic fields are effective in altering the trajectories of ion beams. In light of this discovery, Wilhelm Wien is often considered the forerunner of Mass Spectrometry (for a review, see Downard 2007). The production of secondary ions was first reported by Woodcock and Thompson in 1931 (Woodcock 1931; Thompson 1931). In their experiments, Li$^+$ primary ions were directed at NaF and CaF substrates with the negative secondary ion population recorded. Between 1936 and 1937, Arnott and Milligan, considered the forerunners of SIMS, used a magnetic field to separate the secondary ions on the basis of their $m/q$ ratio (Arnott and Milligan 1936) in much the same manner as that used by Aston.

The first experimental SIMS installation did not, however, appear until 1949 (Herzog and Verlock 1949), with the first dedicated Magnetic Sector-based instruments not constructed until the 1960s (Liebl 1967; Castaing and Slodzian 1962). Note: This timeline is closely associated with the development of the capability to produce the vacuum conditions required for surface analysis and the recognition of the potential of this methodology. The construction of Quadrupole-based SIMS instruments followed (Benninghoven 1971; Wittmaack 1975; Magee et al. 1978), with Time-of-Flight-based SIMS instruments appearing shortly thereafter (Chait 1981). These instrument types have since been fully commercialized (the first being the ims-101 constructed by Liebl in 1963 (Liebl 1967)) to increased levels of sophistication with each new generation. A discussion on instrument types is presented in Chapter 4.

The vast majority of the early work concerned the development of Dynamic SIMS for analyzing both extraterrestrial samples and samples for the semiconductor industry (e.g., see Magee and Honig 1982; Benninghoven et al. 1987; Zalm 1995). Since then, the prospect of examining molecular distributions from an undamaged outer surface has been introduced (Benninghoven 1969), with the true capabilities only fully realized with the development of Time-of-Flight-based SIMS instrumentation (Benninghoven 1994). Most recently, the possibility of carrying out three-dimensional molecular imaging using large cluster ion impact has been demonstrated (for reviews, see Vickerman 2009; Mahoney 2013), thereby opening up new areas of research.

The relatively late development and commercialization of SIMS can be traced to

1. the lack of knowledge concerning the fundamentals of secondary ion generation that, to some degree, still exists,
2. the extreme variability in secondary ion yields even for the same element emerging from different matrices, an observation termed the *matrix effect*,
3. the difficulty in generating the required vacuum (although analysis can be carried out at vacuum as low as of $10^{-6}$ torr, $10^{-10}$ torr, or better is preferable),
4. the complexity of the technique (numerous different instrumental conditions are available even within a specific instrument, with specific conditions required for specific types of analysis),
5. the large amount of data produced, as is particularly evident when using Time-of-Flight SIMS instrumentation.

1.2.2 Physical Basis

Conceptually, SIMS can be considered a straightforward and direct technique. In practice, there are many complexities introduced as a result of the various methodologies that can be applied, whether in the static or in the dynamic mode of SIMS. This exists because there are numerous conditions under which SIMS can be carried out. Each condition is optimized to deal with the analysis of a different elemental or molecular species, from different solid matrices. In addition, relating the output to the compositional variations that may occur on or within the solid being examined can be problematic. This stems, in part, from the complexities surrounding secondary ion generation, or more precisely, the matrix effect. As the term suggests, the matrix effect describes the effect of the matrix on the population of ions emitted. Matrix effects and their associated transient effects are discussed in Section 3.3.3.1.2.

SIMS can be considered a straightforward technique in that an energetic focused ion beam (∼0.1 and 50 keV) is directed at the solid surface of interest. This beam is referred to as the primary ion beam, with some of the more common species being O−, O2+, Cs+, Ga+, In+, Au+, Bi+, SF5+, C60+, C84+, C24H12+, Ne+, Ar+, Xe+, etc., with n being an integer starting from unity. Some of these species may be multiply charged. This primary ion beam induces the ejection of atoms and/or molecules from the irradiated area. This is referred to as sputtering. A schematic example of a sputtering process is shown in Figure 1.3. The small percentage of the sputtered population existing in an ionized state (+1 or −1, depending on the species, being by far the most common) is then collected, focused, and passed through a mass spectrometer. This ejected ionized population is referred to as the secondary ion beam, hence the name SIMS.

SIMS can be considered a direct technique in that the information of interest is derived from the mass of the secondary ions measured. As outlined in Section 2.1.1.1, the mass of an atom is defined by the number of protons and neutrons within the nucleus. Also mentioned in Section 2.1.1.1 is the fact that the number of protons defines the element (no two elements have the same number of protons) and hence its atomic number (Z). The number of neutrons is roughly the same as that of the number of protons with most elements exhibiting a distribution in the number of neutrons. These are the isotopes which, terrestrially, follow a more or less fixed distribution with the average referred to as the natural abundance of the isotopes (listed in Appendix A.2). Note: The term “more or less” is used as slight variations are noted according to various physical and/or chemical fractionation processes (Coplen 2002). Molecular mass is simply the sum of the masses of the isotopes of the elements that makes up the molecule. SIMS is thus
1.2.2.1 Sensitivity and Detection Limits

Prime attributes associated with SIMS are its detection limits (ability to detect low concentrations) and its concurrent sensitivity (ability to detect concentration differences) to certain elements when analyzed under the appropriate conditions. Indeed, SIMS when operated in the Dynamic mode can routinely provide elemental detection limits extending to parts per billion or even sub parts per billion levels. As an example, Boron in Silicon can be detected to $\sim 0.4$ ppb or $\sim 2 \times 10^{13}$ atoms/cm$^3$ under fully optimized conditions. Note: However, that although SIMS can detect all elements and molecules, not all are detectable to the same levels. This is reflected in the detection limits for Hydrogen through Krypton in Silicon, as provided in Appendix A.5.

An understanding of how such detection limits can be attained over highly localized regions can be realized when considering the following Dynamic SIMS example using a Magnetic Sector instrument.

1. A Boron-implanted Silicon wafer is examined on a magnetic sector-based SIMS instrument using a 4-keV $O_2^+$ primary beam. $O_2^+$ is used as this enhances the $B^+$ ionization yields (see Section 3.3.1) while a Magnetic Sector instrument provides for best sensitivity/detection limits.

2. This primary beam is set to a current that results in an etch rate (sputter rate) of $\sim 1$ nm/s. Typical values range from less than 0.5 to greater than 5 nm/s. A 4-keV $O_2^+$ ion beam is used in this example as this removes $\sim 1$ substrate atom per impinging ion.

3. Fixing the analysis region to $100 \times 100$ µm results in a volume of $\sim 1 \times 10^{-11}$ cm$^3$ being removed per second. Note: As discussed in
Section 5.3.2.3.2, the analyzed region is made much smaller than the sputtered area to remove crater edge effects and thus to improve depth resolution.

4. As the atomic density (volume) of Silicon is $5 \times 10^{15}$ atoms/cm$^3$, the number of atoms within this volume that is removed approximates $1 \times 10^{-11}$ cm$^3 \times 5 \times 10^{22}$ atoms/cm$^3$ or $\sim 5 \times 10^{11}$ atoms/s.

5. SIMS, however, records the emitted ion population. If the emitted atoms experience an ionization efficiency of 1% (typical values range from greater than 10% to less than 0.0001% as discussed in Section 3.3.1), the number of ions approximates as $5 \times 10^9$ ions/s.

6. The likelihood that an ion formed at the sample surface reaches the detector is referred to as the instrument’s transmission function (see Section 4.2.3). For the analysis of Boron, this can be maximized to a peak value of around 50% (see Table 4.3).

7. Using the above values, the number of ions reaching the detector per second can be approximated as $1 \times 10^9$ ions/s. As discussed in Section 4.2.3.3, an electron multiplier is capable of detecting every ion impinging on the first dynode (typical background values are less than 0.1 cps).

8. If one of these ions was to have a different mass than that of the elements making up the substrate (Boron has a different mass than Silicon), the detection limit under the above conditions equates to $\sim 1 \times 10^9$ ions/s, or 1 ppb.

These conditions can be further adjusted to fully optimize the detection efficiency to the specific ions of interest, thereby further improving the respective detection limits. Note, however, that although all elements are detectable, such detection limits are noted only for a limited number of elements. This arises from differences in ionization yields (Step 5) as is discussed further in Section 3.3.2. The concept of volume densities and surface densities are discussed in Section 2.1.1.2.

In the case of static SIMS, a reduced volume is examined. To offset the parallel loss in detection limits/sensitivities associated with the analysis of smaller volumes, the secondary ion transmission functions of Time-of-Flight SIMS instruments (these are best suited to Static SIMS applications) can approach 100%, with all ions simultaneously recorded. As a result, surface detection limits for Iron on a Silicon substrate is in the low $10^8$ atoms/cm$^2$ range, whereas that for Boron on Silicon is in the mid $10^7$ atoms/cm$^2$ range (note the different units used). These detection limits can extend further for the more electropositive/electronegative elements when analyzed under appropriate conditions.

The advantage of increased transmission and simultaneous collection in Time-of-Flight SIMS utilizing pulsed primary ion beam instruments does not, however, translate to Dynamic SIMS studies. This is realized as a sizable portion of the analyzed volume is not recorded during the analysis. This stems from the fact that two ion beams are used, one for sputtering and the other for analysis, with the population arising from the sputter beam not recorded. This is further
Concentration fractions (atomic % equivalents)

- 1000 ppth (100 atomic %)
- 100 ppth (10 atomic %)
- 10 ppth (1 atomic %)
- 1 ppth (0.1 atomic %)
- 100 ppm (1e-2 atomic %)
- 10 ppm (1e-3 atomic %)
- 1 ppm (1e-4 atomic %)
- 100 ppb (1e-5 atomic %)
- 10 ppb (1e-6 atomic %)
- 1 ppb (1e-7 atomic %)
- 100 ppt (1e-8 atomic %)
- 10 ppt (1e-9 atomic %)
- 1 ppt (1e-10 atomic %)

Volume density (atoms/cm$^3$)

- 5e22
- 5e21
- 5e20
- 5e19
- 5e18
- 5e17
- 5e16
- 5e15
- 5e14
- 5e13
- 5e12
- 5e11
- 5e10

Surface density (atoms/cm$^2$)

- 1e15
- 1e14
- 1e13
- 1e12
- 1e11
- 1e10
- 1e9
- 1e8
- 1e7
- 1e6
- 1e5
- 1e4
- 1e3

Figure 1.4 Concentrations in fractions and percentages. These are translated into volume and surface atomic densities for the Silicon (110) surface. Note: As discussed in Section 2.1.1.2, these densities are a function of the substrate as well as the surface plane. Engineering notation, where e refers to the base 10 (not to be confused with the exponential $e$), is used for the sake of simplicity. Also shown are some additional analytical techniques along with the approximate best possible detection limits noted for specific elements when using fully optimized analysis conditions. Note: ICP-MS, in this case, would either require solid digestion, be coupled with Laser Ablation (LA), or coupled with Vapor Phase Decomposition (VPD) for dissolving surface films.

compounded by limitations in the detection of multiple ions of the same mass within the same pulse.

To put these detection limits into perspective, the volume and the surface atomic densities of Silicon are related to atomic concentrations (in fractions and atomic percent) as shown in Figure 1.4. Note: Different substrates can exhibit different densities (that of Silicon is $4.98 \times 10^{22}$ atoms/cm$^3$). Likewise, different surface planes of a crystalline substrate can exhibit different surface densities. For example, the Silicon (100) plane has a density of $6.78 \times 10^{14}$ atoms/cm$^2$, whereas the (110) plane has a density of $9.59 \times 10^{14}$ atoms/cm$^2$. The (110) plane is used in Figure 1.4 for the sake of simplicity, i.e., is closest to $1 \times 10^{15}$ atoms/cm$^2$. Surface and volume densities are discussed further in Section 2.1.1.2.

Note: Such detection limits cannot be reached when examining large molecular ions because of the lower sputter and ion yields observed. These topics and the elemental emissions are discussed further in Chapter 3.

Also shown in Figure 1.4 are the relative detection limit ranges for SIMS when operated in both its Static and Dynamic modes, as well as the detection limits...
displayed by some other analytical techniques applied in the analysis of solids or solid surfaces. These include:

1. Auger Electron Spectroscopy (AES),
2. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) whether by itself (digestion required) or coupled with Laser Ablation (LA) or Vapor Phase Decomposition (VPD),
3. Low-Energy Ion Spectroscopy (LEIS),
4. Total reflectance X-Ray Fluorescence (TXRF),
5. XPS (X-ray Photoelectron Spectroscopy)

From this list, only ICP-MS of a digested solution or when combined with LA or VPD, displays, superior detection limits compared to SIMS. It should be noted, however, that ICP-MS and VPD-ICP-MS are not true probe-based techniques, i.e., these are not useful when concentration variations over micro-volume to nano-volume regions are of interest. Furthermore, VPD-ICP-MS is a highly specialized technique developed specifically for the semiconductor industry. Of the micro-probe techniques, SIMS displays the highest elemental detection limits, whether used in the areas of micro-volume analysis/nano-volume analysis (both are forms of Dynamic SIMS) or surface analysis (Static SIMS). Optimal detection limits pertain to those noted from specific element–substrate combinations when examined under optimized conditions.

With the exception of SIMS, the above techniques along with various other related spectrometric and spectroscopic techniques are summarized in Appendix A.10. For completeness sake, various microscopies of interest are covered in Appendix A.11., whereas various diffraction and reflection-based techniques are summarized in Appendix A.12.

1.2.3 Application Fields

As SIMS is the solid-state analog of Mass Spectrometry, it has found extensive use in many highly diverse areas within both industry and academia, in which the distribution of isotopes, elements, and/or molecules on or within a specific region of the substrate is of interest. Three areas in which SIMS has found heavy application (listed in the order in which SIMS has been applied) are as follows:

1. Materials Sciences
2. Earth Sciences along with the Environmental Sciences and Cosmology
3. Biosciences

Note: This order does not necessarily relate to the impact SIMS has had in these respective fields. Moreover, of course, there are other fields in which SIMS has been applied, many in niche applications.

The Material Sciences cover an extremely broad field stemming from many disciplines. As a result, SIMS has been applied in this field more extensively than
SECONDARY ION MASS SPECTROMETRY

any other, with all the commercially available instrument types (Magnetic Sector, Quadrupole, and Time-of-Flight SIMS instruments) being applied accordingly. The analysis requirements are also the most diverse because of the range of samples encountered. This is realized as this field examines relationships between the structure of matter at the atomic/molecular scale and the resulting macroscopic properties displayed. For some reviews, see Benninghoven et al. 1987; Wilson et al. 1989; O’Connor et al. 2003; Riviere and Myhra 2009.

Some of the properties include but are not limited to (these are listed in alphabetical order):

1. chemical properties
2. electrical properties
3. mechanical properties
4. magnetic properties
5. optical properties
6. thermal properties

Recall: as mentioned in Section 1.1, the physical properties of matter are defined in one form or another by the elements present (the types of atoms) and how these elements bond with each other.

As an example, adding small amounts (<2%) of Carbon along with other elements to Iron during the forging process enhances alloying and thus the strength/hardness albeit at the cost of ductility. The result, otherwise known as Carbon steel, was heavily used in the development of the sword during the Iron Age and also played a pivotal role in the development of structural materials during the industrial revolution. A more recent example lies in the substitution of trace amounts of Boron, Phosphorus or Arsenic into the Silicon lattice in a highly localized manner. This modifies the local electrical properties, without which the Silicon-based semiconductor industry as we know today would not have developed. Moreover, there are many more examples.

Surface science is a subset of materials science concerned with the macroscopic properties of solid and/or liquid surfaces, and how these properties relate to atomic structure in the surface regions. Note: Most forms of matter present in the solid or liquid phases exhibit a surface layer that is different from that of the underlying material. This difference could be chemical (composition and/or bonding), structural (differences in bond angles, bond lengths, or long range order, i.e. the crystalline structure), or both. How a material is perceived by the outside world thus primarily depends on the form or more precisely the physical properties of the outermost layer, i.e. the surface. These may be in the form of (in alphabetical order)

1. adhesion and wettability
2. adsorption/desorption
3. biocompatibility
interfacial electrical properties
5. optical properties in the form of reflectivity
6. reactivity inclusive of corrosion, heterogeneous catalysis, and so on
7. texture
8. wear and tear (also referred to a tribology), and so on.

Note: A solid’s or liquid’s surface can be defined in several different ways. The more obvious definition is that a surface represents the outer or topmost boundary of an object. When getting down to the atomic level, however, the term “boundary” loses its definition as the orbits of the bound electrons are highly diffuse. An alternative definition would then be that a surface is the region that dictates how the solid or liquid interacts with its surroundings. This can also be applied to a solid–solid interface. Applying this definition, a surface or interface can span as little as one atomic layer (0.1–0.3 nm) to many hundreds of atomic layers (100 nm or more) depending on the material, its environment, and the property of interest.

One example of a surface modification lies in the corrosion resistance exhibited by stainless steel. Stainless steel is composed of a range of alloys exhibiting stain resistance, hence its name. Indeed, 316-stainless steel is composed of Iron with 16–18% Chromium, 10–14% Nickel, 2–3% Molybdenum, less than 2% Manganese along with sub 1% levels of Silicon, Phosphorus, and Carbon. The corrosion resistance arises from the segregation of Chromium to the surface whereupon it forms a corrosion resistant oxide ($\text{Cr}_2\text{O}_3$) of only a few nanometers in thickness. Without this, the bulk material would corrode at a significantly greater rate similar to that noted from pure Iron. Moreover, there are many more examples.

The capabilities of SIMS when applied in this field vary according to the information required, the time constraints, and, of course, the capabilities of the instrumentation used. Indeed, imaging to a spatial resolution of $\sim$1 μm and below is routinely possible on commercially available SIMS instrumentation. This can be pushed to the physical limit of 10 nm imposed by the sputtering process or more precisely the collision cascade (see Section 3.2.1) using highly specialized instrumentation (McPhail et al. 2011; Wirtz et al. 2012).

Likewise, depth resolution values to 1 nm and below are within reach or commercially available instrumentation equipped with Ultra Low Energy (ULE) primary ion impact capabilities (Dowsett et al. 1994). This, however, generally comes at the expense of detection limits. Lastly, detection limits for specific elements can extend down to sub parts per billion levels (see Section 1.2.2.1 and Appendix A.5), albeit at the expense of spatial/depth resolution.

The Earth Sciences, Environmental Sciences, and Cosmology have all long recognized the strengths of SIMS. A prime example of this lies in the fact that NASA funded the instrument built by Liebl (Leibl 1967) for such purposes. Some of the requirements of the application of SIMS in this area include the following:

1. The high mass resolution (see Section 5.2.2.2) at high sensitivity over micron scale regions when isotope measurements for chronology are of interest,
2. Effective sample preparation required to support the small and often insulating but highly stable grains prevalent in these fields. These are covered more in Section 5.1.1.2.

3. Understanding of the Instrument Mass Fractionation (IMF) effect. This results in small but measurable deviations from true isotope ratios as discussed in Section 3.3.1.2.3.

The first requirement has since resulted in the availability of commercial purpose built Magnetic Sector instruments. Examples include the SHRIMP™ series of instruments from the Australian Scientific Institute (ASI™) and the ims-1270/1280™ from Cameca™. These instruments provide the sensitivity to measure mass fractionation effects intrinsic to the samples because of the full transmission at a mass resolution \( \frac{m}{\Delta m} \) of \( \sim 5000 \) accomplished using large radii electrostatic and magnetic sectors with ultimate mass resolution values extending well past this value. For further discussion on instrumentation, see Chapter 4.

SIMS is primarily applied in these fields for measuring stable and radiogenic isotope ratios from highly localized micron scale volumes as well as for measuring light element distributions not accessible to other techniques (for reviews, see Reed 1989; Fayek 2009). Moreover, there are other applications.

Radiogenic isotope ratios are used in Chronology. Measurement of such ratios is generally carried out using the Ar–Ar, Sm–Nd, or U–Pb radiometric techniques (and there are others) with the latter being the most prevalent. Here, the age of a rock (Zircon being the most popular) can be defined as between 1 million and 4.5 billion years by measuring specific Lead and in some cases Uranium isotope levels (Ireland and Williams 2003). These are of interest since once trapped within the Zircon sample, \(^{238}\text{U}\) decays into \(^{206}\text{Pb}\) with a half life of 4.47 billion years, whereas \(^{235}\text{U}\) decays into \(^{207}\text{Pb}\) with a half life of 704 million years. Zircon is used as it readily incorporates Uranium and Thorium (this decays into \(^{208}\text{Pb}\)), and once crystallized, it is highly stable, thereby forming an effective time capsule. As a result of the power of SIMS to derive such information, it has become the technique of choice in this area with such studies being of both academic and industrial interest.

Measurement of stable isotope factions of Hydrogen, Lithium, Boron, Carbon, Oxygen, Sulfur and even Chlorine, and so on are also studied as these elements provide a chemical history of the region of interest. Other areas of interest include trace element detection, diffusion analysis, and surface analysis (Reed 1989). SIMS has also been used to examine, among other things, Arsenic levels in various pyrite grains (Chryssoulis et al. 1989) as this provides evidence for the presence of Gold. Such studies can be carried out on less specialized SIMS instrumentation. Note: Gold and Arsenic are seen in close proximity. Indeed, owing to the increased sensitivity of Canaries to Arsenic, these were used during the early days of Gold mining, hence the term “Canary in a gold mine.”

The Biosciences present a huge and as yet largely untapped field for SIMS (for some recent reviews, see Boxer et al. 2009; Vickerman and Gilmore 2009;
INTRODUCTION

Passarelli and Winograd 2011; Mahoney 2013). Reasons for this apparent slow adoption lies in the following:

1. The extensive and often highly specific sample preparation procedures required in supporting the often unstable (vacuum sensitive) samples. These are covered further in Section 5.2.3.

2. The challenges in effectively identifying and/or relating many high mass molecular ions (Note: Both low mass and high mass ions are measured in the Biosciences). Two methodologies proving effective in this area are:
   a. cluster ion SIMS discussed in Section 4.1.1.3,
   b. the G-SIMS methodology discussed in Section 5.4.1.1.1.

3. The need for high sensitivity and good detection limits at high mass resolution when constrained to sub micron regions. As will be noted in Chapters 4 and 5, improving one generally comes at the price of the others.

In the case of the third requirement, instrument manufacturers have developed highly specialized Magnetic Sector mass filter-based instruments and time-of-flight mass filter-based instruments. Quadrupole mass filter-based SIMS instruments are ineffective in this area because of their inability to provide the high mass resolution required. Fourier Transform Ion Cyclotron Resonance (FT-ICR) as well as Orbitrap mass filter-based instruments, on the other hand, show significant promise. Mass filters are discussed in Section 4.3.2.1.

An example of a Magnetic Sector-based SIMS instrument that has proved effective in this area is the Cameca nanoSIMS-50. Indeed, this instrument is capable of full transmission at a mass resolution up to $m/\Delta m$ of $\sim2000$ (higher mass resolution obtained at the expense of transmission). This instrument also incorporates a multi-detection system and normal incidence primary ion beams that can be focused to below 50 nm. Mass resolution, along with definitions, is covered in Section 5.2.2.2.

To date, such instruments have proved useful in probing metals in biological specimens with examples including Sodium, Potassium, Calcium, and Zinc (these are detected as $\text{Na}^+$, $\text{K}^+$, $\text{Ca}^+$, and $\text{Zn}^+$). This is generally accomplished by preparing time-sequenced slices of the region of interest. Other high yield ions of interest in biological specimens include isotopes of hydrogen, carbon, nitrogen, oxygen, fluorine, sulfur, and combinations thereof (recorded as: $^1\text{H}^+$, $^2\text{D}^+$, $^{12}\text{C}^+$, $^{13}\text{C}^+$, $^{16}\text{O}^-$, $^{18}\text{O}^-$, $^{19}\text{F}^-$, $^{32}\text{S}^-$, $^{12}\text{C}^2\text{D}^-$, $^{12}\text{C}^1\text{H}_2^-$, $^{12}\text{C}^{14}\text{N}^-$, $^{13}\text{C}^{14}\text{N}^-$, $^{12}\text{C}^{15}\text{N}^-$, $^{13}\text{C}^{15}\text{N}^-$, etc.), some of which are introduced through isotopic labeling/spiking. An example of these capabilities is illustrated in Figure 1.5 in which the $^{15}\text{N}$ uptake resulting from $^{15}\text{N}_2$ spiking of Trichodesmium trichomes is tracked as a function of depth (Finzi-Hart et al. 2009). Such studies provide the much needed information on metabolic uptake mechanisms. Further discussion on these capabilities along with additional examples can be found in reviews by Lechene et al. 2006 and Orphan and House 2009.
Figure 1.5 $^{15}$N spatial distribution maps collected at four different depths (images A–D) on a nanoSIMS 50 instrument. These were recorded from the $^{12}$C$^{15}$N$^{-}$ secondary ions emanating from multiple *Trichodesmium* trichomes spiked with $^{15}$N$_2$. The white and black circles highlight the increased levels noted on two distinct cyanophycin granules. The scale bar (white horizontal line in image D) represents 1 μm. Reprinted with permission from Finzi-Hart et al. (2009) Copyright 2009 National Academy of Sciences.

Time-of-Flight-based SIMS instruments that have proved effective in this area include the Ion-Tof™ TOF-SIMS series, and the Physical Electronics nano-TOF and TRIFT™ series. These instruments provide the capability of analyzing higher mass secondary ions than possible in their Magnetic Sector-based counterparts and to retrospectively examine signals not originally thought of interest (in Magnetic Sector-based instruments, all signals of interest must be defined before the experiment). The ability to follow specific molecular species or fragments intrinsic to the sample being examined (as opposed to molecules formed as a result of the collision cascade) also eliminates the need for isotopic labeling (Belu et al. 2003; Fletcher et al. 2011).

Although such instruments have proven effective, limitations resulting in poorer detection limits (due to the poorer molecular ion yields) and some reduction in spatial resolution are noted. Indeed, for the analysis of extremely large molecular ions, techniques such as Matrix-Assisted Laser Ablation and Ionization (MALDI) become more effective. That being said, the introduction of large cluster primary ion beams is opening up new areas not previously accessible to SIMS. This is realized as such beams can allow for three-dimensional mapping of specific molecular species to a spatial resolution of between 1 and 30 μm depending on whether a continuous (former value) or pulsed (latter value) primary ion source is used. Some recent reviews on these capabilities can be found in Vickerman 2009; Passarelli and Winograd 2011; Mahoney 2013.

Lastly, SIMS analysis has been carried out using a FT-ICR mass filter-based instrument. The example reported in the literature (Smith et al. 2011) describes the capability of imaging high mass molecular secondary ions resulting from $^{12}$C$_{60}^+$ cluster ion impact to a mass resolution better than 100,000 from micron scale regions. Such mass filters also provide greater detection limits for high mass secondary
ions, but at the expense of analysis times. FT-ICR-based SIMS is presently, only available in research environments. Further discussion on instrumentation can be found in Chapter 4.

1.3 SUMMARY

SIMS is one of the many chemical analysis techniques presently available. Chemical analysis describes the act of elucidating the chemical constituents (elements and/or molecules) making up the material of interest and how these constituents interact with each other (bonding type, etc.). This then affords the possibility of defining the physical properties of the substance of interest.

SIMS can be summarized as a mass spectrometric technique that is applicable to solids (most other mass spectrometric techniques require the sample to be in the liquid or gaseous state). Mass spectrometric techniques differentiate between the different elements and molecules based on their mass-to-charge ratio. To simplify matters, the vast majority exists in the $+1$ or $-1$ charge state. Their mass, in turn, is defined by the number of protons and neutrons making up the element with molecules made up of elements. Note: All matter is made up of the elements with the physical properties of matter thus derivable from the elements present and the way in which they are bound.

SIMS probes a solid by directing a focused energetic ion beam (this is most typically in the 0.1–50 keV range) at the solid’s surface of interest. These ions, defined as the primary ions, initiate the emission of atoms from the surface, with a small percentage departing in the ionized state. The emitted ions are referred to as the secondary ions. These are extracted and focused such that the beam can be directed into a mass spectrometer. Some primary ion beams include, but are not limited to, $O^-$, $O_2^+$, $Cs^+$, $Ga^+$, $In^+$, $Au^{+}$, $Bi^{+}$, $SF_5^+$, $C_{60}^+$, $C_{84}^+$, $C_{24}H_{12}^+$, $Ne^+$, $Ar^+$, and $Xe^+$. In some cases, multiply charged ions may also be used with some examples being $Bi_n^{2+}$ and $Bi_n^{3+}$.

The advent/development of SIMS initially hinged on the capability to produce the high vacuum conditions needed. Indeed, it was not until the 1950s that true ultra high vacuum conditions could be reached even though the first secondary ions were recorded in 1910. Note: The first mass spectrometer was not constructed until 1919 with the first experimental SIMS installation not appearing until 1949. Dedicated instruments did not appear until the 1960s. Owing to the popularity of SIMS, this technique has since seen extensive sophistication and diversification, some of which can be traced to the parallel development in computational power.

This sophistication is evident in all forms of SIMS as they exist today. Indeed, SIMS is now routinely used to measure isotopic, elemental, and/or molecular distributions (whether existing at the outermost surface or within a substrate) through the application of highly specific instrumentation. Likewise, SIMS, which has long been able to measure atomic ion emissions, can now do so to unprecedented sensitivity, detection limits, dynamic range, mass resolution, spatial resolution, and depth resolution.
Traditionally, SIMS has been subdivided into the areas otherwise referred to as Static SIMS and Dynamic SIMS. Static SIMS analyzes the undisturbed population of elements and molecules that are present at the outermost surface of a solid. Dynamic SIMS probes the constituents present at the surface and below through the removal of many layers per analytical cycle. This is carried out using primary ion beams of significantly higher current densities. This form of SIMS also introduces the possibility to derive depth distributions of any element and in some cases, molecular species with relative ease. The ability to derive molecular depth profiles and even three-dimensional images is a recent advent introduced using large cluster primary ion sources on specific substrates.

The popularity of SIMS stems from multiple factors, some of which simply arose as a result of the sophistication driven by both industrial and academic needs. This drive resulted from the initial realization that SIMS was capable of deriving both isotopic ratios and elemental depth distributions over highly localized volumes to extreme sensitivity and detection limits with relative ease. As a result, Dynamic SIMS has, for example, become the technique of choice in such areas as dopant profiling in the semiconductor industry and chronological studies using Zircon in the Earth Sciences. Increased use is also noted in the Biosciences, which is being further facilitated by the development of new methodologies. Indeed, new application fields continue to emerge with the new capabilities being developed.

The full power of SIMS is realized in that it provides insight into past events (when applied in the Earth Sciences inclusive of Cosmology), as well as present-day events (when applied in the Materials and Biosciences), thereby allowing predictions of future events (all sciences).