

Time-of-Flight Secondary Ion Mass Spectrometry

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Introduction

The properties of many modern products are not only governed by their surface morphology and structure but also by their surface chemistry. For example, in some cases a contamination of less than a monolayer of molecules can be responsible for the failure of a coating with all its consequences (aesthetics, protection, life time, and so on). Other areas affected by surface chemistry are adhesion, staining, corrosion, and so on. Thus, powerful analytical techniques for the identification, as well as the localization and quantification, of substances on a surface or at the interface between different layers are of increasing importance for fast and efficient failure analysis. However, surface analysis is not only limited to failure analysis but can be also used in research and development of, for example, methods of surface modification on the molecular level as well as in production and quality control, such as the evaluation of cleaning procedures.

Secondary ion mass spectrometry (SIMS), especially in combination with a time-of-flight mass analyzer (ToF-SIMS) [1], is one of the most powerful surface analytical techniques available today. Improvements over the last decade have made the method suitable for industrial as well as research applications. A good overview of recent developments and a variety of applications is given in the proceedings of the international SIMS conference [2]. This article gives an overview of the principle and instrumentation behind ToF-SIMS and will discuss some typical examples of the kind of information one can obtain about the surface chemistry of a sample.

Principle of SIMS

In SIMS, a sample surface is bombarded with a high-energy primary ion beam. The primary ion energy is transferred to target atoms via atomic collisions resulting in a so-called collision cascade. Part of the energy is carried back to the surface and subsequently atomic and molecular particles are emitted from the outer layers. A fraction of these particles, which can vary over several orders of magnitude depending on the ionization probability of the respective species, is charged. These secondary ions are extracted by an electric field into a mass spectrometer, where their mass and thus their chemical structure are determined. The emission process of secondary ions is limited to the uppermost one to three monolayers (typically less than one nanometer in thickness) of a solid sample. Secondary ions can be elemental ions, clusters, molecular fragments and/or intact molecules that are desorbed from the surface. The detection limits are generally in the ppm to ppb range. These capabilities make SIMS a highly sensitive analytical technique delivering information about the chemical composition of a sample's surface.

Time-of-flight mass spectrometry has the ability to detect in parallel all generated ions, making it the optimum spectrometer for surface analysis by SIMS. Other types of mass spectrometers (quadrupole, magnetic sector) are also used for SIMS, but spectra must be developed sequentially because

only selected ions pass through a slit. Parallel detection, on the other hand, in combination with unlimited mass range ensures that all of the generated ions (inorganic and organic) are used for the analysis. Thus, it is possible to only consume a minimal part of the surface during analysis leaving the sample effectively undamaged ("static SIMS"). Alternatively, the surface can be eroded layer by layer (dynamic SIMS) in order to gain information about the in-depth distribution of elements and compounds in surface-near regions.

Surface Spectroscopy

The typical result from a ToF-SIMS analysis is a mass spectrum of secondary ions reflecting the chemistry on the sample surface. Figure 1 shows a detail of a mass spectrum of positively charged secondary ions around the nominal mass of 27 amu. Two peaks are clearly resolved in this spectrum and have been identified as Al^+ and the small organic fragment ion C_2H_3^+ . A mass resolution of at least 650 (defined as the nominal mass 27 amu divided by the mass difference between the masses of Al^+ and C_2H_3^+) is needed to separate these peaks. This demonstrates that a high mass resolution is necessary for unambiguous identification of the collected ions. Modern ToF mass spectrometers deliver mass resolutions over 13,000 in the higher mass range and approximately 9,000 around mass 27 amu.

Although the low mass range (1–200 amu) delivers information about elemental and small molecular fragment

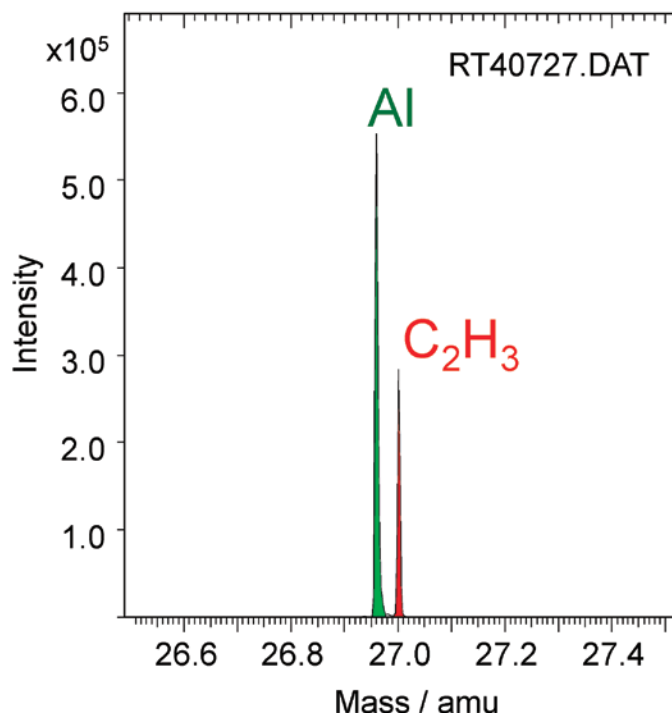
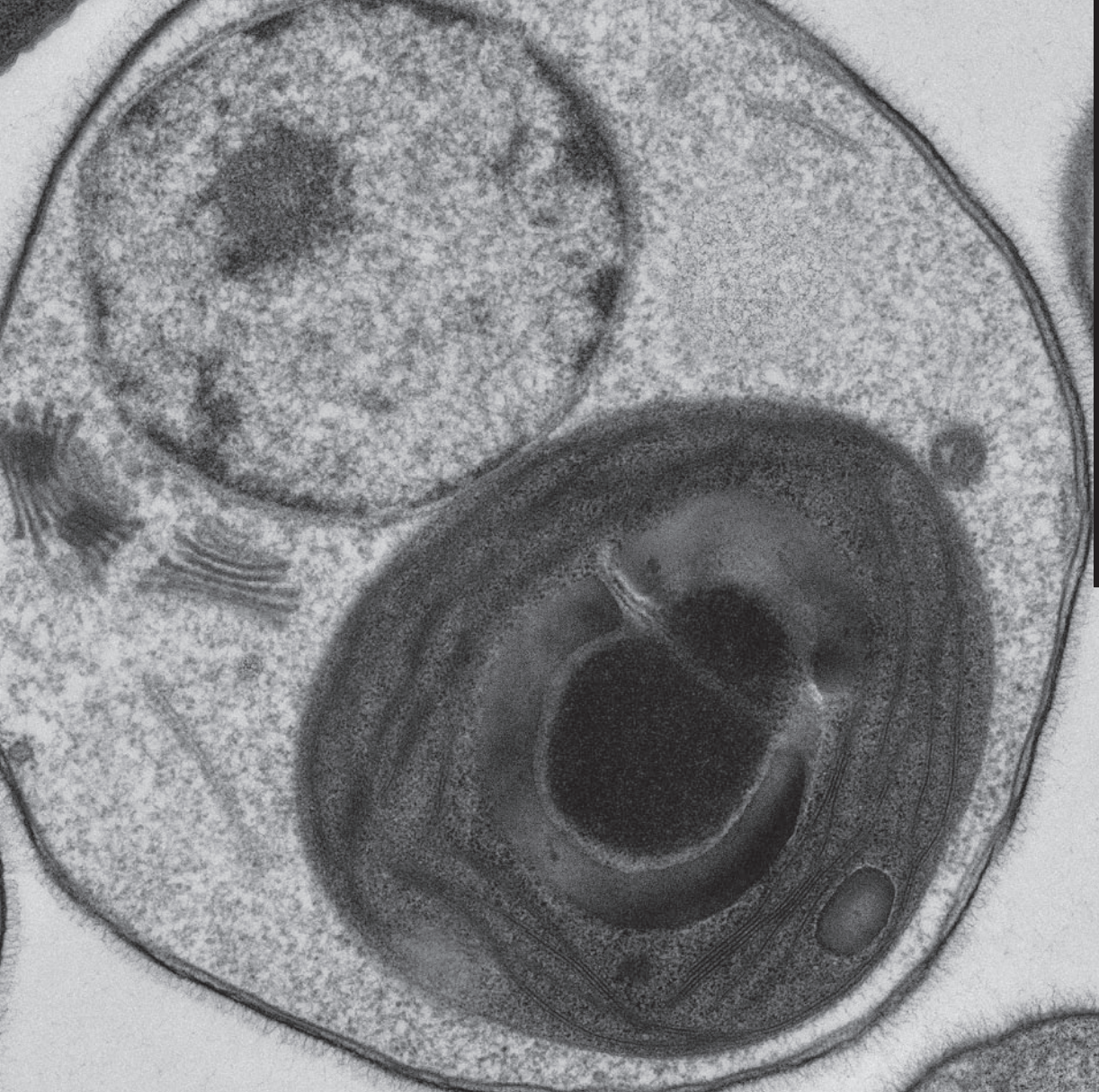


Figure 1: Detail of a positive secondary ion mass spectrum demonstrating the need for good mass resolution. The Al^+ -peak and the C_2H_3^+ -peak are clearly separated.



Antarctic Algae. HPF freeze-substitutes in 2% OsO₄ in acetone. Sample provided courtesy of Dr. Kirk Czymmek and Shannon Modla, Delaware Biotechnology Institute Bio-Imaging Center



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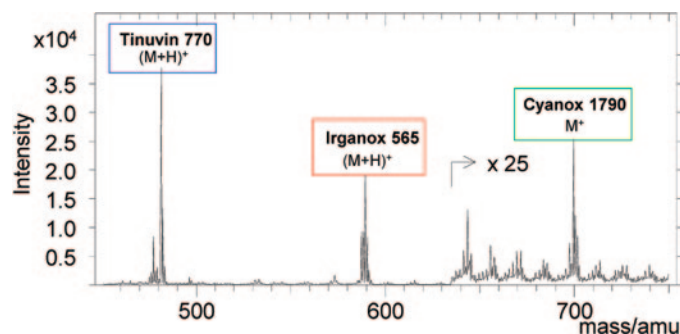


Figure 2: Detail of a positive secondary ion mass spectrum of a polypropylene surface. Three additives were identified: the UV stabilizer Tinuvin 770, the thermal stabilizer Irganox 565, and the antioxidant Cyanox 1790.

ions, the full strength of ToF-SIMS comes into play when evaluating the higher mass range of a spectrum. Molecules with masses of up to several 1000 amu are often represented in the mass spectrum by their molecular ions or as large characteristic fragments after the loss of a functional group like a hydroxyl-group (OH). Therefore, it is possible to characterize even chemically complex systems on a surface. A typical example is given in Figure 2, which shows the range between 450 amu and 750 amu of a mass spectrum of positively charged secondary ions generated from a polypropylene surface. Three distinct peak groups are detected, which can be identified as the molecular ions of the polymer additives Tinuvin 770 (a UV-stabilizer), Irganox 565 (a thermal stabilizer), and Cyanox 1790 (an antioxidant).

Chemical Imaging of Surfaces

ToF-SIMS analysis is not limited to the spectral characterization of chemical compounds on a surface. By scanning the finely focused primary ion beam over the sample surface, it is possible to generate chemical maps (up to $500 \times 500 \mu\text{m}^2$) showing the lateral distribution of compounds on the surface. Imaging of larger samples (up to $90 \times 90 \text{mm}^2$ or up to

300 mm in diameter for circular samples) is accommodated by physically scanning the specimen stage under the primary ion beam. During imaging analysis, all ions generated in each pixel are collected by the mass spectrometer and stored in a data file (a spectrum image), making it possible to display distribution maps for all elements and compounds detected on the sample. The achievable lateral resolution is limited by the focus of the probing ion beam. Modern liquid-metal ion guns can be focused down to some 10 nm in DC-beam operation and to approximately 50 nm in pulsed-beam operation. (Pulsing of the primary beam is necessary for ToF-SIMS.)

Figure 3 gives an example of such an imaging analysis. The analytical task was to detect the origin of a blooming of whitish crystals on the surface of a car bumper. A small piece was cut from the bumper and placed into the mass spectrometer for analysis. Figure 3a depicts a light optical image of the sample inside the mass spectrometer. The whitish crystals on the surface can easily be seen. Figure 3b shows a three color overlay of chemical maps of several compounds detected on the surface (Figures 3c to 3e). The crystals on the surface were identified as a segregation of the phosphate antioxidant Ultrinox 626 (Figure 3d, green color). Unrelated to the crystal formation, residues of the release agent Li stearate (Figure 3e, blue color) were also found on the sample.

Until recently, this type of analysis was not commonplace, because it was often not possible to achieve good image contrast. Despite the good focus of the primary beam, the intensity for many structurally significant secondary ions (like molecular ions) in the higher mass range was too low. This has changed with the use of polyatomic primary ions as projectiles resulting in a dramatic increase (typically by two orders of magnitude) in the number of secondary ions that can be generated from a certain surface area compared to monoatomic primary ions [3]. This rise in efficiency combined with the focus quality of modern liquid metal ion sources, using bismuth or gold cluster ions, has pushed the lateral resolution of ToF-SIMS images of organic compounds into the range of 100 nm.

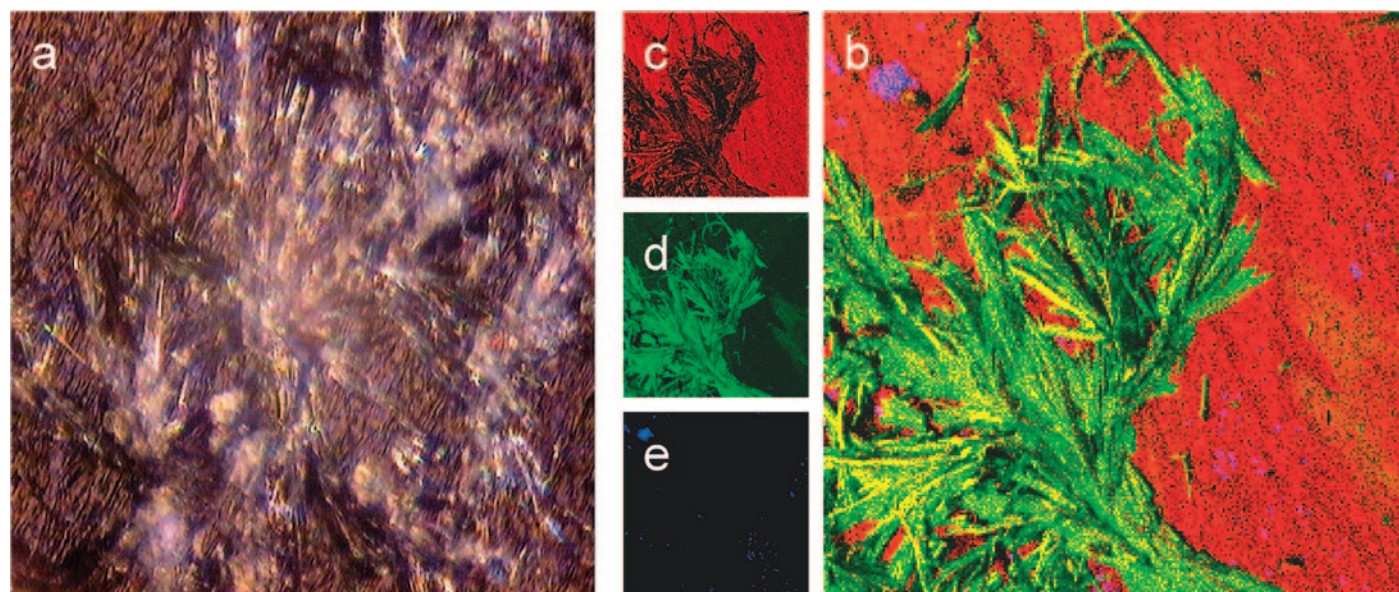


Figure 3: (a) Light optical image of white crystals blooming on a car bumper (field of view about $800 \times 800 \mu\text{m}^2$). (b) 3-color overlay of secondary ion images detected on a blooming area (field of view $500 \times 500 \mu\text{m}^2$). (c) (Red) base polymer of bumper. (d) (Green) antioxidant Ultrinox 626. (e) (Blue) release agent Li stearate.

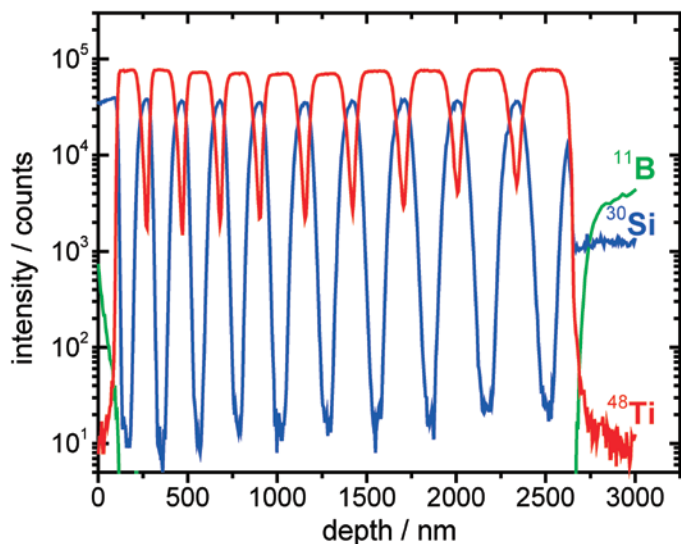


Figure 4: ToF-SIMS depth profile of a multilayer coating on a halogen spotlight reflector.

Depth Profiling

ToF-SIMS also can be applied to analyze the in-depth distribution of chemical compounds in sub-surface regions and to characterize the interfaces between different layers. This is done by using ion bombardment for the controlled erosion of a sample and analyzing the freshly exposed surface in parallel. With the proper selection of the analytical conditions, ToF-SIMS can be used for high-performance, ultra-shallow depth profiling with sub-nanometer-depth resolution as well as for the analysis of several micrometer-thick layers. Figure 4 shows a profile of a multilayer system on glass. The sample is a piece of a halogen spotlight reflector consisting of 10 double layers of titanium oxide and glass. The thickness of the layers increases with depth in order to accomplish a broadband reflection of the visual spectrum of the halogen bulb. As expected, the boron intensity rises again in the glass bulk.

3D-Analysis

Combining depth profiling with imaging analysis, ToF-SIMS can even be used to produce three-dimensional analyses of small volumes. An example from the field of metallurgy is shown in Figure 5. The sample is a polycrystalline

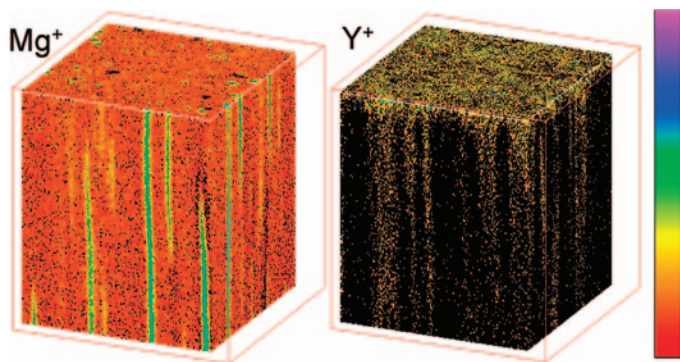


Figure 5: 3D-distribution of Mg and Y in a polycrystalline metal oxide $O_{2.8}Mg_{0.2}Ga_{0.8}Sr_{0.2}La_{0.8}$ with an overlayer of Cr, Fe, and Y. The analyzed volume is $60 \times 60 \times 0.8 \mu m^3$.

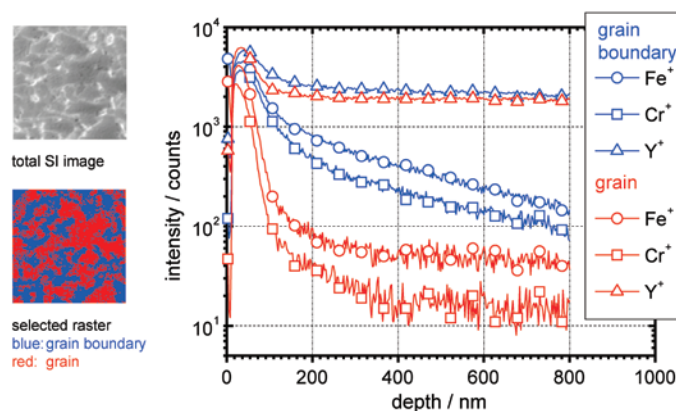


Figure 6: Depth profiles on different areas (blue: grain boundaries; red: grains) reconstructed from the raw data of the 3D-analysis of a polycrystalline metal oxide $O_{2.8}Mg_{0.2}Ga_{0.8}Sr_{0.2}La_{0.8}$ with an overlayer of Cr, Fe, and Y (see Figure 5). The diffusion is more pronounced along the grain boundaries. The total field of view is $60 \times 60 \mu m^2$.

metal oxide with the nominal composition $O_{2.8}Mg_{0.2}Ga_{0.8}Sr_{0.2}La_{0.8}$ and a thin overlayer of Cr, Fe, and Y on the top. ToF-SIMS was used to study the diffusion from the overlayer into the polycrystalline bulk. Figure 5 shows the distribution of Mg (bulk) and Y (from the overlayer) in a cube of the size of the analyzed volume ($60 \times 60 \times 0.8 \mu m^3$). A complete mass spectrum is saved for every voxel (the volume equivalent of a pixel) in the analyzed volume. It is possible to reconstruct spectra, images, and profiles from any region of interest inside the analyzed volume as demonstrated in Figure 6. After identifying the grain structure of the polycrystalline material from the secondary ion images, depth profiles from the grain boundaries and from the grains themselves were reconstructed. It is obvious that the diffusion of the elements from the overlayer is more pronounced along the grain boundaries. This possibility of retroactively mining a data set has proven to be very powerful, especially for these complex types of analyses.

Conclusion

ToF-SIMS is a powerful surface analytical tool suited for all materials compatible with vacuum environment (including powders, insulators, and even frozen liquids and biological materials). It can detect all elements (H to U), is isotope-sensitive, and delivers chemical information (molecules, clusters, fragments) about the analyzed sample surface with high sensitivity and small detection limits (ppm–ppb). Spatially resolved analysis can be achieved with high lateral resolution ($<100 \text{ nm}$) and high depth resolution ($<1 \text{ nm}$).

Acknowledgment

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