12 *Ion beams for material analysis*

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Ion Scattering Spectrometry

Fundamentals

Ion Scattering Spectrometry is an analytical method, which uses various range of incident energies. The ions are irradiated onto a sample surface, then the scattered ions or neutrals from surface and inside of the material are detected. Those scattered ions have information on surface composition, compositional change in depth, structure, and so on. For this ion scattering, 4 fundamental physical concepts are important to understand the acquired spectrum. So first of all these 4 concepts are described in this section.

Kinematic factor

Figure 12.1 shows the schematic of elastic collision between a projectile of mass M_1 , energy E_0 and a target mass M_2 which is initially static. After the collision, the projectile of mass M_1 is scattered to the direction of angle θ with energy E_1 = KE_0 and target particles of mass M_2 are recoiled in direction of angle ϕ with energy E_2 .



FIGURE 12.1

Schematic of elastic collisions

 E_1 can be calculated with E_0 , M_1 , M_2 , and θ , by using momentum conservation law. The ratio, between the kinetic energy of scattered particle E_1 and incident particle E_0 is called "Kinematic factor", K, is given by:

$$K = \frac{E_1}{E_0} = \left[\frac{M_1 \cos\theta + \sqrt{M_2^2 - M_1^2 \sin^2 \theta}}{M_1 + M_2}\right]^2$$
(1.1)

Since the parameters M_1 , E_0 , and θ are usually known, M_2 is determined and then the target element is identified.

Scattering cross section

Next, the probability that the projectile is scattered by the target atom is called as scattering cross section, σ , which is expressed by the value of scattered particles per unit area divided by the

number of incident particles. The scattering cross section per d Ω , which is the solid angle per unit of the detector, is defined as "differential scattering cross section", $d\sigma/d\Omega$. $d\sigma/d\Omega$ can be analytically calculated from

$$\frac{d\sigma}{d\Omega} = \left(\frac{Z_1 Z_2 e^2}{4E_0}\right)^2 \times \frac{4\left[\sqrt{M_2^2 - M_1^2 \sin^2 \theta} + M_2 \cos \theta\right]^2}{M_2 \sin^4 \theta \sqrt{M_2^2 - M_1^2 \sin^2 \theta}}$$
(1.2)

where Z_1 and Z_2 are the atomic numbers of the incident and target ions, respectively.

By measuring the energy of scattered particles and using kinematic factor K, it is possible to decide what element is of the target atom. Also, as the yield of the scattered particles is proportional to the concentration of target atom, by measuring the number of the scattered particles and using the differential cross section $d\sigma/d\Omega$, the concentration of the target atom can be calculated. Because $d\sigma/d\Omega$ is proportional to Z_2^2 , the sensitivity of heavy element is much higher than that of light element, which is also shown in Figure 12.2. Generally, the sensitivity of heavy element, for example Ta or W, is around several ppm, and that of light element like C or O, is approximately several %.



FIGURE 12.2

Calculated relative yield of scattered He ions from various elements. The incident energy is 2.0 MeV and scattering angle is 160°

Stopping power

When incident ion goes through in a solid, the ion loses its energy by the interaction with electrons in a solid. The energy loss is proportional to the distance which the ion traveled in the material. That means, by using the energy loss per unit length, which is defined as "stopping power", the energy loss can be converted to depth information. Figure 12.3 shows a scattering event, where a projectile of energy E_{in} with incident angle α is scattered at depth t, to the direction of angle β .



Schematic diagram of the energy loss of incident particle, scattered at the depth t

The energy E_{out} , which is the energy of the scattered particle at the surface of the material, is given by:

$$E_{out} = K \left[E_{in} - \frac{t}{|\cos \alpha|} \cdot \left(\frac{dE}{dx}\right)_{in} \right] - \frac{t}{|\cos \beta|} \cdot \left(\frac{dE}{dx}\right)_{out}$$
(1.3)

where $(dE/dx)_{in}$, $(dE/dx)_{out}$ are the stopping power during the incident and exit path, respectively. From the energy loss, $\Delta E = E_{in}-E_{out}$, the information of depth can be acquired. In most cases, as the stopping powers of target materials are unclear, the stopping power per areal density, ex. eV/atoms·cm⁻², is usually used. As for the values of stopping power, the semi-empirical formula, which is based on LSS model and is derived by Ziegler [1], is widely used.

Energy straggling

The last concept is "energy straggling". When the incident ion goes through the material, the projectile gradually loses its energy as described before. At the same time, this energy loss has some statistical broadening because this energy loss is derived from the independent collisional process. This energy fluctuation was first suggested by Bohr [2], based on LSS (Lindhard-Scharff-Schiøt) theory. For several MeV regions, the energy distributioncan be approximate with Gaussian and its standard deviation is given by:

$$\Omega_B^2 = 4\pi Z_1^2 Z_2 e^4 Nt$$
 (1.4)

where N is an atomic density of a material, and t is a distance where the ion passes through the material, respectively. As shown (1.4), the energy straggling becomes larger as the scattering event occurs in a deeper region.

High Energy Ion Scattering (HEIS, RBS)

Ion scattering spectrometry is often categorized into three fields, shown in Table 1, depending incident energy.

TABLE 1.1

The category of ion scattering analysis, depending on the incident energy

Name	Incident energy
HEIS : High Energy Ion Scattering	1 - 10 MeV
MEIS : MediumEnergy Ion Scattering	200 - 400 keV
LEIS: LowEnergy Ion Scattering	1 – 10 keV

Generally speaking, HEIS means Rutherford backscattering spectrometry (RBS), so in this section RBS is used instead of HEIS.

Equipment

Figure 12.4 shows a basic configuration of RBS equipment.



FIGURE 12.4

Schematic diagram of basic RBS instrument: (1) Ion source, (2) Accelerator, (3) Switching magnet, (4) Collimator, (5) Vacuum chamber, (6) Solid state detector

Incident ions are generated at the ion source, and are accelerated to MeV region by the accelerator. The ion source is placed inside or outside of the accelerator, depending on the type of the accelerator. The ions, with desired valence and energy, are selected with switching magnet and paralleled with collimator. Then the ions are irradiated to the sample surface in the vacuum chamber. In this situation, the incident ions are implanted into the sample. Then some of the incident ions are scattered by the atoms in the material. RBS spectrum is acquired by measuring the energy and yield of the scattered particles with silicon surface barrier detectors (SSBDs). Preamps, linear amp, and multichannel analyser are usually used for detection system.

Application



FIGURE 12.5 RBS spectrum of NiSi film

Figure 12.5 shows a RBS spectrum of NiSi film, formed on a Si substrate. The thickness of NiSi film is approximately 100 nm. 2.0 MeV He⁺ is irradiated onto the sample surface and the backscattered particles are measured with SSBDs set at 160°.

The dotted line is the observed data, and the solid line is the simulated spectrum by theoretical calculation. Considering the scattering of He ions between Ni and Si atoms. As the kinematic factor of Ni is larger than that of Si, the scattered He by Ni atoms in the top surface layer, are detected at the highest energy (1530 keV). These rising edge for each element is called surface edge. The scattered He ions by Ni atoms, which exist in the deeper region from the surface, are detected with lower energy than surface edge, because the ions lose their energy through the path before and after the scattering. The intensity of Ni around the surface edge is higher than that of in the low energy region (1250 - 1450 keV), which means the concentration of Ni near the surface is higher than that of in the deeper region. The surface edge of Si can be seen at 1180 keV and the range from 1180 to 870 keV is the scattering by Si substrate (The concentration of Si in the substrate is much higher than that of in the NiSi film).

In order to obtain compositional depth information from this RBS spectrum, Simulation fitting is widely used. Ion scattering, especially in the case of RBS, since the principle of elastic collisions are quite simple (energy and momentum conservation), the expected RBS spectrum can be accurately calculated by using the basic concepts as shown in 1.1. For this simulation fitting, some useful programs are available and widely used [3] [4]. Figure 12.6 shows the obtained depth profile of this sample, which is the result of simulation fitting.



FIGURE 12.6 RBS depth profile of NiSi film, calculated from the RBS spectrum in Figure 12.6

As already mentioned, the concentration of Ni in the surface region is higher than that of in the deeper region. Ni composition decreases gradually to the deeper region, and the composition of Ni and Si in the deeper region is turned out to be almost 1 : 1. Silicon oxide layers are also observed on the top surface and at the interface between NiSi and silicon substrate.

Medium Energy Ion Scattering (MEIS, HR-RBS)

Equipment

For RBS and ERDA (see section entitled 'Elastic Recoil Detection Analysis (ERDA)') analysis, SSBDs are usually used to acquire the energy spectrum. The energy resolution of SSBDs is generally ~15keV, and this energy resolution limits the depth resolution of the analysis, because the energy loss in a material is converted into depth. Because of this fact, the depth resolution of RBS / ERDA

can be improved if the energy resolution of the detector is improved. In the case of MEIS, the basic idea to improve the energy resolution is to calculate from the particle position after using the energy analysing magnet. Kimura suggested a new system for high-resolution depth profiling, which uses a magnetic spectrometer with a position sensitive detector (PSD) and medium energy ions (e.g. 400 keV) [5]. The energy resolution in this work was ~1 keV for scattered 400 keV He⁺. The use of medium energy He⁺ has some advantages: the higher stopping power which leads to a better energy resolution, and larger scattering cross sections compared with HEIS, which cover the smaller solid angle of the magnetic spectrometer than that of SSBDs.



FIGURE 12.7

Schematic drawing of MEIS system consisting of a magnetic spectrometer and a small accelerator in Kyoto, Japan [6]

Figure 12.7 shows a schematic drawing of MEIS system consisting of a magnetic spectrometer and a small accelerator in Kyoto, Japan, which Kimura has developed [6]. In this system, He⁺ ions are irradiated onto a sample surface, and the energy of the scattered ions is analyzed by a magnetic spectrometer. Then they are detected by a micro-channel-plate position-sensitive detector (MCP-PSD). This type of MEIS system with magnetic analyzer and MCP-PSD is generally called as High-resolution RBS (HR-RBS), which is designed for high energy resolution and high efficiency of ion detection.

Application

Figure 12.8 shows the MEIS spectra of Si wafers, which are implanted As at different energy and different areal density. For this measurement, [111] channeling conditions were used (See section entitled 'Channeling'). From 340 to 350 keV, rectangular-shape spectra from Si were observed, which shows a surface amorphous layer formed by the ion implantation. Comparing the thickness of the amorphous layer, the one formed by As_2^+ implantation is thicker than that of formed by As^+ implantation. This indicates that there is some effect of molecular ions on the process of forming an amorphous layer.



MEIS spectra for 2 keV As⁺ and 4 keV As₂⁺ implanted Si(001) observed under [111] channeling conditions when 400 keV He⁺ ions are incident on the sample [6]. The scattering angle and the incident angle are 50° and 54.7°, respectively

Figure 12.9 shows As depth profiles derived from the observed MEIS spectra. The result of the TRIM simulation [7] for 2 keV As⁺ is also shown for comparison.



FIGURE 12.9

Arsenic depth profiles in Si(001) implanted by 2 keV As⁺ and 4 keV As₂⁺ ions. The result of TRIM simulation is also shown for comparison

Thanks to the good depth resolution of MEIS, a small difference in depth profile between As_2^+ and As^+ implantations. As shown here, MEIS is one of the powerful analyses, which provide us the accurate, quantitative depth profile with sub nm depth resolution.

Figure 12.10 is an example of the application of MEIS which shows the difference of intermixing layer for different annealing temperature. Figure 12.10(a) shows MEIS spectra [8] from 0.26 nm of BaO on 2.7 nm SiO₂ thin film. By annealing, Ba peak becomes broadened, because of diffusion with SiO₂ layer. After the sample was heated to 900 °C, the Ba peak has expanded until almost the same width as the oxygen peak. The inset in Figure 12.10(a) is the multiplot of Ba and oxygen depth profiles, which shows that the Ba has spread throughout the dielectric. This behavior of Ba is much different from other silicate-forming compounds, such as La₂O₃ or Y₂O₃ [9-11]. When a 0.23 nm La₂O₃ on a 3.4 nm SiO₂ is annealed, the La does not fully intermix with the SiO₂, which is shown in Figure 12.10 (b). Annealing causes the La to intermix with SiO₂ but the peak width saturates before the entire SiO₂ layer is consumed. The inset in Figure 12.10 (b) shows that La and oxygen depth distributions are quite different, with a nearly La-free layer existing below the silicate. Evidently, a

silicate phase nucleates for La, and this occupies the upper part of the sample. For Ba, a silicate phase does not nucleate, and instead the Ba dissolves into the SiO₂.



FIGURE 12.10

MEIS spectra showing the effect of annealing on (a) BaO/SiO_2 sample and (b) La_2O_3/SiO_2 . Only the metal part of the spectra is shown. The annealing broadens the metal peak due to the intermixing with SiO₂. The insets show the metal and oxygen depth distributions after a 900°C annealing. While the Ba fully intermixes with the SiO₂, La is confined to the near-surface region

Low Energy Ion Scattering (LEIS)

Equipment

Atoms at the top surface of materials generally have a different chemical state from that of in a bulk. In addition, the composition of the top surface is crucial for many phenomena such as adhesion, corrosion, and catalysis reaction. Because of this background, the analysis of outermost layer has become of importance. This is quite challenging because the analytical technique should distinguish between signals originating from the top surface and bulk. Also, the technique should possess high sensitivity, because the volume of the top surface is quite small. Without high sensitivity, the top surface will be somehow damaged before obtaining information from the outermost layer.

LEIS has existed as a surface analytical technique since the late 1960's, but recently there is a great advance in instrument and its capability and applicability are dramatically improved [12-16]. As mentioned before, LEIS is sensitive to the outermost layer, on the other hand, for example, X-ray photoelectron spectrometry (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS), acquire information from the first few nanometers of the surface. This means, that XPS and ToF-SIMS give useful information such as composition and chemical state, but that information is to

some degree averaged. By comparison, LEIS has become a unique, powerful tool for evaluating the surface composition only of the outermost layer, which is quite useful to understand the relationship between surface top composition and phenomena such as adhesion, catalysis, and reaction [17-20].

LEIS is based on the scattering of noble gas ions that are directed at the surface with 1-8keV. In a binary collision, like HEIS and MEIS, some of the ions are scattered back from an atom in the surface and can be detected by an energy analyzer. As mentioned above, the sensitivity of the detector is a key factor in order to realize "static analysis", which means collecting the spectrum before any damage on outermost layer is caused by ion irradiation.



FIGURE 12.11

Schematic of the double toroidal energy analyzer of the Qtac¹⁰⁰ LEIS instrument [22]

Recently a new type of LEIS instrument has been developed: the Qtac¹⁰⁰, supplied bz ION-TOF GmbH [21]. In the Qtac¹⁰⁰ instrument a double toroidal energy analyzer is used, which is described in Figure 12.11 [22]. This analyzer collects the scattered ions for a given scattering angle (145°) from all azimuth angles. The analyzer images the energy distribution of the ions on a position sensitive detector, which enables parallel energy detection. Its sensitivity is orders of magnitude higher than that of conventional LEIS.

In this instrument, samples can be treated with atomic oxygen in the prechamber of the Qtac¹⁰⁰. This procedure removes organic contamination from the surface. In addition to atomic oxygen, hydrogen is also used for cleaning. Then the samples are transferred under vacuum to the analysis chamber.

Figure 12.12 illustrates how LEIS spectrum can be interpreted. Like MEIS and HEIS, scattering may also take place in layers beneath the surface. However, since noble gas ions are used for the primary beam, the ions are effectively neutralized while traveling within the sample. The ions that survive the interaction with the material have only interacted with a single surface atom, which means, in the outermost layer. Because the electrostatic analyzer, like Qtac¹⁰⁰, can detect only ions, the information will be only from the outermost surface. These ions give rise to the peaks in the

LEIS spectra, as shown in Figure 12.11 (B), that is why they are often called "surface peaks" (ex. Zr_{surf} or O_{surf}).



FIGURE 12.12

(A) Noble gas ion scattering of a ZrO_2 film on Si. Shown are: (1) ion scattering from the top surface, and (2) particle penetration, neutralization, backscattering, and reionization. (B) Illustration of LEIS spectrum for the material shown on the left [23]

The scattered ions from layers beneath the surface lose their energy, not only due to the scattering event, but also from the depth-proportional energy loss on their way into the sample and back to the surface. Those ions can be detected, only if they are re-ionized when leaving the surface. This results in a lower intensity of the ions scattered in deeper layers compared to those scattered at the surface by the same element. These signals can be distinguished from the surface peak, and can be used to obtain depth information.

Application

First example of LEIS technique is an analysis of Pt catalysis [24]. Figure 12.13 (A) shows LEIS spectra of Pt_3Fe alloys supported on carbon, which is a comparison between sputtered and annealed surface. In the spectrum of sputtered surface, Pt and Fe peaks are detected, which indicates that, after mild sputtering the composition of the first outermost layer is the same as that in a bulk Pt_3Fe alloy (that is, 75 % of Pt and 25 % of Fe). On the other hand, in the spectrum for annealed surface shows only Pt peak, which means, after the annealing the surface atomic layer was pure Pt because of the surface segregation, as described in Figure 12.13 (B).





LEIS surface characterization of a Pt_3Fe alloy [24]: (A) LEIS spectra of mildly sputtered and annealed surfaces. The spectra was obtained using $Ne^+ 1$ keV. (B) Schematic model for Pt_3Fe and Pt-skin surfaces. In this Figure M means Fe

As discussed above, this information is not able to be obtained using another surface analytical method, such as XPS and TOF-SIMS, because of the limitation of information depth. The top surface property, for example, plays an important role for catalysis or solid oxide fuel cell (SOFC). In this way, LEIS has become one of the most useful analytical method for catalysis or SOFC [24-26]. Second example is an application of LEIS to semiconductors. Stokhof et al. reported a LEIS

application to study the nucleation and growth of ALD-WNC films [27]. It can be used to determine the growth rate even for the initial ALD stage, to minimize the number of cycles for a pin hole-free layer closure. In this application, LEIS has been used to evaluate coverage ratio of ultrathin WNC layer on silicon. Figure 12.14 shows some LEIS spectra obtained after different number of ALD cycles [28].



FIGURE 12.14 LEIS spectra for WNC layers grown with various numbers of reaction cycles [28]

The signal intensities of the detected elements derive from their atomic concentrations in the outermost atomic layer. After a number of ALD cycles, a low energy tail was observed after the W surface peak. This derives from the growth of multiple layers. The intensity and width of the tail is a direct measure for the thickness distribution of the WN_xC_y layer. A weak Si surface signal is observed even after 40 ALD cycles. This means that with 40 cycles the Si surface is not fully covered by WN_xC_y . This film growth estimated from the LEIS analysis is illustrated in Figure 12.15 [28].



FIGURE 12.15 Schematic of island formation corresponding to 1 (top), 20 (middle), and 40 (bottom) ALD cycles [28]



A detailed evaluation of the Si and W surface coverage is shown in Figure 12.16. The WN_xC_y surface coverage after 40 cycles is estimated to be 93 %. For the applied process conditions a layer growth of 0.08 nm per ALD cycle can be observed once the coverage is complete. After 50 cycles, the Si peak has disappeared completely. This indicates that the SiO_x surface is fully covered with a complete, pin hole-free WN_xC_y layer. As shown here, by using the surface sensitivity of LEIS, the coverage ratio of ultra-thin films can be evaluated, which would have been difficult by XPS or ToF-SIMS.

Elastic Recoil Detection Analysis (ERDA)

Introduction

Elastic recoil detection analysis (ERDA) was first introduced by L'Ecuyer [29] as a useful analytical technique for depth profiling of light elements. As mentioned in the previous section, in the case of RBS, the incident particles that are backscattered by the target atom are detected. However, in the

WN_xC_y and SiO_x coverage as a function of the number of reaction cycles [28]

case of ERDA, the target atoms that are recoiled by the incident ions are directly detected. In this chapter, the basic principles of ERDA, measuring method, and some applications are described.

Instruments and examples

Stopper foil technique (Conventional ERDA)

Similar to RBS, ERDA depends on only four physical basic concepts, which were already described in 2.1—kinematic factor, scattering cross section, stopping power, and energy straggling. By using these four physical concepts, the elastic recoil spectrum can be transformed into a quantitative compositional depth profile. The main difference between the treatment of ERDA and RBS data lies in accounting for the difference in stoppage between the incident particle and recoiled atom.

Figure 12.17 shows the schematic configuration of the ERDA experiment. In this case, He ion beam is irradiated onto the sample surface, and hydrogen atoms in the sample are recoiled in the forward direction. These recoiled hydrogen atoms are detected by the SSBD. A thin film is arranged in front of the SSBD in order to stop the He ions scattered in this direction. This thin film is usually called absorber or stopper foil. A polymer foil, such as polyethylene terephthalate (PET), or thin aluminum foil is used as an absorber.



FIGURE 12.17

Schematic configuration of an ERDA experiment. In this case, He ion is used as an incident beam, and recoiled hydrogen atoms in the material are detected by the SSBD using an absorber

If PET foil is used, since the stopping power of H in PET is approximately one-tenth that of He at the same energy, it is possible to stop the scattered He by setting an appropriate thickness of the PET foil. This method is widely used in ERDA setup owing to its simplicity. Using this simple setup, a quantitative depth profile of light elements such as hydrogen can be obtained. The disadvantage of this technique is that the depth resolution will be deteriorated owing to the energy straggling of the recoiled atoms in the absorber.

Figure 12.18 shows the RBS and ERDA spectrum of diamond-like carbon (DLC) thin film deposited using the plasma chemical vapor deposition (CVD) method on Si wafer. The depth profile generated from simulation fitting is also displayed. He ion beam of 2.3 MeV is used as the incident beam, and recoiled hydrogen atoms are detected by the SSBD, whose scattering angle is set at 30°. The backscattered ions are detected by another SSBD, which is set at 160°. From this analysis, it is revealed that the hydrogen in DLC film exists uniformly in the depth direction within the depth resolution of this analysis, and the hydrogen content is 37.8 atomic %.



(1) RBS and (2) ERDA spectrum of DLC film deposited on Si substrate. Depth profile generated by simulation fitting of these spectra is also shown (3)

Time of flight ERDA (TOF-ERDA)

The absorber foil technique is originally intended to determine hydrogen and its isotopes using He ion beams of million electron volts. Using a heavy ion beam such as chlorine or iodine, the ERDA technique can be extended to the depth profile of elements heavier than hydrogen [30]. However, with a heavy ion beam, a multitude of different recoil masses is detected, with the recorded energy spectrum being the sum of energy spectra of all the recoiled particle types. In order to separate the contributions from various elemental components, the recoil particle detector must employ some form of mass or atomic number identification in conjunction with the energy detection. Time of flight ERDA (TOF-ERDA) is one such technique; it is typically applied to medium mass and heavy ion beams of ³⁵Cl, ¹²⁷I, or ¹⁹⁷Au in the range of 10–200 MeV.

The experimental geometry of TOF-ERDA is very similar to that of the conventional ERDA. A representation of the TOF-ERDA setup at the Wakasa Wan Energy Research Center is shown in Figure 12.19 [31]. The ion beam from the accelerator is transported to the scattering chamber. A TOF pipe is connected to a 40° port of the scattering chamber. In this configuration, the TOF-ERDA measurement system consists of a time detector and SSBD. The detection angle is 40° with respect to the beam direction. The time detector positioned in the flight pass includes a micro channel plate (MCP) detector and an electrostatic mirror grid [32]. The recoiled particles traveling to the TOF detector first pass through two electrostatic mirror time detectors, which measure the time of flight. Subsequently, they are stopped in an SSBD that provides the energy information. The time detectors produce fast timing pulses generated by the secondary electrons as the recoil particle travels through a thin carbon foil. Since the time of flight depends on the mass of recoiled atoms,

this flight time and energy measurement system provides sufficient information to identify the mass of the recoiled particle.



FIGURE 12.19

Typical experimental geometry for TOF-ERDA measurements [31]

Figure 12.20 shows an application of the TOF-ERDA for thin film depth profiling. The coincident detection of the ion velocity and energy produces a histogram such as the one shown in Figure 12.20 (a), where the signals generated by different masses lie on different curves. Thus, each element can be analyzed separately. Through TOF-energy calibration, the time signals are converted first to energy signals and subsequently to energy spectra, which can be compared to the simulated spectra. By using TOF-ERDA, a depth profile of light elements, such as H, Li, C, and O in this example, can be evaluated with good depth resolution.



FIGURE 12.20

(a) Time-of-flight versus energy histogram of the raw data. (b) Elemental depth profile extracted from the raw data. The measurement was performed with a 16 MeV ⁶³Cu beam on a 144-nm LiLaO film on Si substrate [33]

Moreover, other methods have been reported for the detection of recoiled atoms, such as electrostatic spectrometer [34] or magnetic spectrometer [35-37], in order to improve the depth resolution. If medium-energy ion is used, good depth resolution can be obtained using a magnetic spectrometer. This method is also known as high-resolution ERDA (HR-ERDA). By using HR-ERDA, a depth resolution of approximately 0.8 nm is achieved for the measurement of hydrogen distribution in the silicon crystal [38].

Nuclear Reaction Analysis (NRA)

General principles

RBS is a useful method for analyzing atoms whose mass is heavier than that of matrix atoms. In the case of light elements, the signal from light elements is detected with a large background of the scattering signal from heavy elements. Moreover, as described in Figure 12.18, the scattering cross section is proportional to Z_2^2 , and it is difficult to determine the concentration of light elements accurately in a matrix that includes heavy elements. However, there are many nuclear reactions between energetic ions of several million electron volts and light elements. Considering the advantage of this nuclear reaction, by detecting particles or γ -rays emitted from the reaction, light elements can be evaluated with relatively high sensitivity. This method is called nuclear reaction analysis (NRA). RBS and NRA can be used as complementary approaches to evaluate the material composition of light to heavy elements.

Figure 12.21 shows the relationship between the cross-section of ${}^{1}H({}^{15}N, \alpha\gamma){}^{12}C$ and incident ion energy.



FIGURE 12.21

(a) Cross-section for the reaction ${}^{1}H({}^{15}N, \alpha\gamma){}^{12}C$. (b) Schematic representation of hydrogen depth profiling technique. ${}^{15}N$ reacts with hydrogen within the resonance window at a certain depth in the target. Measuring the γ -ray yield and beam energy determines the depth profile of hydrogen concentration [39]

In the case of ${}^{1}H({}^{15}N, \alpha\gamma){}^{12}C$, when ${}^{15}N$ of 6.385 MeV is irradiated to a sample surface, the incident ion induces a nuclear reaction with ${}^{1}H$ existing on the surface. Subsequently, γ -rays of 4.43 MeV are emitted from the reaction. In Figure 12.21 (a), the cross-section has a peak at the energy of 6.385 MeV, and is more than four orders of magnitude greater than the other energy region. This type of reaction is called a resonant reaction, and has a narrow resonant width. In this reaction, the resonant width is 0.005 MeV. When the sample is bombarded with ${}^{15}N$ above the resonance energy, as the ${}^{15}N$ ions penetrate the sample, they lose energy and reach the resonance energy at some depth. By measuring the γ -ray yield as a function of the beam energy, the hydrogen concentration as a function of depth is obtained. This procedure is shown in Figure 12.21 (b).

Furthermore, Figure 12.22 shows the cross-section change for the reaction ⁷Li(p, α)⁴He [40]. In this

case, the cross-section gradually increases as a function of the incident energy. This reaction is called a non-resonant reaction.



FIGURE 12.22

Laboratory differential cross-section for the reaction 7 Li(p, α) 4 He [40]

In the case of reactions that emit particles, sometimes a stopper foil, such as the conventional ERDA, is used to separate the emitted particle and incident ions. When the reaction emits γ -rays, the detector for γ -rays can be placed outside the scattering chamber because the scattering and absorption of γ -rays by the chamber wall can be almost ignored.

Applications

As MeV energetic ion beams can travel several millimeters or centimeters in air, the incident ion can be extracted into air by using a thin foil between air and a vacuum chamber. This thin foil is usually called an "exit window". The exit has to be sufficiently strong to withstand the pressure differential and sufficiently thin to transmit the proton beam. The majority of exit windows in use are polymers such as Kapton and Mylar. Recently, thin SiN film has gained popularity as an exit window owing to its mechanical durability and stability against radiation. As γ -ray loses an extremely small amount of its energy in air, it is possible to perform NRA measurement in air if the ion beam is extracted into air.

Figure 12.23 shows 1 H(15 N, $\alpha\gamma$) 12 C NRA yield curve measured for a hydrogenated Y film (80 nm) deposited on a glass plate [41]. 15 N ion beam was extracted into an in-air chamber through a 100 nm SiN membrane, and the measurement was performed with different N₂ gas pressures. Each curve reveals a maximum corresponding to hydrogen in the Y film, which is shifted to a higher energy region with an increase in pressure owing to the energy loss of 15 N beam in the N₂ gas. Notably, the yield curve is broadened and exhibits a tailing feature at the high-energy side as the N₂ gas pressure is increased. The broadening is partly due to the energy straggling of the incident 15 N beam in the N₂ gas. By using the external beam and NRA technique, it is possible to analyze various samples that are difficult analyze in vacuum, such as ancient documents or biological specimens.

The second example is an NRA depth profiling that uses a non-resonant reaction. Although the reaction is non-resonant, depth information is extracted by using simulation fitting of the spectrum. In the field of next generation Li-ion batteries (LIB), solid-state batteries are one of the most promising candidates in terms of high safety and wide potential window. Extensive research has been carried out to pursue higher ionic mobility and processibility. However, in order to realize all-solid state LIB, fundamental research is still required to understand the mechanism of Li-ion transportation in a solid electrolyte. Various analyses are necessary to research and evaluate the

property of solid-state electrolytes. Furthermore, the depth profile of Li provides important information, especially if the depth profiling at the operating status is possible.



FIGURE 12.23

In this experiment, ${}^{7}Li(p, \alpha)^{4}He$ nuclear reaction was used to obtain Li depth profile. A Li_{1.5}Al_{0.5}Ge_{1.5}P₃O₁₂ (LAGP) solid electrolyte pellet (4 mm) was used as an analyte. Au electrode was deposited on both sides of LAGP. Alternating current (AC) impedance is measured in the chamber, followed by NRA measurement, in order to study the movement of Li under the application of voltage. Figure 12.24 shows the schematic of this experiment.



FIGURE 12.24

Schematic of NRA measurement for Li depth profiling of LAGP under the application of voltage

NRA yield curve measured for a hydrogenated Y film (80 nm) deposited on a glass plate in N_2 gas of various pressures of (a) 0, (b) 1×10^4 Pa, (c) 3×10^4 Pa, (d) 7×10^4 Pa, and (e) 1×10^5 Pa [41]



(a) Nyquist plot of LAGP solid electrolyte. (b) NRA spectra of ${}^{7}Li(p, \alpha){}^{4}He$ reaction for each voltage application. (c) Depth profile of Li for each voltage applied, generated from the NRA spectra

Figure 12.25 (a) shows a Nyquist plot by applying a voltage of 0 and +5 V measured in the NRA chamber. The irradiated surface was set as the positive electrode. A clear difference in the Nyquist plot was observed between the two voltages applied, which indicates a new layer with a different impedance generated by the application of voltage. Figure 12.25 (b) is a comparison of the NRA spectra from the reaction ⁷Li(p, α)⁴He obtained for each voltage applied. The inset is a sample structure that shows the correspondence between the depth and energy of the NRA spectra. From the spectrum obtained at 0 V, Li exists uniformly in the direction of the depth in LAGP. However, at +5 V, the intensity of the spectrum is low in the region of the interface between Au and LAGP. Figure 12.25 (c) shows the Li depth profiles generated from the NRA spectra. The result demonstrates that, when a positive voltage is applied, Li⁺ moved from the interface between the Au positive electrode and LAGP interface in the range of 8.8 µm. As this nuclear reaction can acquire depth information without using ion etching, which sometimes seriously damages and destroys material surface, it has an advantage of acquiring accurate depth profile in an *in situ* condition such as the one demonstrated here.

Particle Induced X-ray Emission (PIXE)

Measurements and quantifications

When H or He ion beam with MeV energy is irradiated to a material, not only the ions are scattered by host atoms, but also characteristic X-ray is emitted. The cross section of this X-ray emission is so large that even trace elements in a material can be detected and quantified. This method is called as PIXE, which means Particle Induced X-ray Emission. 1-4 MeV H⁺ beam is usually chosen as incident beam, because the cross section of X-ray emission is highest in this energy region. For X-ray detection, lithium-drifted Si(Li) detectors are widely used. These detectors combine the advantages of high efficiency in the X-ray energy region of interest, typically 2-20 keV, with a good energy resolution. The resolution is typically 100-200 eV, that means one can fully resolve the K X-rays of neighboring elements in the transition element region of the periodic table. From the yield of characteristic X-ray of each element, the content of those elementcan be obtained. PIXE has some advantages as follows:

- (1) Almost all elements can be analyzed at the same time for one measurement.(By using a Si(Li) detector with Be window, from Al to U can be detected.)
- (2) Very small amount of sample, such as several μ g of specimen, is needed for the measurement.
- (3) With a help of μ -beam, 2D map of trace elements in a material can be acquired.
- (4) By applying external ion beam, samples can be analyzed in atmospheric condition. That means, liquid or biological samples can be evaluated.

PIXE is one of methods of EDX (Energy dispersive X-ray spectrometry). Compared with EDX using electron beam as a probe, PIXE has much higher sensitivity. This is because, the intensity of characteristic X-ray in PIXE is much higher than that of bremsstrahlung X-ray, which leads to a background in X-ray spectrum. On the other hand, when electron beam is used as a probe, bremsstrahlung by atomic nucleus of material is much higher than that of PIXE. Because of this, PIXE has advantage of detecting trace elements than other EDX methods.

Thanks to this advantage, PIXE is now used in various fields, such as medicine, biology, geology, environmental science, and so on.

Applications

First Example is a combination of RBS and PIXE. Figure 12.26 shows RBS and PIXE spectrum for InGaAsP (1 μ m) on InP substrate.

From RBS spectrum, because of low mass resolution of RBS for heavy elements, it is difficult to separate the surface edge of Ga and As. On the other hand, PIXE can clearly distinguish of X-ray peak from Ga and As. The atomic ratio of Ga and As can be evaluated from this PIXE spectrum. By using this information, the composition of InGaAsP layer was obtained as In_{0.44}Ga_{0.06}As_{0.10}P_{0.40} from RBS spectrum. As shown in this example, RBS and PIXE are complementary method. By combining RBS and PIXE analysis, the composition including heavy and close-mass elements can be evaluated.



(a)RBS and (b)PIXE spectrum of InGaAsP (1 μ m) on InP substrate. 2.3 MeV He⁺ beam was irradiated, and both spectra were collected at the same time. The detector angle was 160° for RBS and 135° for PIXE, respectively



FIGURE 12.27

Quantitative spatial distribution maps of Fe, Zn and Mn in two cultivars of pearl millet grain, cross-sectioned longitudinally [42]. Top row, ICMH 1201; bottom row, ICMH 1301. Color scales represent concentrations ($\times 10^4 \mu g \cdot g^{-1}$). Scale bar = 1 mm

The next application is an elemental distribution map of grain tissue of two cultivars of pearl millet, using a micro beam (Micro-PIXE) [42]. Mature, dried pearl millet grains of two cultivars, namely ICMH 1201 and ICMH 1391, were used as analyte. A proton beam of 3.0 MeV energy, a current of ~100 pA and a spot size of $3 \times 3 \ \mu\text{m}^2$ was raster scanned. X-ray spectra were detected with a Si(Li)

detector. By collecting PIXE spectrum at each point and integrated the signal in region of interest, quantitative elemental maps were obtained. Figure 12.27 shows quantitative elemental maps of Fe, Zn, and Mn in two cultivars of pearl millet grain. Mn has the most distinctive pattern of distribution in the embryo, which is localized in the tissues surrounding the embryonic root. This distribution pattern for Mn was also reported in similar studies which is done on mature wheat [43] and barley grains [44].

Since the energy loss of emitted X-ray in air is much smaller than that of charged particles, this PIXE analysis is often performed in atmospheric condition, like NRA analysis, which detects γ -ray.

Channeling

Basic concepts of channeling

Channeling is a steering of incident ions into open spaces, which is called channel, between rows and planes in a crystal. This is illustrated in Figure 12.28



FIGURE 12.28

Illustration of the channeling of ions directed at an angle ψ to a close-packed row of atoms in a crystal



Energy of backscattered particle

FIGURE 12.29 Comparison of random and aligned RBS spectra

The steering is the result of a correlated series of small-angle screened Coulomb collisions between ions and the atoms which border the channel. Thus when the incident angle is aligned to a crystal axis or row, the number of scattered ions dramatically decrease. This is what we call channeling. The spectrum, which is obtained with aligned ion beam, is called "aligned spectrum", and the one without channeling is called "random spectrum". Figure 12.29 shows a schematic of those two spectra. The ratio of yield, between aligned and random spectra in a same region (same energy or same channel), is defined as χ_{min} . χ_{min} indicates the crystallinity of the specimen. The higher the crystallinity is, the smaller χ_{min} becomes.

When analyzing amorphous thin films deposited on a single crystal substrate, since the signal from the substrate often becomes large background, this channeling technique is sometimes used in order to reduce the intensity of signals from the substrate, as shown in Figure 12.8.



FIGURE 12.30

(1) Comparison of RBS spectra of GaN epitaxial film, with and without ion implantation. (2) Damage depth profile of Ga

Examples

Figure 12.30 (1) shows a comparison of aligned and random RBS spectrum of GaN epitaxial films. In one of the samples was implanted Si, with 1×10^{16} atoms·cm⁻² at 50 keV, in order to produce crystal damage in a surface region. The aligned spectrum was acquired with 2.3 MeV He⁺ beam, aligned at <0001> channel of GaN film. In the case of non-irradiated sample, the yield of aligned sample decreases significantly at around 1 % of that of random spectrum. On the other hand, the yield of aligned spectrum for implanted sample increases, especially in the region of 1600~1750 keV. That means because of the damage by ion implantation, more Ga atoms exist within <0001> axis. This damage depth profile, calculated from those spectra, is shown in Figure 12.30 (2). By using the channeling technique, damage depth profiles by ion implantation, or re-crystallization by annealing can be evaluated.

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