Chapter 5

Ion methods of surface analysis

5.1   Ion sources

In case of surface and thin films analysis can ion sources can be used. Suitable sources provide proper ion beams for surface cleaning and for surface layer sputtering in order obtain a depth profile (such as XPS or AES), primary beam for static and dynamic SIMS. Another sources are represented by the particles accelerators used for energetic ion analysis (such as RBS, PIXE, NRA, ERDA etc.)

The ionization methods can be classified according to:

- electron impact

- fast atom bombardment

- electro-spray ionization

- gas discharge ion sources

- solid state surface atom ionisation sources

- high electric field desorption

Ion beam focus:

- wide ion beam sources

- narrow focused ion beam sources

5.1.1   Electron impact ionisation sources

The principle of ionization source is similar as a ionisation gauge. The only modification include a geometry of gauge and ion collector must be replaced by the system which is able to extract the produced ions. Ionisation space is inside the cylinder - screened by anode with the ion trap at the end. Electrons are accelerated from a thermionic emission cathode by high voltage (100 - 500 V). The electrons travel through the ionisation space and ionize gas molecules around them.

The resulting ions are collected at a negative trap electrode - thus resulting in an ion beam. The operating pressure is lower 0.01 Pa and the source provides high focused ion beam with beam current to 10 μA. Due to its properties it is possible another manipulation in ion optics.

Another source modification - double anode source. Two parallel bars - anodes - are placed along the cylindrical cathode (voltage up to 10 kV). Electrostatic field with a saddle point is form on anode axis. Electrons oscillate around this point and they are effectively ionise the gas. The produced ions are accelerated along the plane symmetry to cathode with the outlet. Operation pressure is tenths of Pa, ion current is tens of μA. Electrons are ejected in the form of diverging beam with wide energy distribution $\rightarrow$ they are inappropriate to another manipulation in ion optics. It causes a high chromaticism. In consequence, it is use to surface sputtering.

5.1.2   Plasma sources

Plasma sources generate plasma - excitation of the gas requires ionization of neutral atoms and molecules. High intensity electric field extracts ions from the plasma surface (negative charged electrode). The dependency of extracts ion current I and electrode surface voltage U_{ex} on the thickness d is described by Child-Langmuir law

$$I \approx U_{\text{ex}}^{3/2}/d^2. \tag{5.1}$$

Two types of plasma sources are most often use to surface and thin films analyses. In van der Graff accelerators, high frequency discharge are the ion sources generally use to analysis with ion energy in order MeV. The duoplasmatron is a type of ion source compresses the plasma by a magnetic field in front of the extraction system. The plasma is so dense that matching to the extraction field strength requires an expansion cup to lower the current density. Most often is used as a source of Ar and O ions.

High frequency ion source

Ions can be created in an inductively or capacitively coupled plasma. The electric field has a frequency in order tenth of MHz, the power is tenth to hundreds of W, the pressure is units of Pa, current is from tenth of μA to tenth of mA. The ionization efficiency can be enhanced by magnetic field.
Two types of inductively coupled RF structures are most common. In one type, the induction coil is placed outside a glass or quartz cylindrical tube in which the plasma is generated. The other type has a metallic discharge chamber with an RF antenna inside the discharge plasma.
Although capacitively coupled RF sources are widely used in plasma etching processes, they are seldom employed for the production of ion beams. Capacitively coupled discharges form a very high positive plasma potential. As a result, material is sputtered from the chamber wall to form impurity ions in the extracted beam.

Duoplasmatron

The duoplasmatron operates as follows: a cathode filament emits electrons into a vacuum chamber, then the gas is introduced in very small quantities into the chamber, where it becomes charged

or ionized through interactions with the free electrons from the cathode, forming a plasma. The plasma is then accelerated through a series of at least two highly charged grids, and becomes an ion beam, moving at fairly high speed from the aperture of the device. Duoplasmatrons are characterized by high efficiency - usually above 90 %.

The duoplasmatron components are:

- cathode (K)- generally the heated cathode (thermionic emission), sometimes (for oxygen ions) is use the hollow cold cathode

- intermediate electrode (IE),

- anode (A).

The intermediate electrode and anodes are ferromagnetic and create the part of magnetic circuit. Demirkhanov installed a ferromagnetic anticathode electrode to ensure oscillation of electrons in the anode region of the duoplasmatron. The anticathode was located behind a copper anode and had a potential close to the cathode potential. Electrons oscillating in the magnetic field (1500 G) efficiently ionize the gas at a low pressure of $\sim$5–10^{-3} Torr. When the anticathode negative bias relative to the anode was increased from 0 to 100 V, the ion current increased by a factor of five. The source, which had an outlet aperture 6 mm in diameter and an expansion cup 50 mm in diameter, provided a pulsed hydrogen ion current of up to 1.5 A at a discharge current of 20 A.
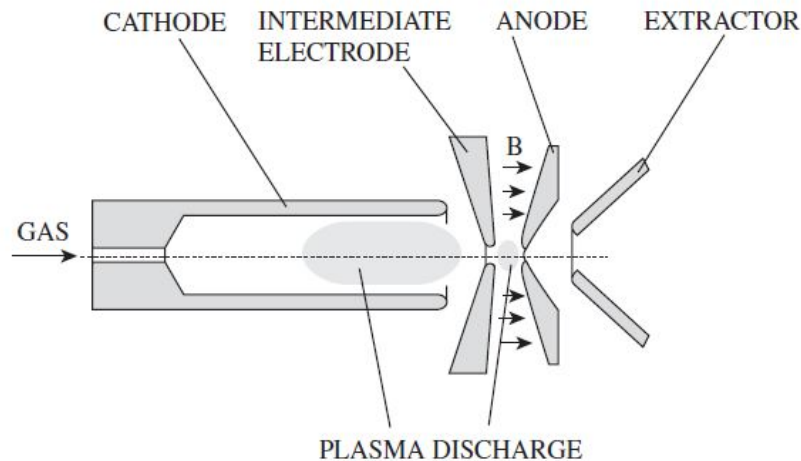

Figure 5.1: Duoplasmatron scheme.

Duoplasmotrons can have different ion sources:

- Penning-type electrode system (PIG) to maintain a high current discharge by electrons supplied through a double electric layer from a plasma cathode, has been embodied most completely in the DuoPIGatron type ion source. The magnetic field diverges toward the ion optics, ensuring oscillation of primary electrons between the intermediate and screen electrodes and formation of a large, uniform plasma surface. To increase the cathode lifetime,

an inert gas (argon) is fed into the cathode stage and oxygen into the anode stage of the source. An ion optics system with 13 holes of diameter 5 mm provided an ion beam current up to 170 mA at an accelerating voltage of up to 50 kV. After mass separation of the beam and acceleration of ions to energy of 200 keV, a beam of O^+ ions with current 100 mA was obtained. The filament cathode lifetime is over 25 hours.

- periplasmatron-type ion source has a unique electrode system design, which decreases heating of the screen electrode by thermal radiation of the cathode, reduces the effect of secondary electron back flow from the accelerating gap, and ensures a high uniformity of plasma flow to the screen grid. A rectangular variant of this source provided a hydrogen ion current of 96 A from an extractor 40 x 16 cm in size.

- magnetic-field-free source for use in neutral beam injectors has been developed in which the plasma is generated by a diffuse low-pressure high-current discharge, with a distributed thermionically emitting cathode. Twenty hairpin filaments, 0.5 mm in diameter, are installed around the periphery of the discharge chamber, 14 cm in diameter, near the cylindrical wall, which serves as the anode. The peripheral placement of the cathode provides generation of uniform ($\pm$ 6 %), oscillation-free plasma of 12 cm diameter. For a discharge current of 1000 A the deuterium ion beam current density is 0.5 A cm^{-2} and the beam current 15 A at an extraction voltage of 15 kV.

5.1.3   Surface ionization sources

Surface ionization sources are commonly used for producing a Cs^+ ion beam. The surface ionization source emits ions from a hot plate. This configuration is ideal for designing beam optics with minimum aberration because the emitting surface is a solid boundary. In fact, the surface ionization source can be designed to produce a beam with very large aperture (and therefore high current per beam) because of the rigid emitting surface. The ion temperature from a surface ionization source is typically low, of the order of a fraction of an eV; therefore the beam emittance is kept low, even when the source diameter is large. The two main types of surface ionization sources are contact ionizers and aluminosilicate sources.

The ration of density of emitted positive ions flux j_+ to density of emitted atoms flux j_a is defined

$$j_+/j_\mathrm{a} = \frac{g_+}{g_\mathrm{a}} e^{-\frac{V_i - \phi}{kT}}, \tag{5.2}$$

where g_+ a g_a are statistical weight of ionized and atomic state of adsorbed atom, V_i is ionization energy of adsorbed atom, ϕ represents work function of solid, T is the temperature of solid and k is Boltzmann constant.

5.1.4   Field ionization

Field emission from sharp needle points at which very intense electric fields are created can be used to extract either electrons or ions from the solid (or liquid) state:

- liquid metal ion sources (LMIS) - is used in liquid metal ion sources to produce beams of species of low melting point metals such as Ga, In, Bi, Al, Sn, ... with extraordinarily high brightness

- gas field ion source (GFIS)

In both types the electric field with intensity 10 V/nm is use.

5.2   Ion scattering spectroscopy - ISS

Sometimes called Low Energy Ion Scattering Spectroscopy (LEIS) is a surface sensitive analytical technique used to characterize the chemical and structural properties of materials. The range of ion energies is from hundreds of eV to units keV. When a beam of ions hits a solid surface part of the projectiles will be scattered back into the vacuum after one or more collisions with target atoms of the layer. Measurement of the energy of the backscattered particles is use to identify chemical structure of solid. primary ion energies of $0.5 - 5$ keV are used with noble gas ions (He, Ne, Ar) and also alkali ions (Li, Na, K). With this method, information is obtained from the topmost atomic layer, under certain circumstances also from the second or third layer.
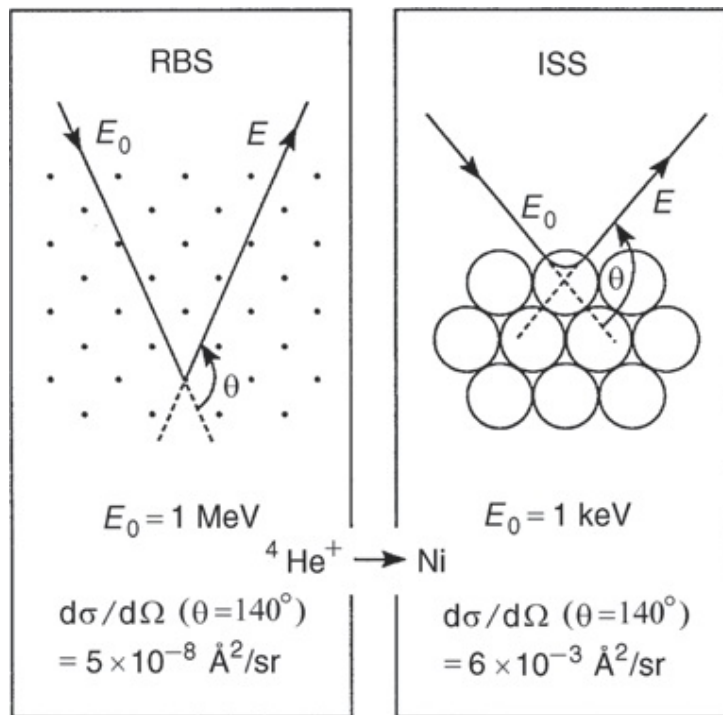

Figure 5.2: Comparison of RBS and ISS techniques.

5.2.1   Qualitative analysis

From the applied conservation and momentum laws in the case of two-body collisions it is possible to calculate the ion kinetic energy after a collision with a surface atom without knowing the interaction potential.

If the incident ion has energy E_0, the mass M_1 and the surface atom M_2, we obtain the energy and mass conservation relation for the backscatter energy E_1:

$$\frac{E_1}{E_0} = \left[\frac{\cos\theta \pm [(M_2/M_1)^2 - \sin^2\theta]^{1/2}}{M_2/M_1 + 1} \right]^2, \tag{5.3}$$

When this relation is derived, the kinetic energy of atom should be neglected

For 90° and 180°: backscattering angles the relation is simplified:

$$\frac{E_1}{E_0} = \frac{M_2 - M_1}{M_2 + M_1} \quad \text{for} \quad \theta = 90° \tag{5.4}$$

$$\frac{E_1}{E_0} = \frac{(M_2 - M_1)^2}{(M_2 + M_1)^2} \quad \text{for} \quad \theta = 180° \tag{5.5}$$

The ration $K = E_1/E_0$ is named kinematic factor. The above relations show that the energy of ion after collision is given by the projectile and the target atom weight and the backscattered angle (for constant E_0) $\Longrightarrow$ determination of target atom mass M_2. The corresponding expression for the recoiling target atom is:

$$\frac{E_2}{E_0} = \frac{4A}{(1 + A)^2} cos^2\theta_2 \tag{5.6}$$

Scattered-ion energy spectra are transformed into mass spectra by the backscattered relation for $\theta = 180°$. Consequently, the mass resolution also can be calculated from this equation for the special case of $\theta = 90°$:

$$\frac{M_2}{\Delta M_2} = \frac{E}{\Delta E} \frac{2A}{A^2 - 1} \tag{5.7}$$

Assuming a constant relative energy resolution of the detector of $E/\Delta E = 100$ the mass resolution is better for large scattering angles and about equal ion and target atom masses. So the primary projectile mass has to be selected accordingly if mass resolution is important.

5.3   Rutherford backscattering spectroscopy - RBS

In Rutherford Backscattering Spectroscopy (RBS) the primary ion energy ranges from about 100 keV (for H^+) to several MeV (for He^+ and heavier ions). The ion-target atom interaction can be described using the Coulomb potential from which the Rutherford scattering cross-section is derived,which allows absolute quantification of the results. Information in principle arises from a thickness of the order of 100nm (10^{-5} cm), but analysis of surface layers is also possible by using channelling/blocking techniques. Scattering of H^+ with energies around 100 keV is sometimes referred to as MEIS (Medium Energy Ion Scattering), probably because it only needs a smaller type of accelerator, but physically it is within the RBS regime.

The physical principles are the same for both techniques (ISS and RBS): an ion beam is directed onto a solid surface, a part of the primary projectiles is backscattered from the sample and the energy distribution of these ions is measured. Since the ion–target atom interaction can be described by two-body collisions, the energy spectra can be easily converted intomass spectra. The difference between ISS and RBS arises from the difference in the cross-sections and the influence of electronic excitations and charge exchange processes, which result indifferent information depths. In both cases, structural information is obtained from crystalline samples by varying the angles between beam and sample. Deduction of structural information from the data is straightforward, since both techniques are "real space" methods which are based on fairly simple concepts. With ion scattering only the individual atoms of an element can be detected and no information on compounds or molecules can be gained.

In terms of analytical characteristics, is important the variable cross section for elastic scattering, which integrates a number of dispersed particles with the number of atoms in the substance to be examined. Differential scattering cross section at the angle θ in the laboratory system is then:

$$\frac{d\sigma_R}{d\Omega} = \left(\frac{Z_1 Z_2 e^2}{2E_0}\right)^2 \frac{\left[(M_2^2 - M_1^2 \sin^2\theta)^{1/2} + M_2 \cos\theta\right]^2}{M_2 \sin^4\theta (M_2^2 - M_1^2 \sin^2\theta)^{1/2}}, \tag{5.8}$$

where Z_1 and Z_2 are the atomic numbers of the ion and the target.

Analysis using heavier particles and lower energies can play a significant role in electron screening. In such cases the first correct approximation of the cross section is multiply by the correction factor F in the form:

$$F = \frac{\sigma}{\sigma_R} = 1 - \frac{0,049 Z_1 Z_2^{4/3}}{E_{\text{CM}}}, \tag{5.9}$$

where E_{CM} is the energy of particles expressed in keV. In a conventional design RBS the correction is below 5 %. Significant deviation of the cross section appear when the energy of the particles is increased , or particles with lower atomic number are used. The effect of nuclear forces appears when the scattered are scattered at large angles and energies $E_0 > E_{\text{critical}}$

$$E_{\text{critical}} = 10^3 Z_1 Z_2 M_2^{-1/3}. \tag{5.10}$$

For example, nuclear effects occur when the α particles ($Z_1 = 2$, $M_1 = 4$)on Si atoms ($Z_2 = 14$, $M_2 = 28$) sat energies$E_{\text{krit}} > 9$ MeV are scattered.

5.3.1 Elemental composition determination

The basic relationship is

$$Y = QN \int_{\Delta\omega} \frac{d\sigma}{d\Omega} d\Omega, \tag{5.11}$$

where Y is the number of the dispersed particles registered, Q is the number of incident particles, N is the area density in the layer (atoms/cm^2) and $\Delta\omega$ is the interval of the solid angle from which is detected the scattered particle. The equation can be applied in a layer containing multi-elements or a thin layer on a stronger substrate.

5.3.2   Energy loss

Only a small fraction of the primary ions come close enough to a target nucleus (impact parameters of the order of 10^{-12} cm) to undergo an elastic nuclear collision which is described by the kinematics given in the previous section. If such an ion is backscattered, its final energy is determined by the *elastic* nuclear collision in a certain depth of the sample and the additional *inelastic* energy loss to electrons on its way in and out of the target.

The relation for energy loss per unit length, $--dE/dx$ given in eV/Åand commonly called **stopping power**:

$$S = -\frac{dE}{dx} \qquad (\text{keV.cm}^{-1}), \tag{5.12}$$

The stopping cross section ϵ (eV/(atoms/cm^2)) relates this quantity to the atomic density N and is therefore more specific for a

$$\epsilon = \frac{1}{N}S \qquad (\text{keV.cm}^2), \tag{5.13}$$

The stopping power curve exhibits a broad maximum around 1 MeV and that is the operational regime of RBS: here, the stopping power does not depend very much on the ion energy and hence can be assumed to be constant as a sufficient approximation in many cases; the stopping power there has its maximum value and therefore RBS its best depth resolution and in this energy range the nuclear interaction is exactly given by the Coulomb potential, giving RBS the advantage of an absolute analytical method. Stopping cross section for a particle with energy E and a mixture of $A_m B_n$ elements is

$$\epsilon^{A_m B_n} = m\epsilon^A(E) + n\epsilon^B(E), \tag{5.14}$$

where $\epsilon^A(E)$ ans $\epsilon^B(E)$ are the stopping cross sections for the elements A and B.

5.4   Detection of ejected atoms - ERDA

Detection of light elements by RBS is difficult due to the low effective elastic scattering cross-sections and often because the signal lies on a high background originated by scattering on heavier elements. Therefore, the method used is ERDA (Elastic recoil detection analysis).

In this method, atoms or ions are detected which are removed from the surface by one single collision with an incoming projectile. They can therefore be identified by their kinetic energy. Directly recoiling particles are therefore different from those secondary particles that originate from a collision cascade in a sputtering process and have a broad energy distribution around one to two eV. They are used in secondary ion or neutral mass spectroscopy.Recoil cross-sections are generally of the same order as scattering cross-sections. They are largest towards $\theta_2 = 90°$, but then the recoil energy approaches zero. A useful energy range is obtained between 30° and 60°.

ERDA is also often done using a relatively low energy (2 MeV) He beam specifically to depth profile hydrogen. In this technique multiple detectors are used, at backscattering angles to detect heavier elements by RBS and a forward (recoil) detector to simultaneously detect the recoiled hydrogen (the cross-section for which reaction is strongly non-Rutherford at these energies). The recoil detector has to have a *range foil*: a thin film (typically 6 micrometres of PET film) to preferentially stop the incident He beam scattered into the forward direction.

5.5 Secondary ion mass spectrometry - SIMS

Secondary Ion Mass Spectrometry (SIMS) is a relatively new technique for surface chemical analysis compared with Auger enectron spectroscopy (AES) and X - ray photoelectron spectroscopy (XPS). SIMS examines the mass of ions escaped from a solid surface to obtain information on surface chemistry.
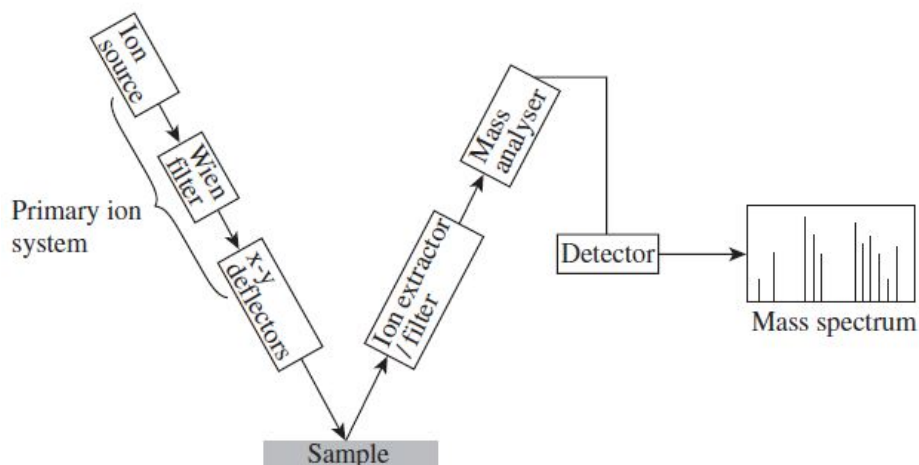

Figure 5.3: SIMS instumentation.

SIMS uses energized primary particles, usually ions such as Ar^+, Ga^+ and Cs^+, to bombard a solid surface in order to induce sputtering of secondary particles from an area. The interactions between primary ions and the solid are rather complicated. First, the secondary particles include electrons, neutral species of atoms or molecules, and ions. The majority of the secondary particles are neutral and not useful in SIMS. Only the secondary ions generated by the bombarding process carry chemical information. Second, the interactions are often more than a simply one-to-one knock-out of a surface ion by a primary ion. Commonly, the primary ions induce a series of collisions (collision cascade) in a solid because the energy of a primary ion is transferred by collisions between atoms in a solid before secondary ions on the surface are emitted.

The ionization probability is strongly affected by the electronic properties of the sample matrix. Ionization directly affects the signal intensity of secondary ions as shown in the basic equation of secondary ion yield.

$$J_s^\pm = J_p c Y \beta^\pm f, \tag{5.15}$$

where J_p is the primary ion flux, Y is the sputter yield, c is concentration of species m in the surface layer, $\beta^\pm$ represents the probability for positive ions and f is the transmission of the detection system. The transmission is defined as the ratio of the ions detected to ions emitted, and it varies from 0 to 1 depending on the analyser. The yield of elemental secondary ions can vary by several orders of magnitude across the periodic table.

5.5.1 Ion sputtering

Emission of secondary particles can result from collision sputtering or from other processes such as thermal sputtering. Collision sputtering includes direct collision sputtering and slow collision sputtering. The former can be considered as a direct impact between a primary ion and a surface atom. Direct collision sputtering is extremely fast, and occurs in the range of 10^{-15} to 10^{-14} seconds after the primary ion strikes a surface. Slow collision sputtering, represents the case that a primary ion never has chance to collide with a surface atom; instead, atoms in the solid transfer the impact energy to surface atoms after a series of collisions. The time scale of slow collision sputtering is in the range of 10^{-14} to 10^{-12} seconds.

Only a small portion of secondary particles ($\sim 1\%$ of total secondary particles) are ionized and become the secondary ions that are analysed in SIMS. A sputtered particle faces competition between ionization and neutralization processes when it escapes a sample surface. Ionization probability represents the chance of a sputtered particle being an ion.

5.5.2 Ion sources

The commonly used primary ions include argon (Ar^+), xenon (Xe^+), oxygen (O^{2+}), gallium (Ga^+) and caesium (Cs^+) ions. Heavier metal ions such as bismuth (Bi^+) are also available in modern static SIMS instruments. The ions of elements normally occurring in gaseous phases, such as oxygen and argon, are produced by electron bombardment sources or plasma ion sources. Electron bombardment sources use a circular filament cathode surrounding a cylindrical grid anode. The gas to be ionized is injected into the open space of the grid, and the gas molecules are bombarded by the electrons emitted from the cathode. The electrons travel in orbit inside the grid in order to increase their chances of striking gas molecules. An extraction field inducted in the grid will draw the gas ion beam through an opening in the center of the extractor. The electron bombardment sources provide moderate brightness of primary ions ($\sim 10^5$ Am^{-2} per solid angle).
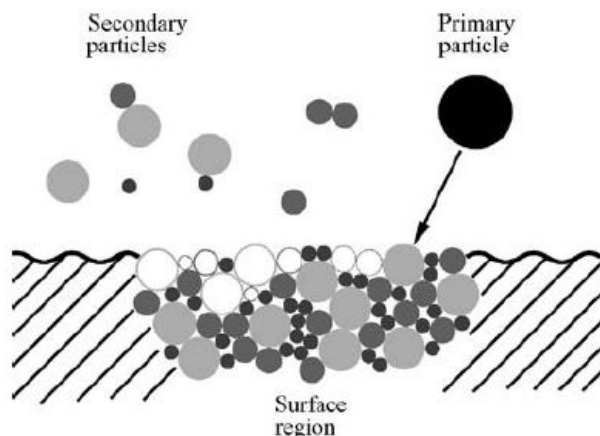

Figure 5.4: Secondary particle generation by an energetic primary particle.

5.5.3 Mass analysis system

The mass analysis system collects and analyses the ion masses to produce mass spectra with the assistance of a computer. The extractor filter extracts secondary ions from the surface, selects a mass range of ions to analyse, and eliminates scattered primary ions from a mass spectrum. The mass analyser, the critical component for secondary ion mass analysis, can be one of the following types:

- magnetic sector analyser,

- quadrupole analyser,

- time-of-flight analyser.

Magnetic sector analyser

This analyser was the oldest type used for mass spectroscopy. Secondary ions are accelerated by an extraction potential of 4 kV before entering a magnetic field. The magnetic field in the magnetic sector will impose a field force in a direction orthogonal to the direction in which the ions travel.
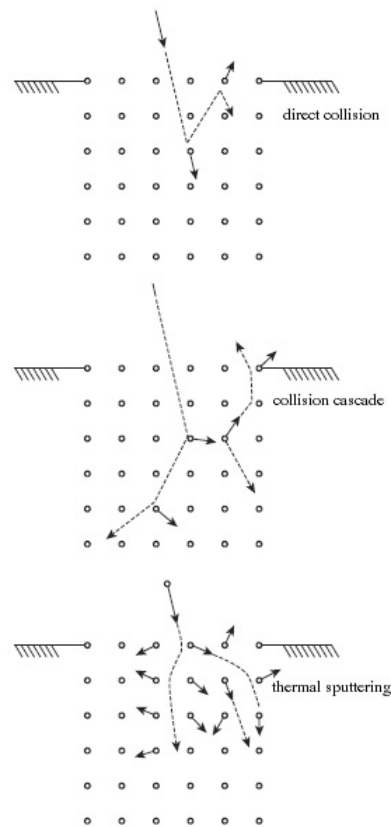

Figure 5.5: The sputtering proces: (a) direct collision sputtering;(b) collision cascade; and (c) thermal sputtering.

The ions with a given kinetic energy will change their travel path to a circular trajectory. The radius of path curvature R has the following relationship with the ion mass.

$$R = \frac{(2V)^{1/2}}{B} \left(\frac{m}{z}\right)^{1/2} \tag{5.16}$$

where the extraction potential (V) is constant. We can adjust the magnetic field strength B, to select ions with a certain mass-to-charge ratio (m/z) with a fixed radius of magnetic sector R.

Quadrupole mass analyser

The quadrupole mass analyser selects ions with a certain mz^{-1} by generating unstable oscillation travels for the non-selected ions. Oscillations of ion trajectories are created by an electric field combining a constant direct current (DC) and alternating current with a radio frequency (RF). The secondary ions are accelerated by an extraction field, and then the ions travel through the center of four circular rod electrodes. Combined DC and RF voltages are applied to one pair of rods and equal but opposite combined voltages are applied to another pair of rods. Such an arrangement of electric fields generates ion oscillation. The oscillation can be so severe that ion trajectories become unstable and ions strike the rods. Ions with unstable trajectories cannot travel through the exit slit of the analyser to reach the mass detector. Only the ions with a certain mz^{-1} have stable trajectories and can pass through the exit slit under a given ratio of DC:AC voltages. The analyser is a sequential type that only allows the ions with single mz^{-1} values to reach the detector. Thus, the quadrupole analyser is a device with low transmission, as less than 1% of ions can reach the detector at any time. To obtain a whole mz^{-1} spectrum, the analyser increases the voltages but keeps the ratio of DC:AC voltages constant.

Time-of-Flight analyzer

The time-of-flight (ToF) analyser is the most widely used analyser in static SIMS. As its name indicates, for this analyser the flight time of an ion is the parameter for measurement. When ions are obtained with a constant kinetic energy from an acceleration potential (V) of $3 - 8$ kV, the flight time of ions through a distance (L) of flight tube to reach a detector is calculated.

$$t = L(2V)^{-1/2} \left(\frac{m}{z}\right)^{1/2} \tag{5.17}$$

Thus, the mz^{-1} of ions is analysed by measuring their flight time in the analyser. Heavier ions will have longer flight times in the tube. To measure the time of flight, precisely pulsed primary ions should be used. The pulse is controlled by a highly accurate clock. The pulse periods are typically in the order of 10 ns. The flight time of ions to the detector is electronically measured and converted to mz^{-1}. In a pulse period, all the ions can be measured and a whole mass spectrum can be obtained almost simultaneously. Again, the initial kinetic energy of secondary ions will affect the resolution of mass analysis, because the velocity could be different when ions with the same mz^{-1} enter the flight tube.