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The matrix effect - A challenge for quantitative secondary ion mass spectrometry

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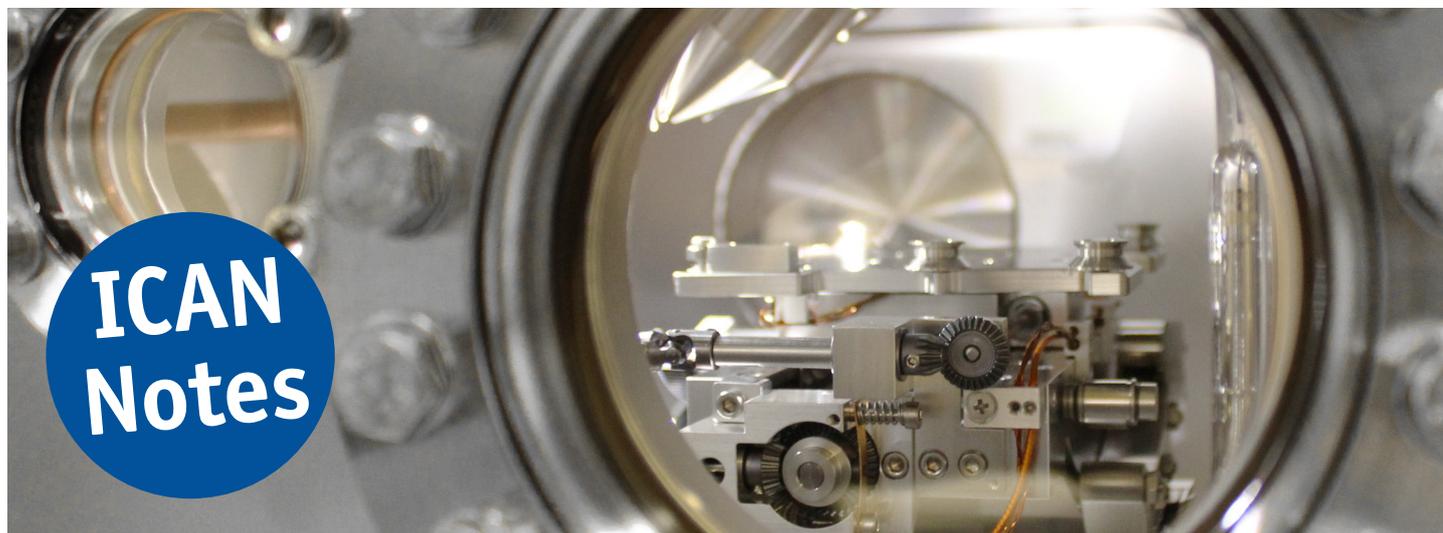


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The matrix effect - A challenge for quantitative secondary ion mass spectrometry

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Secondary ion mass spectrometry (SIMS) is a powerful and versatile tool for surface analysis, depth profiling and 3D analysis of thin films and interfaces. Perhaps most notably, among the surface and nanoanalytical methods available in ICAN, it provides the highest sensitivity in chemical analysis. Depending on the material and the analysis parameters dopants, trace elements and contaminations with concentrations in the ppm range and below are detectable. For analysis, a focused primary ion beam is used. Primary ions hitting the sample surface result in the ejection of secondary ions including atomic ions, cluster ions, and molecular ions. A time-of-flight (TOF) analyzer allows one to determine the masses of these secondary ions and obtain a mass spectrum of the analyzed surface area. The overall process leading to the formation of secondary ions is highly complex. Besides other analytical and instrumental parameters, this ionization process depends on the type, energy and angle of incidence of the primary ions, and on the analyzed material itself. Most notably, it not only depends on the elements or species which finally become ionized throughout this process but also sensitively depends on the local chemical composition and structure of the material where the primary ions hit the sample surface. It is for this reason why quantitative TOF-SIMS measurements generally are particularly challenging and in many cases not feasible at all. The ionization probability of a given element, for example, may vary over several orders of magnitude depending on the matrix, i. e., the material composition of the analyzed sample. In addition, the structure, crystallinity and surface orientation affects the overall ejection of secondary ions. This phenomenon in SIMS is called the matrix effect [1].

In this note, the matrix effect is illustrated via analysis of a classic system [2], an ordinary piece of Al foil as used for lab purposes in ICAN (EN AW 8006 O, Al content 96.1 - 98.5 %, packpack.de GmbH). Al exhibits a native oxide layer with a thickness of a few nanometers [3 - 5], whereas the bulk consists of elemental Al. The

analysis is carried out via dual beam depth profiling using a TOF-SIMS 5-100 (IONTOF GmbH) in the ICAN microscopy center [6]. As a primary ion gun a Bi⁺ nanoprobe operated in spectrometry mode at 15 kV and an analysis field of 100 x 100 μm² with the TOF-analyzer operated in positive polarity are used. For non-interlaced sputtering a Xe⁺ source operated at 500 V and a sputter field of 400 x 400 μm² is employed. After each analysis cycle material is removed from the top atomic layers of the surface in the subsequent sputter cycle. The resulting depth profiles are shown in Figure 1, displaying the intensities of Al⁺, AlO⁺ and O⁺. As expected, both the AlO⁺ and O⁺ intensities rapidly decrease with increasing sputtering time and reach the noise level once the oxide layer is completely removed. It is noteworthy that also the Al⁺ intensity rapidly decreases by nearly two orders of magnitude, even though the concentration of Al, i. e., the atomic density of Al, is indeed higher in elemental Al compared to aluminum oxide. For reference, respective values calculate to 6.0·10²² cm⁻³ vs. 4.7·10²² cm⁻³. The measurement nicely illustrates the aforementioned matrix effect. Oxygen is in fact known to strongly enhance the ionization probability of electropositive elements yielding higher ion intensities. For this reason O₂⁺ sources are routinely used in depth profiling particularly if high sensitivity for electropositive elements is desired.

The key consequence of the matrix effect is, that ion intensities do generally not scale linearly with the concentration of the respective species in the analyzed material. In fact, increasing concentrations may result in decreasing intensities and vice versa (cf. Figure 1). Clearly, this has to be taken into account when interpreting and discussing TOF-SIMS data. All ICAN users should be aware of this. In case of any ambiguities please contact ICAN prior to the publication of TOF-SIMS data. Typically, for quantitative SIMS, suitable reference materials of known composition are required for calibration. Also, if the matrix is largely constant, variations of ion intensities of minor components in good approximation represent relative concentration changes. A constant matrix generally is given when ≥99 at.% of the material composition is constant and concentration

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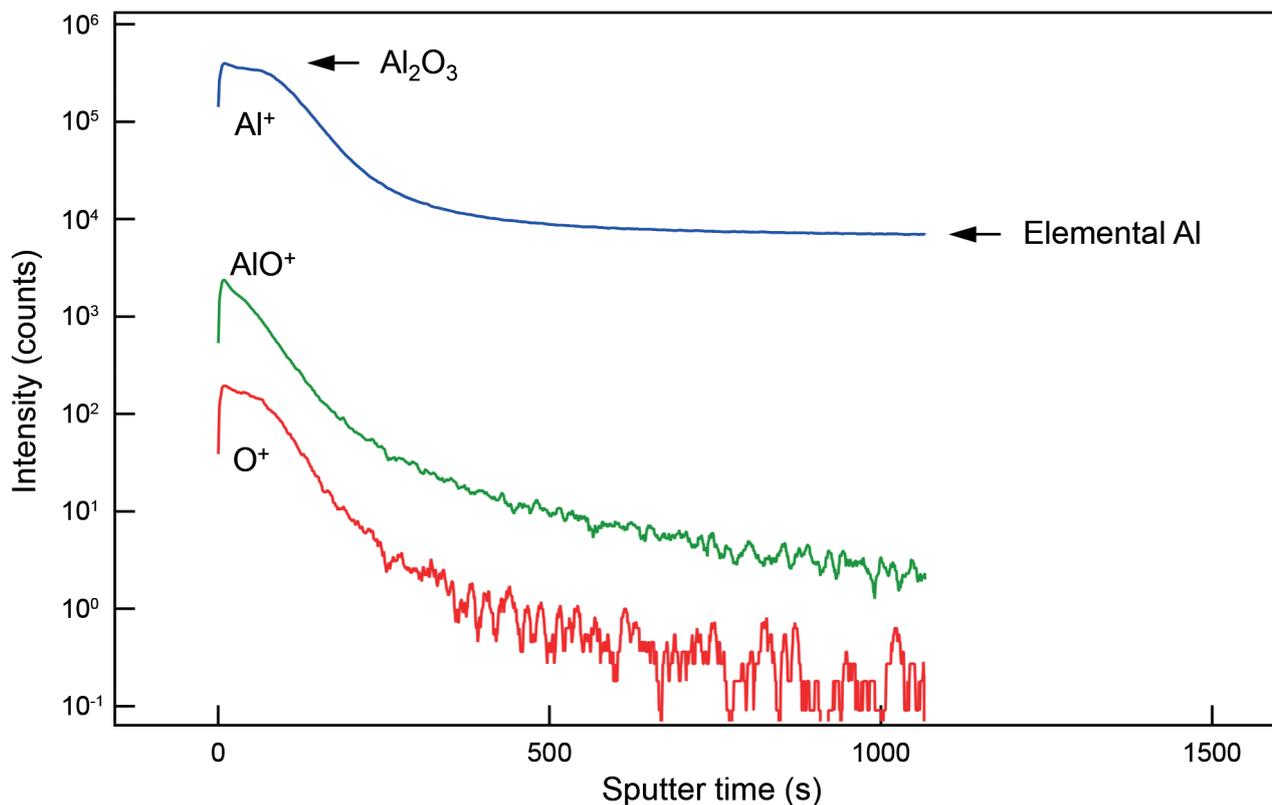


Figure 1: Semilogarithmic graph showing the Al^+ , O^+ , AlO^+ intensities with increasing sputter time during depth profiling of Al foil.

changes of a minor component are ≤ 1 at.%. An example where this is exploited is the measurement of doping profiles in semiconductor technology, where ppm level doping concentrations are routinely used and analyzed.

In contrast to the intensities of secondary ions M^+ of electropositive elements M, the corresponding intensities of MCs^+ clusters have been shown to be much less dependent on the matrix [7]. This offers an opportunity for semiquantitative or quantitative depth pro-

filings of metals with varying compositions using a Cs^+ source for sputtering. Note, that compared to M^+ , corresponding secondary cluster ions MCs^+ typically exhibit a lower intensity. Hence, quantitative analysis of MCs^+ cluster ions usually comes at the expense of the sensitivity of these measurements. In many cases, though, sensitivities $\ll 1$ at.%, i. e., well below those sensitivities of common surface-sensitive spectroscopic techniques, such as X-ray photoelectron spectroscopy (XPS), can be reached.

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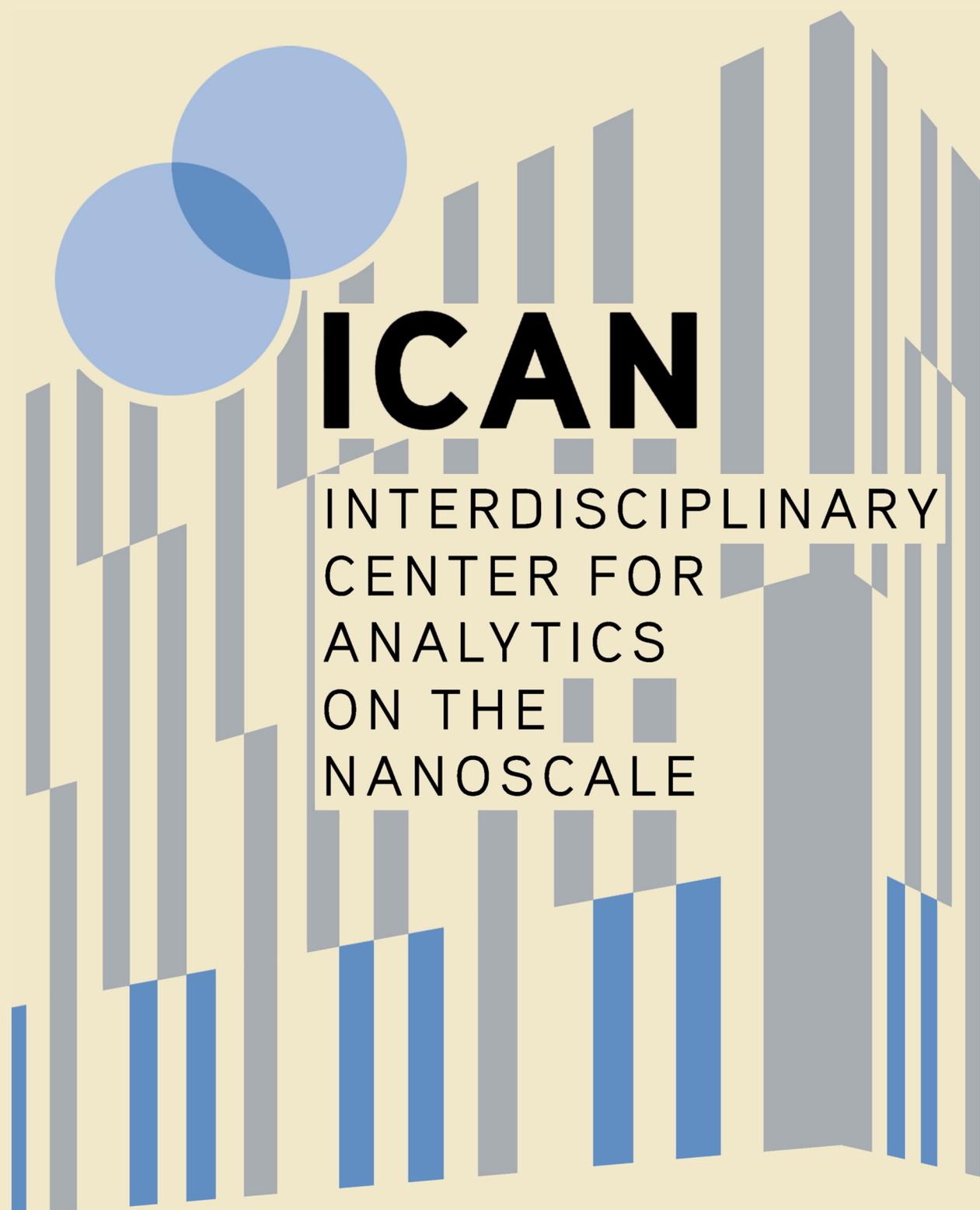
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