9
ION SCATTERING TECHNIQUES

9.0 INTRODUCTION

In this chapter three ion-scattering methods for determining composition and geometric structure (for single crystal material) are discussed. They are Rutherford Backscattering Spectrometry, RBS, which typically utilizes high-energy He or H ions (usually 1–3.4 MeV energies), Medium-Energy Ion Scattering, MEIS (ion energies from 50 keV to 400 keV), and low-energy ion scattering (100 eV to 5 keV) which is more commonly known as Ion-Scattering Spectroscopy, ISS. A fourth technique, Elastic Recoil Spectrometry, ERS, is an auxiliary to these methods for the specific detection of hydrogen. All the techniques are performed in vacuum.

For the three ion-scattering techniques there are differences in information content that are a consequence of the different ion energy regimes involved, plus some differences in instrumentation. For RBS, the most widely used method, the high-energy ions penetrate well into the sample (up to 2 μm for He ions; 20 μm for H ions). On its way into the sample an individual ion loses energy in a continuous manner through a series of electronic scattering events. Occasionally an ion undergoes a billiard ball-like collision with the nucleus of an atom in the sample material and is back scattered with a discrete, large energy loss, the value of which is characteristic of the atom struck (momentum transfer). Since this major energy loss is atom specific, whereas the small continuum energy losses depend on the depth traveled, the overall energy spectrum of the emerging back scattered ions reveals both the elemental composition and the depth distribution of those elements in a nondestructive manner. Since the scattering physics is quantitatively well understood at
these high energies (Rutherford Scattering) a standardless depth profile is obtain-
able with a few percent accuracy. Other important factors are: the separation in
backscattering energy of adjacent elements in the backscattered spectrum decreases
with increasing mass such that Ni and Fe are not separable, whereas C and O are
easily distinguished; the backscattering cross section is essentially proportional to
$Z^2$ and therefore heavy elements in light matrices have much better de-
tection limits (by about a factor of 100) at 10–100 ppm than vice versa; the depth-resolution
depends on ion energy, angle of incidence, and depth below the surface such that a
resolution of 20 Å is achievable (low ion energy, grazing angle, analysis done right
at the surface), but more typical values are several hundred angstroms.

For single crystal materials, aligning the ion beam with a crystallographic direc-
tion suppresses the signal from below the first few layers, since the atoms in these
layers shadow bulk atoms below from the incoming ion beam. This technique,
known as channeling, is used both to enhance the surface sensitivity and to deter-
mine the extent of crystalline defects, since if atoms are displaced from their correct
positions the degree of shadowing in the channeling mode will be decreased.

MEIS is a more sophisticated form of RBS that uses lower energy ions (usually
100–400 keV) and a higher resolution ion energy analyzer. The lower energies
restrict the probing depth. The better energy resolution improves the depth resolu-
tion down to a few angstroms. It also improves the ability to distinguish elements at
high mass. When used for single crystal materials in conjunction with channeling
of the incoming ions, and blocking of the outgoing backscattered ions, the method
provides atomic positions at a surface, or an interface up to 4 or 5 layers below the
surface, to an accuracy of a few hundredths of an angstrom. In addition it retains
the standardless quantitation of the RBS method with sensitivities to submonolayer
amounts. Both RBS and MEIS are extremely expensive, requiring an ion accelera-
tor. The lower energy accelerator of MEIS is cheaper, but this is counteracted by
the greater expense of the more sophisticated ion energy analysis. Both techniques
typically cost around $1,000,000 and take up large laboratories. Beam diameters
are usually millimeters in size, but microbeam systems with spatial resolution down
to 1 μm exist. Ion-beam damage can be a problem, particularly for polymers. It can
be mitigated by using low ion doses and by rastering the beam.

ISS involves the use of ions (usually He or Ar) in the 100–5000 eV range. At
these energies essentially only backscattering from atoms in the outermost atomic
layer produces peaks in the ion energy spectrum due to nearly complete neutraliza-
tion of any ions scattered from below the surface. As with RBS and MEIS the abil-
ity to resolve adjacent elements becomes rapidly poorer with increasing $Z$. This can
be mitigated, but not solved entirely, by changing the mass of the ion (eg Ar for
He), the ion energy, and the angle of detection. All these variations significantly
affect the scattering cross section and background, however, which complicates
quantitative use. Quantitation is not standardless at these energies but requires suit-
able standards to determine relative cross sections for the set of scattering parame-
ters used. Cross sections still depend roughly on $Z^2$, however, so the technique is much more sensitive to high-Z materials. Owing to its extreme surface sensitivity ISS is usually used in conjunction with sputter profiling over the top 50 Å or so. Spatial resolution down to about 150 μm is routinely obtained. The technique is not widely used owing to the lack of commercial equipment and its poor elemental resolution. Instrumentation is quite cheap, and simple, however, since an ordinary ion gun replaces the ion accelerator used in RBS and MEIS. It can be used as an auxiliary technique on XPS or AES spectrometers by reversing the voltage on the analyzer to pass ions instead of electrons.

In ERS, also known as Forward Recoil Spectrometry, FRS, Hydrogen Recoil Spectrometry, HRS, or Hydrogen Forward Scattering, HFS, hydrogen atoms present in a sample recoil from He ions striking the sample at grazing angle with sufficient forward momentum to be ejected. They are then separated from any He that also emerges by using a thin stopping foil that allows energetic H to pass but not He. In this way the hydrogen content can be quantitatively determined. The technique can be applied in RBS, MEIS, or ISS spectrometers and is used because a target atom that is lighter than the incident ion is only scattered in the forward direction; it is never backscattered. Therefore regular RBS cannot be used for H detection. The depths analyzed and depth-profiling capabilities are similar to those of the equivalent backscattering methods, but the depth resolution is poor (~500 Å at 1000-Å depths). NRA (Chapter 11), an alternative technique for detecting hydrogen, has greater sensitivity than ERS. SIMS (Chapter 10) has far greater sensitivity for hydrogen (down to trace amounts) than either technique and better depth resolution, but it is a destructive sputter-removal method and is difficult to quantify. Sample damage can also be a problem with ERS, particularly for polymers.
### Introduction

Ion Scattering Spectroscopy (ISS) is one of the most powerful and practical methods of surface analysis available. However, it is underutilized due to a lack of understanding about its application and capabilities. This stems from its history, the limited number of high-performance instruments manufactured, and the small number of experienced surface scientists who have actually used ISS in extensive applications. Ironically, it is one of the easiest and most convenient surface analytical instruments to use and it provides useful information for almost any type of solid material.

The most useful application of ISS is in the detection and identification of surface contamination, which is one of the major causes of product failures and problems in product development. The surface composition of a solid material is almost always different than its bulk. Therefore, surface chemistry is usually the study of unknown surfaces of solid materials. To better understand the concept of “surface analysis,” which is used very loosely among many scientists, we must first establish a definition for that term. This is particularly important when considering ISS
because of its extreme sensitivity to the surface. In most applications surface analysis implies the analysis of a finite thickness or depth of the outermost layers of a material, generally from the outer few atomic layers to a depth of 100–200 Å. Techniques encompassing layers greater than that are better described as thin-film analyses, or as depth profiles directed at obtaining other information. Techniques like Energy-Dispersive X-Ray Spectroscopy (EDS) and FTIR with ATR (Attenuated Total Reflection) generally do not fit the description of surface analysis. Other techniques, such as Auger and ESCA, meet the definition by obtaining spectra that originate from a depth of up to approximately 50–80 Å.

ISS is the most surface sensitive technique known. It is routinely sensitive to the outermost layer of atoms. At this level of depth sensitivity, it can be shown by ISS that most practical solid materials have the same outer atomic layer, i.e., a layer of surface water molecules, or organic material, with the hydrogen oriented upward. Therefore in ISS, as in SIMS using low-energy ions, it is important to include spectra from several different sputtered depths into the surface or to specify the sputtered depth from which the spectrum was obtained. Usually a series of ISS spectra are obtained at successively greater depths into the surface and the resulting spectra are displayed to show the changing composition versus depth. Because of the extreme surface sensitivity of ISS, these depth profiles offer details about changes in surface composition in the outer 50 Å that are generally not obtainable by other techniques. These details are extremely important in many applications, such as the initiation of corrosion, adhesion, bonding, thin-film coatings, lubrication, and electrical contact resistance. Typical data and applications will be discussed.

History

Earlier studies of ion scattering were directed primarily at gas–ion interactions. As studies of ion–solid surfaces became common the energy of the scattered ions was eventually related mathematically to a simple binary elastic event involving a single atom on a surface element and a single probe ion.

The practical use of ion scattering was not developed until the late 1960s when David P. Smith of 3M Company first reported the use of low-energy inert ion scattering to analyze the composition of surfaces. This early pioneering work established ion scattering as a very useful and viable spectroscopy for studying surfaces. The first studies and instruments consisted of simple systems where the ion beam scattered through an angle of 90°; thus accepting only a small solid angle of the signal. Modern systems use ion beams that are coaxial with the detector and exhibit orders of magnitude higher sensitivity. These devices make use of a Cylindrical Mirror Analyzer (CMA) and include detection of ions scattered about a 360° solid angle. A typical device is shown in Figure 1. ISS has since become readily available commercially and is recognized as one of the four major surface techniques, generally including ESCA (XPS), Auger, and SIMS as well.
Basic Principles

ISS is relatively simple in principle and application. When a low-energy (100–5000 eV) beam of positive ions of some inert element, such as He, Ne, or Ar, strikes a surface, some of the ions are reflected back from the surface. This scattering process involves a single surface atom and a single incident ion. It is, therefore, a simple binary elastic collision that follows all the rules of classical physics. The incident ion scatters back with a loss of energy that depends only on the mass of the surface atom (element) with which the collision occurred. The heavier the surface atom, the smaller the change in energy of the scattered ion. Thus carbon, which is a light atom of mass 12, is readily displaced and the probe ion loses most of its energy, whereas a heavy atom like Pb, having mass 208, is not easily moved. An ion scattering from Pb retains most of its incoming energy. To obtain a spectrum, one merely records the number of scattered ions as their energy is scanned from near 0 eV to the energy of the primary incoming beam. Each element has a unique mass and therefore a unique energy at which the probe ion scatters. The energy of the scattered ion is mathematically related to the mass of the surface atom by the following equation:
where $E_0$ is the energy of the incident probe ion, $E_1$ is the energy of the ion scattered from surface atom, $E_t$ is the ratio of the energies of the scattered and probe ions, $M_1$ is the mass of the primary ion, $M_2$ is the mass of the surface atom, and $\theta$ is the scattering angle measured from the direction of the ion beam.

Penetration of the incident beam below the very outermost atomic layer causes excessive and nondiscrete loss of energy such that the scattered ions do not yield sharp, discrete peaks. Only ions scattered from the outer atomic layer of a surface give rise to a sharp peak. ISS is therefore extremely sensitive to the surface and essentially detects only the outermost surface layer. To obtain more extensive surface information, it is therefore common to continuously monitor the ISS spectrum while sputtering into the surface. When the sputtering is done very slowly using a light atom, such as isotopically pure $^3$He+, complete spectra can be obtained at successively greater depths into the surface. In routine practice, sputter rates on the order of about 1 to 5 Å per minute are used and approximately 15–20 ISS spectra are obtained throughout a sputtered depth of about 100 Å. Since the most important information is obtained near the surface, the majority of these spectra are obtained in the first few minutes of sputtering.

As the scattering angle $\theta$ is decreased to 90°, the physical size of the CMA must increase, until finally one cannot use a CMA but must resort to a sector analyzer. This decreases detection sensitivity by 2–3 orders of magnitude, increases multiple scattering at energies above the primary peaks, and requires much more precise positioning of the sample. Changing the mass of the primary ion beam gas controls not only the sputtering rate of the surface but also changes the spectral resolution and detection sensitivity. For example, using $^3$He+ permits good detection of C, N, and O, whereas using $^4$He+ does not. Using Ar+ provides high sputtering rates for deeper profiles but does not permit the detection of elements having mass less than Ca. Argon also provides increased spectral resolution for higher elements not resolved by He. It is common to sometimes mix Ar and He to detect all elements while obtaining a high sputtering rate. Increasing the energy of the primary beam to above about 3000 eV dramatically increases the overall spectral background, thus decreasing sensitivity, but the spectral resolution increases. Decreasing the beam energy decreases this background and dramatically decreases the sputtering rate. It is possible to obtain useful ISS spectra at energies below 200 eV of He at less than a few nA. The sputtering rate under these conditions is extremely low.

During normal operation, the entire ISS spectrum, covering all elements, is scanned in about 1 second. A number of these scans are then added for signal enhancement and to control the predetermined depth to which sputtering is
9.1 RBS

Rutherford Backscattering Spectrometry

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Introduction

Rutherford Backscattering Spectrometry (RBS) is one of the more quantitative depth-profiling techniques available, with typical accuracies of a few percent. The depth profiling is done in a nondestructive manner, i.e., not by sputtering away the surface layers. Results obtained by RBS are insensitive to sample matrix and typically do not require the use of standards, which makes RBS the analysis of choice for depth profiling of major constituents in thin films. Detection limits range from a few parts per million (ppm) for heavy elements to a few percent for light elements. RBS depth resolution is on the order of 20–30 nm, but can be as low as 2–3 nm near the surface of a sample. Typical analysis depths are less than 2000 nm, but the use of protons, rather than helium, as the probe particle can increase the sampling depth by as much as an order of magnitude. Lateral resolution for most instruments is on the order of 1–2 millimeters, but some microbeam systems have a resolution on the order of 1–10 μm.
Three common uses of RBS analysis exist: quantitative depth profiling, areal concentration measurements (atoms/cm²), and crystal quality and impurity lattice site analysis. Its primary application is quantitative depth profiling of semiconductor thin films and multilayered structures. It is also used to measure contaminants and to study crystal structures, also primarily in semiconductor materials. Other applications include depth profiling of polymers, high-Tc superconductors, optical coatings, and catalyst particles.

Recent advances in accelerator technology have reduced the cost and size of an RBS instrument to equal to or less than many other analytical instruments, and the development of dedicated RBS systems has resulted in increasing application of the technique, especially in industry, to areas of materials science, chemistry, geology, and biology, and also in the realm of particle physics. However, due to its historical segregation into physics rather than analytical chemistry, RBS still is not as readily available as some other techniques and is often overlooked as an analytical tool.

**Basic Principles**

RBS is based on collisions between atomic nuclei and derives its name from Lord Ernest Rutherford who first presented the concept of atoms having a nucleus. When a sample is bombarded with a beam of high-energy particles, the vast majority of particles are implanted into the material and do not escape. This is because the diameter of an atomic nucleus is on the order of 10⁻⁴ Å while the spacing between nuclei is on the order of 1 Å. A small fraction of the incident particles do undergo a direct collision with a nucleus of one of the atoms in the upper few µm of the sample. This “collision” actually is due to the Coulombic force present between two nuclei in close proximity to each other, but can be modeled as an elastic collision using classical physics.

The energy of a backscattered particle detected at a given angle depends upon two processes: the loss of energy by the particle due to the transfer of momentum to the target atom during the backscattering event, and the loss of energy by the particle during transmission through the sample material (both before and after scattering). Figure 1 is a schematic showing backscattering events occurring at the surface of a sample and at a given depth d in the sample. For scattering at the sample’s surface the only energy loss is due to momentum transfer to the target atom. The ratio of the projectile’s energy after a collision to the its energy before a collision \( E_1 / E_0 \) is defined as the kinematic factor \( K^{3,4} \)

\[
K = \left( \frac{\sqrt{1 - \left( \frac{M_1}{M_2} \sin \theta \right)^2 + \left( \frac{M_1}{M_2} \cos \theta \right)^2}}{1 + \left( \frac{M_1}{M_2} \right)} \right)^2
\]

where \( M_1 \) is the mass of the incident particle (typically \(^4\)He); \( M_2 \) is the mass of the target atom; and \( \theta \) is defined as the angle between the trajectory of the He particle before and after scattering.
As shown in Figure 1, when the probing particles penetrate to some depth in a sample, energy is lost in glancing collisions with the nuclei of the target atoms as well as in interactions with electrons. For a 2-MeV He atom, the energy loss is in the range of 100–800 eV/nm and depends upon the composition and density of the sample. This means that a particle that backscatters from some depth in a sample will have measurably less energy than a particle that backscatters from the same element on the sample's surface. This allows one to use RBS in determining the thickness of layers and in depth profiling.

The relative number of particles backscattered from a target atom into a given solid angle for a given number of incident particles is related to the differential scattering cross section:

$$\frac{d\sigma}{d\Omega} = \left( \frac{Z_1 Z_2 e^2}{4 E} \right)^2 \frac{4 \left( \sqrt{1 - \left( \frac{M_1}{M_2} \right)^2 \sin^2 \theta + \cos^2 \theta} \right)^2}{(\sin \theta)^4 \sqrt{1 - \left( \frac{M_1}{M_2} \sin \theta \right)^2}}$$

(2)

where $Z_1$ and $Z_2$ are the atomic numbers of the incident atom and the target atom, $E$ is the energy of the incident atom immediately before scattering, and $e$ is the electronic charge. A rule of thumb is that the scattering cross section is basically proportional to the square of the atomic number $Z$ of the target species. This means that RBS is more than a hundred times more sensitive for heavy elements than for light.
elements, such as B or C. There is much greater separation between the energies of particles backscattered from light elements than from heavy elements, because a significant amount of momentum is transferred from an incident particle to a light target atom. As the mass of the target atom increases, less momentum is transferred to them and the energy of the backscattered particle asymptotically approaches the incident particle energy (see Equation 1). This means that RBS has good mass resolution for light elements, but poor mass resolution for heavy elements. For example, it is possible to resolve C from O or P from Si but it is not possible to resolve W from Ta, or Fe from Ni when these elements are present at the same depths in the sample, even though the difference in mass between the elements in each of these pairs is roughly 1 amu.

Figure 2 shows how the processes combine to create an RBS spectrum by displaying the spectra from two TaSi$_x$ films on Si substrates. Metal silicide films are commonly used as interconnects between semiconductor devices because they have lower resistivity than aluminum or polysilicon. The resistivity of the film depends upon the ratio of Si to metal and on the film thickness, both of which can be determined by RBS. The peak in each spectrum at high energy is due to scattering from Ta in the TaSi$_x$ layers while the peak at lower energy is from Si in the TaSi$_x$ layer and the Si substrate. The high-energy edge of the Ta peaks near 2.1 MeV (labeled $A$) corresponds to scattering from Ta at the surface of both samples, while the high-energy edge of the Si peaks (labeled $D$) near 1.3 MeV corresponds to backscattering from Si at the surface of the TaSi$_x$ layer. By measuring the energy width of the Ta peak or the Si step and dividing by the energy loss of He (the incident particle) per unit depth in a TaSi$_x$ matrix, the thickness of the TaSi$_x$ layer can be calculated. For example, the low-energy edge of the Ta peak corresponds to scattering from Ta at the TaSi$_x$-Si interface and the step in the Si peak corresponds to the increase in the incomplete backscattering.
Si concentration at the TaSi$_x$–Si interface. In this example, one of the films is 230 nm thick, while the other film is 590 nm thick. Particles scattered from Ta at the TaSi$_x$–Si interface of the 230-nm film have a final energy of about 1.9 MeV (labeled $B$) after escaping from the sample, while particles scattered from Ta at the TaSi$_x$–Si interface of the 590-nm film have a final energy of about 1.7 MeV (labeled $C$). Similarly, particles scattered from Si at the TaSi$_x$–Si interface of the 230-nm film have a final energy of about 1.1 MeV (labeled $E$) after escaping from the sample, while particles scattered from Si at the TaSi$_x$–Si interface of the 590-nm film have a final energy of about 0.9 MeV (labeled $F$). In these spectra the greater energy width of the Ta peak and the Si step for the 590-nm TaSi$_x$ film are directly related to the greater thickness of the film.

By measuring the height of the Ta and Si peaks and normalizing by the scattering cross section for the respective element, the ratio of Si to Ta can be obtained at any given depth in the film. Due to the smaller scattering cross section for Si, the Si peaks in Figure 3 have been multiplied by a factor of 5. The height of a backscattering peak for a given layer is inversely proportional to the stopping cross section for that layer, and in this case the stopping cross section of TaSi$_{2.3}$ is 1.37 times greater than that of Si. This explains why, even for the film with a Si/Ta ratio of 2.3, the height of the peak corresponding to Si in the TaSi$_x$ layer is less than $\frac{1}{2}$ the height of the peak corresponding to Si in the sample substrate.

**Channeling**

In addition to elemental compositional information, RBS also can be used to study the structure of single-crystal samples. When a sample is *channeled*, the rows of atoms in the lattice are aligned parallel to the incident He ion beam. The bombard-
ing He will backscatter from the first few monolayers of material at the same rate as a nonaligned sample, but backscattering from buried atoms in the lattice will be drastically reduced, since these atoms are shielded from the incident particles by the atoms in the surface layers. For example, the backscattering signal from a single-crystal Si sample that is in channeling alignment along the (100) axis will be approximately 3% of the backscattering signal from a nonaligned crystal, or amorphous or polycrystalline Si. By measuring the reduction in backscattering when a sample is channeled it is possible to quantitatively measure and profile the crystal perfection of a sample, or to determine its crystal orientation.

Figure 3 shows channeled spectra from a series of Si samples that were implanted with $10^{13}$, $10^{14}$, and $10^{15}$ arsenic atoms/cm$^2$. Only the As peaks for the two highest dose implants are shown, but with a longer data acquisition time the concentration $10^{13}$ As atoms/cm$^2$ could be detected. The damage caused to the Si crystal lattice by the As implants is reflected in the peaks near 1.25 MeV in the aligned spectra. In the case of the $10^{15}$-atoms/cm$^2$ implant there is little or no single-crystal structure remaining in the damaged region of the Si, so the backscattering signal is the same height as for nonaligned Si. Measuring the energy width of the damage peak indicates that the damaged layer is approximately 200 nm thick. Integrating the damage peak and subtracting the backscattering signal obtained for the nonimplanted reference indicates that approximately $1.0 \times 10^{18}$ Si atoms/cm$^2$ were displaced by the $10^{15}$-atoms/cm$^2$ As implant, while $3.4 \times 10^{17}$ and $1.7 \times 10^{16}$ Si atoms/cm$^2$ were displaced by the $10^{14}$-atoms/cm$^2$ and $10^{13}$-atoms/cm$^2$ As implants, respectively. In this case RBS could be used to measure accurately the total concentration of arsenic atoms implanted in each sample, to profile the As implant, to determine the amount of As that is substitutional in the Si lattice and its lattice location, to measure the number of displaced Si atoms/cm$^2$, and to profile the damage in the Si crystal.

**Quantification**

As noted above, the calculation of elemental concentrations and thicknesses by RBS depends upon the scattering cross section of the element of interest and the stopping cross section of the sample matrix. The scattering and stopping cross sections for each element have been carefully measured and tabulated.\(^3\)\(^4\)\(^7\) In general, scattering cross sections follow the Rutherford scattering model to within 5%. It is difficult to accurately describe the stopping cross sections for all elements with a single equation, so semiempirical values are employed. A polynomial equation with several terms is used so that the stopping cross sections for each element can be calculated over a range of energies. In general, the calculated stopping cross sections are accurate to 10% or better. The stopping cross section for a multi-elemental sample is calculated by normalizing the stopping cross section of each element to its concentration in the sample.
Figure 4  RBS spectra from a sample consisting of 240 nm of Si on 170 nm of SiO$_2$ on a Si substrate. The spectrum in (a) was acquired using a scattering angle of 160° while the spectrum in (b) used a detector angle of 110°. This sample was implanted with $2.50 \times 10^{16}$ As atoms/cm$^2$, but the As peak cannot be positively identified from either spectrum alone. Only As at a depth of 140 nm will produce the correct peak in both spectra.

Due to the convoluted mass and depth scales present in an RBS spectrum, it may not be possible to accurately describe an unknown sample using a single RBS spectrum. For example, Figure 4a is an RBS spectrum acquired at a backscattering angle of 160° from a sample implanted with $2.50 \times 10^{16}$ atoms/cm$^2$ of As at a depth of approximately 140 nm. If this were a totally unknown sample it would not be possible to determine positively the mass and depth of the implanted species from this spectrum alone, since the peak in the RBS spectrum also could have been caused by a heavier element at greater depth, such as Sb at 450 nm, or Mo at 330 nm, or by a...