Secondary Ion Mass Spectrometry (SIMS)

Principle of the SIMS method

The method is based on the phenomenon that when the surface of a solid is bombarded with heavy particles (ions or sometimes atoms) with an energy of 1-10 keV, positively and negatively charged atoms and clusters of atoms exit the surface (beside atoms, atomic clusters an electrons). The secondary ions thus leaving can be separated by different types of mass spectrometers. The name of the method comes from this process: Secondary Ion Mass Spectroscopy - SIMS. The first sputtering ion source combined with a mass spectrometer was described by Herzog and Viehböck [1] in 1949. Almost 10 years later, the first complete secondary ion mass spectrometers were made. The practical, routine use of the method began in the mid-1960s (Bradley [2], Beske [3], and Werner [4]).

Secondary ions exit from the uppermost atomic layer of the bombarded surface. Thus, the most important property of secondary ion mass spectroscopy is its high surface sensitivity.

The current, Is,Z,A/q of the secondary ions (where q is the charge number of the isotope - with mass number A - of a given element with atomic number Z) is given by the following relation:

$$I^{\pm}_{s,Z,A/q} = I_p \cdot S \cdot \gamma^{\pm}_{Z,q} \cdot a_{Z,A} \cdot c_Z \cdot \eta_{A/q},$$

where I_p is the current of the primary ion measured in amperes, S is the ionsputtering efficiency in atom/ion units, $\gamma^{\pm}_{Z,q}$ is the ionization probability of the given ion type in ion/atom units, $a_{Z,A}$ gives the proportion of the isotope with mass number A of the element with atomic number Z, c_Z is the concentration of the examined element in atomic fraction ($0 < c_Z < 1$), $\eta_{A/q}$ is the transmission coefficient of the equipment (the detected fraction of the sputtered secondary ions). If $I^{\pm}_{s,Z,A/q}$ is measured not in amperes but in cps (number of counts/s), then $\eta_{A/q}$ includes the conversion factor also and its dimension is cps/A.

During SIMS studies, the directly measured quantity $I^{\pm}_{s,Z,A/q}$ is the secondary ion current of the given ion type, and mostly the primary ion current Ip can be varied.

The $\eta_{A/q}$ transmission coefficient can be determined experimentally for a given device (its value is on the order of 10^{-4}-10^{-2}). The amount of sputtered material can also be measured, as the shape and depth

of the crater formed during sputtering can be measured by a profilometer (Talysurf) with an accuracy approx. of 10nm. From these quantities *S* can be calculated, the typical value of the ionsputtering efficiency is 1-10 atoms / ion. The ionization probability $\gamma^{\pm}_{Z,q}$ depends on many parameters (eg secondary ion atomic number, charge, energy, etc.) and its value is sensitively influenced by the experimental conditions and their changes, such as surface purity, gas composition, pressure, the local composition of the test sample, the microstructure around the emission site, etc. In general, the ionization probability varies between 10^{-1}-10^{-6} ions/atom. The expression of ion sputtering efficiency: $S^{\pm}_{Z,q} = S \cdot \gamma^{\pm}_{Z,q}$ (unit: ion/ion) is also often used. The high sensitivity of the ionization probability to the matrix environment makes quantitative analysis difficult, practically only possible by using well-chosen standard samples. At the same time, it provides an opportunity to determine chemical bonding states.

The use of oxygen, either as a primary ion or in reactive ionsputtering (SIMS measurement at elevated oxygen background pressure), increases the probability of positive ionization of many elements. This is often used to detect poorly ionizing elements. In addition to the sensitizing effect, the so-called “reactive SIMS” has additional benefits:

- the oxygen primary ions and the increased oxygen background pressure reduces the concentration and matrix.dependence of the ionization probability.

- reactive ionsputtering can reduce the effect of the original (and possibly varying) amount of oxygen present in the samples on the ion yield. This is especially important when surface or boundary transition layers are examined.

Nowadays, the following applications of the SIMS method have been developed:

- Surface analysis: Analysis of surfaces, interfaces, thin films with very low primary ion current densities. This method is called static SIMS (SSIMS). The m/e (mass/charge) spectrum of secondary ions emitted from the bombarded surface provides direct information about the chemical composition of the bombarded surface. Figures 1 and 2 show the positive and negative secondary ion spectra obtained from the surface of a vanadium sample. Figure 1 shows the atomic ions ($^{51}V^{+}$) and molecular (cluster) ions ($^{52}VH^{+}$, $^{67}VO^{+}$) of the target, as well as the ions of the electropositive elements present in small amounts in the sample ($^{23}Na^{+}$, $^{39}K^{+}$). It is important to note that $^{1}H^{+}$ ions are also detected, which is a unique opportunity of the SIMS method. The ions of the electronegative elements appear in the negative secondary ion spectrum (Fig. 2) with higher intensity ($^{16}O^{-}$, $^{17}OH^{-}$, $^{32}O_2^{-}$, $^{35}Cl^{-}$). However, ^{51}V, ^{52}VH, and ^{67}VOH ions can also be found, but at lower intensities.

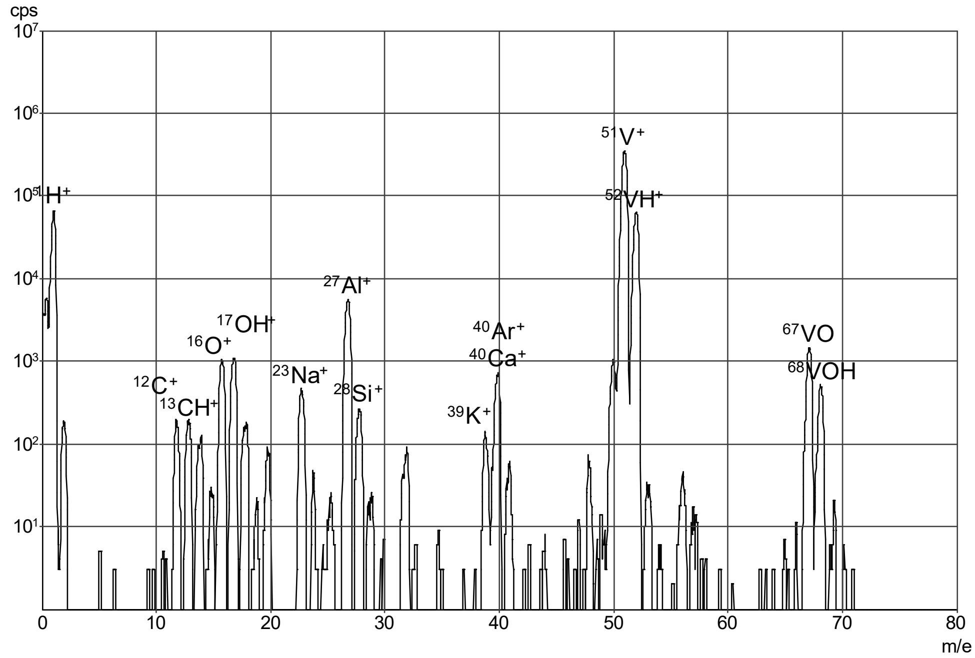

Fig 1.: Positive secondary ion spectrum of a Vanadium sample.

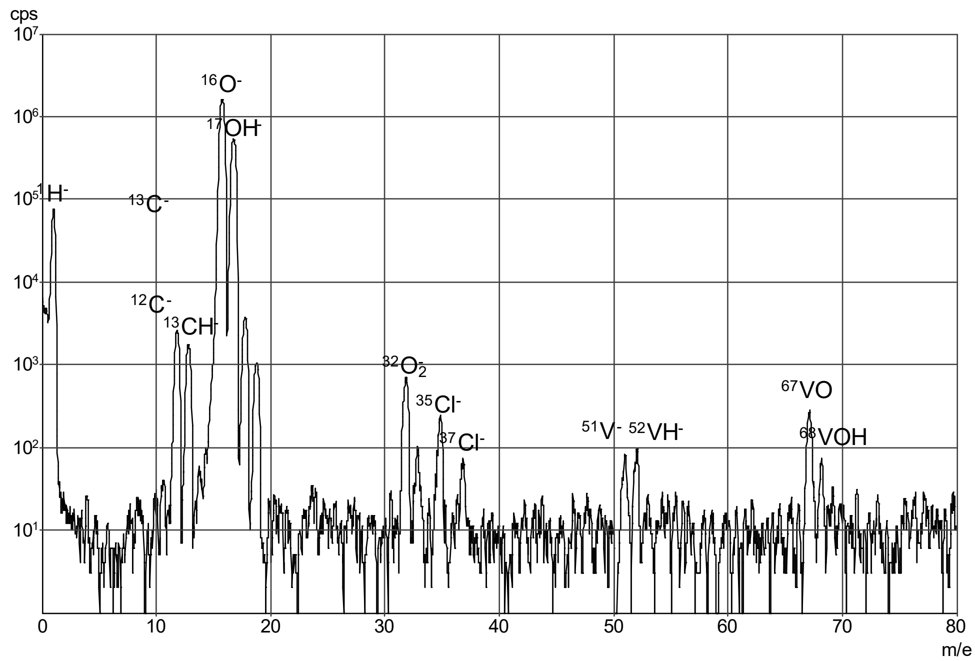

Fig 2.: Negative secondary ion spectrum of a Vanadium sample

- Analysis of composition and bonding state ditribution along the surface by secondary ion microscopy, abbreviated SIIMS (Secondary Ion Imaging Mass Spectrometry).

- Profile analysis: Depth concentration profiles, e.g. recording diffusion profiles. In such investigations, the surface of the sample is ionsputtered from layer to layer with a high (A / cm^2) primary ion current density. The method is called dynamic SIMS (DSIMS). Figure 3 shows the depth concentration profile of Boron implanted in a single crystal sample Si. (Recording was performed using reactive sputtering technique as described below.)

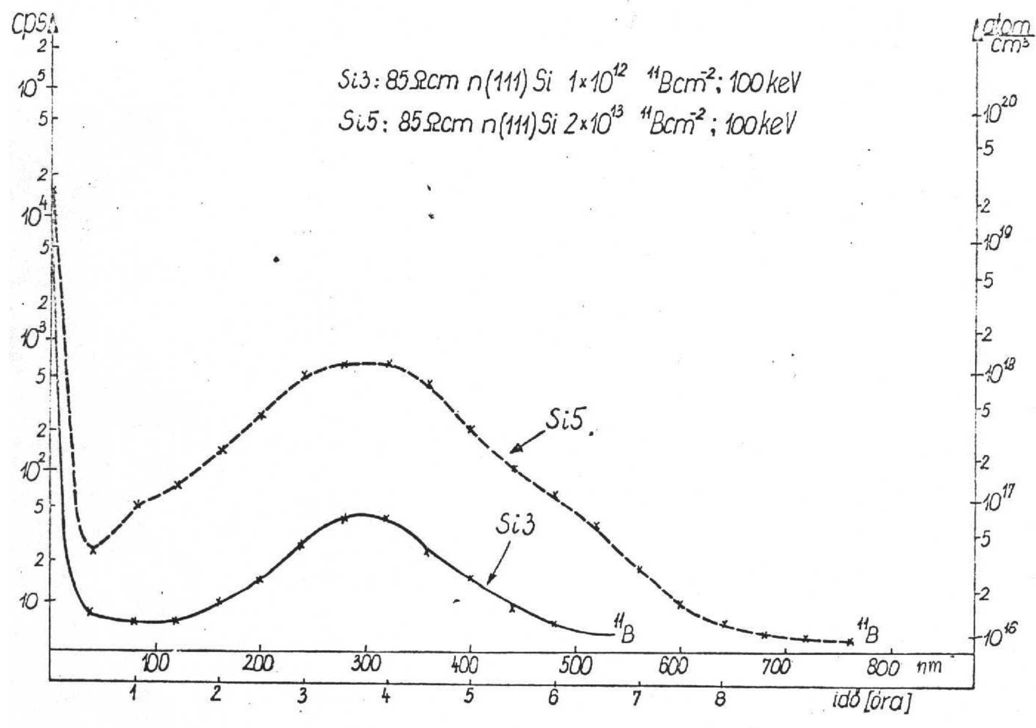

Figure 3: SIMS Depth profile of ^{11}B implanted in Si

The SIMS method has also been made suitable by Oechsner et al [5] for the analytical use of neutral secondary particles with much higher yields than secondary ions by post-ionization of neutral secondary particles exiting the sample surface. This method is called SNMS (Sputtered Neutral Mass Spectroscopy). Its advantage beside higher sensitivity is the possibility of quantitative analysis without standards.

An important parameter for measuring depth profiles is depth resolution. Examining the ion sputtering process in more detail, it turns out that beside the information depth, there are a number of factors and processes that affect/limit the depth resolution:

- instrumental factors: inhomogenity of the primary ion beam, the effect of the crater edge

- properties of the sample: initial surface roughness, crystal orientation, matrix effect

- processes during sputtering: preferential sputtering, movement of atoms towards to the inside of the sample, cascade mixing.

The following table summarizes the features of the SIMS techniques described above:

Technique	Information	best lateral resolution	Infromation depth (monolayers)	Sensitivity	Quantitative analysis
SSIMS	chemical	1μm	2	0.01%	
SIIMS	elemental, chemical	20nm	10	1 ppm	by standards
DSIMS	elemental, chemical	50μm	10	1 ppm	by standards
SNMS	elemental	50μm	10	1 ppm	easy

Experimental techniques

The SIMS method, like other surface analysis methods (XPS, AES), requires ultra-high vacuum conditions. The two main units immersed in the vacuum chamber are the ion source and the mass spectrometer. In the Surface Physics Laboratory the main units of the SIMS equipment is an electron-impact ionization source and a quadrupole mass spectrometer. Furthermore, the equipment is suitable for measuring insulating samples thanks to the built-in FAB (Fast Atom Beam) gun.

In the electron-impact ionization source thermal electrons exiting the glowing cathode collide with gas phase atoms to form ions without plasmaformation. Thus, the number of ions generated is proportional in a broad range to the gas pressure and the electron current. Therefore, by changing these two parameters, the current of ions can be changed and controlled - more than six orders of magnitude - quickly and without hysteresis. Usually the material of the glowing cathode is tungsten, these ion sources

are suitable for the production of noble gas ions. Thorium, zirconium or iridium coated cathodes can also be used to produce ions from O2 and N2 gases. Typical parameters of electron-impact ionization sources:

ion energy: 0.1-5keV

beam diameter: 0.1-2mm

maximal ioncurrent: 10-5A

Re-neutralized ion beam: In SIMS tests, the charging of insulating samples is a major concern. There are several ways to prevent this, one of the most effective methods is to use a FAB (Fast Atom Beam) gun. The point is that the already accelerated and focused ions are passed through a space where a gas of the same material quality as the ions is introduced at a relatively high pressure (~10-3mbar). Here, high-energy directed ions collide with neutral atoms performing disordered thermal motion. During the collision, the ions transfer their charge to the atoms, however, no impulse transfer occurs. As a result, high-energy directed neutral atoms exit the FAB gun, and the remaining low-energy disordered motion ions are removed by a low electrostatic field applied laterally.

The quadrupole mass spectrometer uses only electric field, the device is a relatively simple in construction and small in size. It consists of four parallel rods, in opposite diagonal position two-two of them are galvanically connected. An AC voltage in the MHz frequency range (UAC cosωt) and a superimposed direct voltage (UDC) are applied to this electrode system. The potential of one pair of rods is Uo = UDC + UACcosωt the other is -Uo. By varying the DC and AC voltages applied to the quadrupole rods, ions of different masses pass between the rods without outscattering. The mass resolution, m/Δm, is determined by the ratio of DC to AC voltage (UDC/UAC).

The upper mass range that can be tested with a quadrupole can range from 250 to over 1000 atomic mass units, depending on the size of the rods. Typical transmissivity is 10-4. Quadrupole-operated SIMS devices often have an advantage over the magnetic sector systems described later, although they generally have a smaller transmission, a larger collection area, and are easier to operate. Due to its relatively small size and weight, it is often used in conjunction with electron spectroscopic techniques operating at the same analysis point.

State-of-the-art SIMS equipments already operate with a Time-of-Flight (TOF) mass spectrometer. The principle of operation of a TOF mass spectrometer is quite simple: charged particles are accelerated with

a constant voltage U by starting them at time t = 0. At the end of the acceleration, the velocities of the ions of different masses will be different. The ions are then allowed to run in a force-free space over a given path length, thereby approximately separate ions of different velocities over time. The mass information is given by the time elapsed between departure and arrival. Despite the simple measurement principle, a number of measurement difficulties have to be overcome: A very narrow start pulse is required, i.e. it requires a primary ion source operating in pulse mode. The time resolution of the detection must be extremely good. Another problem is the energy dispersion of the starting ions.

Advantages of TOF SIMS devices: Very high mass ranges can be examined, several mass lines can be analyzed at the same time. An additional advantage of TOF SIMS in contrast to SIMS devices with quadrupole and magnetic mass spectrometers is that transmission can be kept constant even in high mass ranges. Due to these properties, it is particularly suitable for the testing of organic compounds.

General literature:

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