Technical Note: ToF-SIMS

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is an analytical method for the chemical characterization of solid surfaces. With this method, the atomic and molecular composition of the outermost 1 – 3 monolayers is obtained. ToF-SIMS can be used on conducting and insulating samples. With detection limits in the ppm range; small amounts of a compound can be analyzed with high sensitivity.

In SIMS, the surface under study is bombarded with a primary ion beam of high energy (e.g., Au^+ or Bi^+). The projectile's energy is transferred to the region near the surface by collisions between the primary ion and the sample atoms as well as by collisions between sample atoms. This collision cascade transports a small part of the energy back to the surface and leads to the emission (sputtering) of electrons, neutrals, and secondary ions (see Figure 1). Subsequently, the secondary ions are analyzed with respect to their mass to charge ratio in a suitable analyzer.
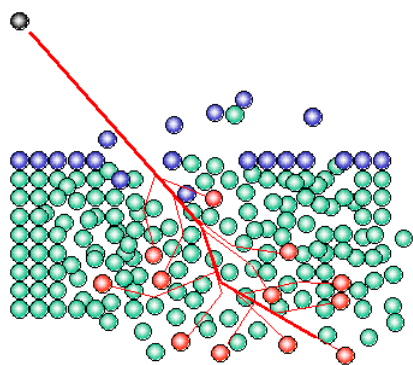

Figure 1 Schematic of the excitation processes in SIMS (collision cascade; grey: primary ion; blue: atoms from the outermost monolayers; green: atoms in deeper layers; red: simple atoms after a direct collision with the primary ion).

In ToF-SIMS the mass of the sputtered secondary ions is determined by means of a time-of-flight (ToF) mass analyzer. For the mass analysis, all secondary ions which are produced by a short primary ion pulse are accelerated to the same energy. From the time needed to travel along a given drift path, the mass of each secondary ion can be calculated. In this way, an accurate determination of the flight time yields the chemical composition of the emitted ions and thus the elemental and molecular composition of the sample surface.

In modern analyzers, this parallel mass detection is combined with the resolution to separate species with similar masses e.g., $^{56}Fe^+$ at 55.9349u and Si_2^+ at 55.9539u.
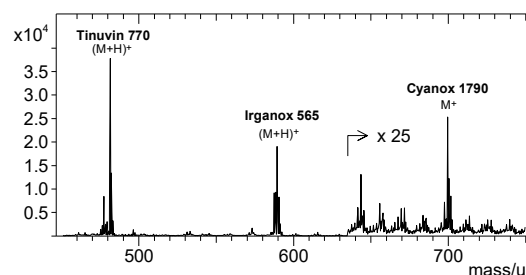

Figure 2 Positive secondary ion spectrum of polymer additives in low density poly(ethylene) (LDPE).

The intensity of the detected secondary ions is influenced by the chemical composition of the surrounding matrix material (SIMS matrix effect). Therefore, SIMS does not give inherently quantitative data. However, it is possible to compare analyses of chemically similar samples. Furthermore, with the analysis of suitable references it is possible to determine absolute concentrations.

The sample bombardment with primary ions leads to changes in the local molecular structures. Therefore, only very few primary ions can be used for the determination of the original composition of the surface (Static SIMS limit). The resulting spectra show secondary ion intensity as a function of secondary ion mass and represent the average composition of the probed area (see Figure 2).

The chemical distribution can be recorded as an image by scanning the area pixel by pixel with a focused primary ion beam (imaging or mapping, see Figure 3). The intensity in each pixel is assigned a color value, leading to mass resolved images. The size of the analyzed surface can be varied from 20 x 20 μm^2 to 500 x 500 μm^2. Large areas of up to 9 x 9 cm^2 can be mapped by automated movement of the sample during the analysis (stage scan). The typical primary ion beam size is < 100 nm.
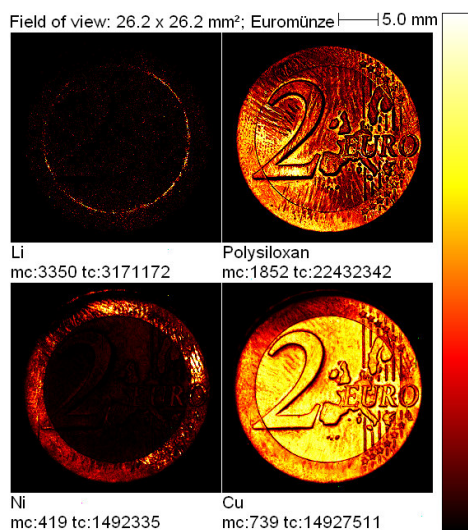

Figure 3 Selected secondary ion images acquired from a 2 euro coin stage scan. MC: number of secondary ions in the brightest pixel; TC: total counts of detected secondary ions. Polysiloxane is a component of hand lotions.

The damaging effect of the primary ion bombardment can be utilized if one wants to investigate the chemical composition of the sample as function of depth. By applying high ion does, so called depth profiles can be generated. Depending on the chosen bombardment conditions profiles can be performed for elemental (e.g., metallic layers) as well as organic (e.g., organic light emitting diodes (OLED)) layer sequences. During the analysis, the chemical composition of the crater bottom is acquired as function of sputter does or time. Depth scales can be established at the end of an analysis when the final crater depth is determined or if a sputter yield of the matrix material is known (see Figure 4).
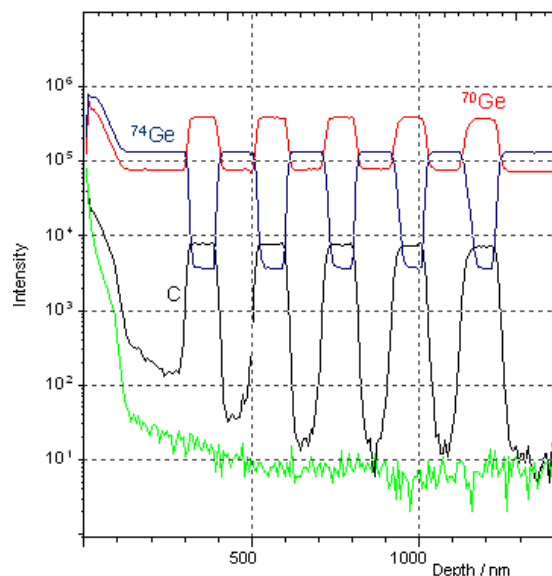

Figure 4 Depth profile for a Ge multi layer system; (Source: Prof. Bracht; Inst. für Materialphysik, WWU Münster)

The combination of imaging and depth profiling yields a "3D-analysis" mode of operation (Figure 5). This mode of analysis makes it possible to probe a complete sample volume with good resolution in all 3 dimensions and serves among others in the identification of point defects in complex layer structures.
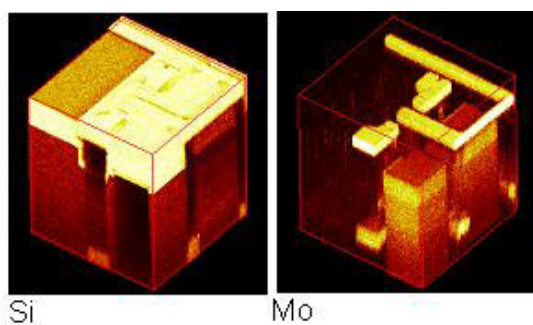

Figure 5 3D-image for the Si and Mo distributions in a pixel from a TFT monitor.