

Cation mass spectrometry: towards an optimisation of SIMS analyses performed in the MCs_x^+ mode

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Introduction

The excellent sensitivity, high dynamic range and good depth resolution make Secondary Ion Mass Spectrometry (SIMS) an extremely powerful technique for the analysis of surfaces and thin films. However, the SIMS technique suffers from one major drawback that gives rise to very significant problems with quantification; the ionisation yield of a given sputtered element may vary by several orders of magnitude depending on the composition of the matrix in which it is located. For example the ionisation probability of Ti will be 10 to 10,000 times (depending on the primary ions used) greater in an oxide sample compared with a metallic sample. This leads to signals measured at the exit of the spectrometer that can vary by a factor of 10 to 10,000, whereas the concentration of Ti remains the same. This phenomenon, which is known as the matrix effect, prevents SIMS from becoming an easy tool for quantitative analysis, except when dealing with ideal samples like a single crystal of silicon for which standard samples can be prepared in order to determine the ionisation probability of the element of interest in silicon (this efficiency cannot be used for quantification in other matrices).

The matrix effect can be circumvented by working in the MCs_x^+ mode. This method consists of incorporating Cs into the material and detecting MCs^+ clusters and, in the case of electronegative elements, MCs_2^+ clusters, where M represents the element to be analysed. The quantitative potential of this method is understood by assuming that the MCs^+ ions are generated by the combination of a secondary neutral M^0 with a resputtered Cs^+ ion in the near surface region above the specimen. Consequently, the emission process for

the species M is decoupled from the subsequent MCs^+ ion formation process by analogy with the ion formation in secondary neutral mass spectrometry resulting in a drastic decrease of the matrix effect. This process is nicely illustrated in Figure 1, which shows the useful yield of Si^+ ions in different samples: silicon, silicon carbide, silicon nitride and silicon oxide. The useful yield expresses the ratio between the number of detected secondary ions and the number of sputtered atoms of the same element. It reflects thus the sensitivity of the measurements and strongly depends on the ionisation probability. The SIMS ions exhibit large changes in ionisation probability (useful yield) from one sample to another under oxygen, cesium or gallium bombardment, whereas the useful yield of the MCs^+ clusters (here SiCs^+) stays practically constant.

It has been shown that the sensitivity of the MCs^+ and MCs_2^+ ions depend strongly on the stationary cesium surface concentration incorporated in the specimen during the primary bombardment.^{1,2} An increasing Cs surface concentration can lower the electron work function below a critical value that is slightly below the ionisation energy of

Cs. If this occurs, according to the electron-tunnelling model for secondary ion formation, the probability of secondary Cs^+ ionisation and consequently the probability of MCs^+ and MCs_2^+ cluster formation strongly decreases, see Figure 2.

The analysis of MCs_x^+ clusters is routinely performed using dynamic SIMS instruments equipped with a primary ion column delivering Cs^+ ions serving both for the incorporation of Cs into the material and for the sputtering of the surface. In this case, the primary bombardment conditions (mainly the impact energy and the incidence angle, which can be adapted only in a very limited way on conventional SIMS equipment) as well as the characteristics of the investigated specimen imply a distinct total sputtering yield Y and consequently determine the cesium surface concentration c_{Cs} according to $c_{\text{Cs}} = 1/(1 + Y)$. As a consequence, the Cs concentration is practically fixed for a given type of sample and cannot be chosen freely. As it is unlikely that the Cs concentration thus obtained will coincide with the optimum concentration for the highest MCs_x^+ useful yields for the material in question, the analysis is not optimised.

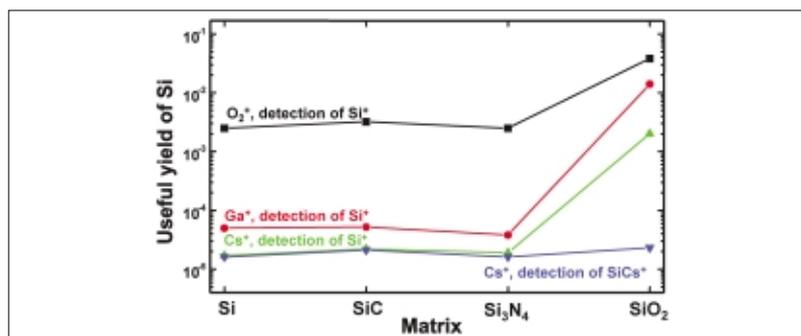


Figure 1. Useful yields of Si in four matrices obtained in the Si^+ mode under three different primary bombardments and in the SiCs^+ mode.

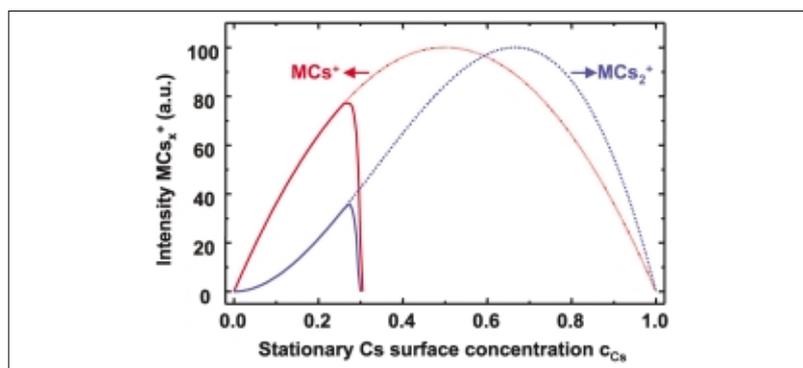


Figure 2. Theoretical evolution of the MCs^+ and MCs_2^+ signals with the stationary Cs surface concentration c_{Cs} for any kind of sample. The dashed line plots were calculated by considering only the direct influence of c_{Cs} and the concentration, c_M , of the analysed species M. The final solid line curves were obtained after additionally taking into account the evolution of the ionisation probability β_{Cs} of a sputtered Cs atom caused by work function shifts. (The critical value of c_{Cs} depends on the sample considered and was chosen arbitrarily for the graph presented.)



Figure 3. Photograph of the Cation Mass Spectrometer.

The Cation Mass Spectrometer, which has been developed and realised in the LAM (Laboratory for the Analysis of Materials) within the framework of the European Community Standards, Measurements and Testing programme, has been designed to optimise the analysis of these MCs^+ and MCs_2^+ clusters.¹⁻⁴ The Cation Mass Spectrometer leads to high MCs^+ and MCs_2^+ useful yields by allowing one to adjust the stationary Cs surface concentration to its optimum value while retaining the high transmission advantage of using a double focussing magnetic sector spectrometer.

The instrument

The Cation Mass Spectrometer (Figures 3 and 4) has been equipped with several newly-developed features:

- a surface ionisation Cs^+ ion gun and a field emission Ga^+ ion gun deliver-

ing a finely focused beam for serving, in particular, imaging applications. These two ion guns can be operated simultaneously in order to adjust the Cs concentration introduced into the sample by means of varying the Cs proportion contained in the primary bombardment;

- a patented column capable of delivering an adjustable flux of neutral Cs that can be used with either (or both) of the two aforementioned ion guns;
- an electron gun allowing for a charge compensation while analysing insulating specimens;
- a sample stage and adapted collection optics which allow variations of the impact angle of the primary beam onto the specimen at a constant primary energy. These variations of the incidence angle imply changes of the sputtering yield Y , and consequently the Cs surface concentration;
- a secondary column with microscope imaging, equipped with a magnetic sector spectrometer.

Cs^0 column

An important and innovating component of the Cation Mass Spectrometer is the specially-developed Cs^0 column. Therefore, we are going to discuss this new item in more detail.

To deposit alkaline metals, one almost exclusively uses getters heated by circulating an electric current in order to release the alkaline atoms. The use of such a getter for analytical purposes requires a Cs deposition rate of the order of 1 \AA s^{-1} . However, this presents several major drawbacks. It results in a very limited lifetime, and contamination of both the analysis chamber, due

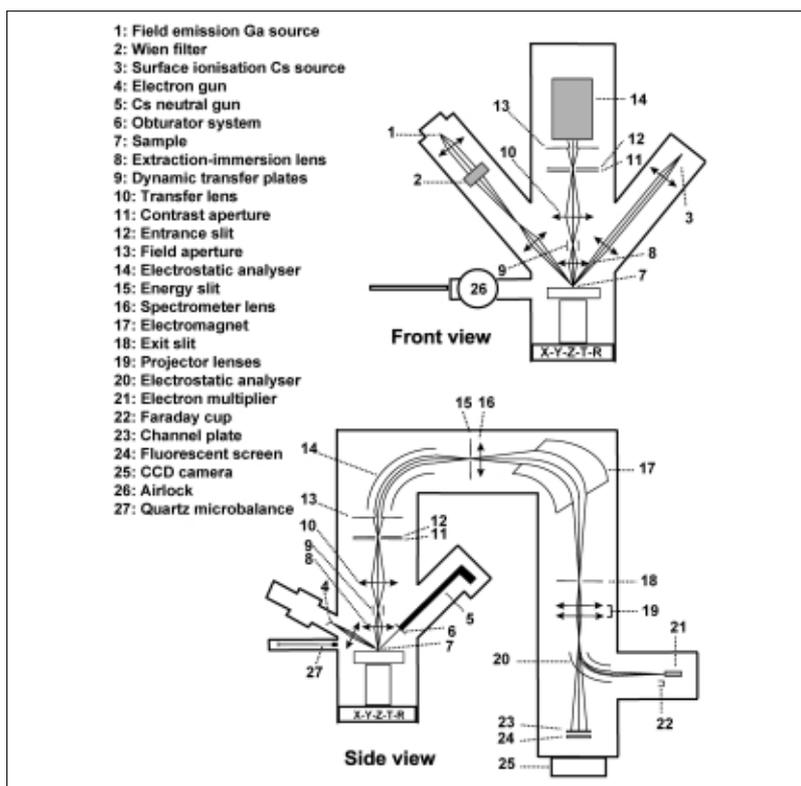


Figure 4. Schematic representation of the Cation Mass Spectrometer.

to a broad non-collimated beam, and the Cs deposit, due to traces of chromates and reducing agents contained in the getter.

As an alternative, we developed a column delivering a stream of Cs from the evaporation of pure metallic Cs. This configuration enables us to eliminate the major disadvantages of conventional getters. Indeed, the service life can be increased enormously (by a factor of up to 1000) given that it is possible to fill the reservoir with a large quantity of Cs (several grams) and given that the Cs beam can be collimated onto the useful zone by using a gun end-piece with a small opening positioned close to the sample. In addition, as the evaporator is loaded with pure metallic Cs, the risk of contaminating the Cs deposit with traces of other elements is reduced considerably.

Calibration curves achieved with a quartz microbalance system show that Cs⁰ deposition rates on the sample of the desired order of 1 Å s⁻¹ can be reached with reasonable temperatures (75–85°C) and corresponding heating powers (75–100 W). Moreover, as the deposition rate exhibits an exponential change with respect to the temperature applied to the reservoir, considerably greater flow rates can be obtained if necessary by increasing the temperature by only a few degrees. Also, the stability of these deposition rates amounts to 2% over a period of 60 min and the Cs⁰

spot produced on the sample has a diameter of a few mm.

The cleanliness of the Cs deposit is a crucial factor for the use of the Cs⁰ evaporator during the analyses. Contamination of the Cs vapour with impurities leads to an increase in the detection limits for certain elements since the signal of the element under study is affected by a background noise of varying degrees of intensity. We have performed several measurements to investigate the cleanliness of our system, and no trace of any contaminant was detected from the produced Cs⁰ stream.

Variation of Cs concentration

The Cation Mass Spectrometer offers three main possibilities for varying the stationary Cs surface concentration c_{Cs} in order to reach high MCs_x⁺ useful yields. These are:

- bombarding the sample with Cs⁺ ions and varying the incidence angle of the primary beam by using the z motion of the sample stage to change the distance d between the sample surface and the extraction nose. These variations involve changes of the sputtering yield Y , which determines the Cs surface concentration according to $c_{Cs} = 1/(1 + Y)$;
- operating simultaneously the Cs⁺ and Ga⁺ ion guns and adjusting the Cs proportion contained in the primary bombardment;

- exposing the sample to an adjustable flux of neutral Cs and use the Ga⁺ ion gun.

Experiments have shown that these three primary bombardment techniques allow one to vary the stationary Cs surface concentration over a complete and continuous Cs concentration range from quasi 0% to 100%. As a consequence, it becomes possible to fix the Cs concentration to its optimum value in order to maximise the detected MCs_x⁺ signals for any kind of sample.

Advantages of the Cs⁰ column

The newly developed Cs⁰ evaporator installed on the Cation Mass Spectrometer opens up several promising new opportunities. Using this new column, it is possible to introduce an analysis technique consisting of a X⁺ ion bombardment (where X stands for any element other than Cs) accompanied by a deposit of Cs⁰ at the surface of the sample. This experimental technique avoids the constraints imposed by a Cs⁺ ion bombardment, namely that it is impossible to separately choose the Cs concentration implanted in the sample and the energetic and angular parameters of the primary beam, given that the latter determine the value of the Cs concentration. These primary bombardment conditions also have a major affect on important analytical considerations such as the depth resolution.

Compared with Cs⁺ ion bombardment, deposition of Cs⁰ provides an additional degree of freedom. It separates the sputtering and Cs introduction phases during analyses in the MCs_x⁺ mode allowing for a simultaneous optimisation of the Cs concentration and of important analytical considerations, such as the depth resolution, which as mentioned depends on the primary bombardment conditions. When the optimum quantity of Cs is deposited in the form of neutral atoms on the surface of the sample, no sputtering process or atomic mixing of the target takes place and the depth resolution of the analysis depends only on the characteristics of the bombardment produced by the sputtering/analysis gun. Consequently, the CMS will soon be equipped with a C₆₀⁺ cluster ion gun to serve as a sputtering gun, thereby allowing for optimum depth resolution.

In addition, the use of the Cs evaporator, which deposits the Cs atoms right on the surface of the sample, enables an optimised signal to be measured from the first atomic layer. This new analysis technique therefore offers a considerable advantage in the analysis of samples in which the interesting zone is directly at or in very close vicinity of the surface.

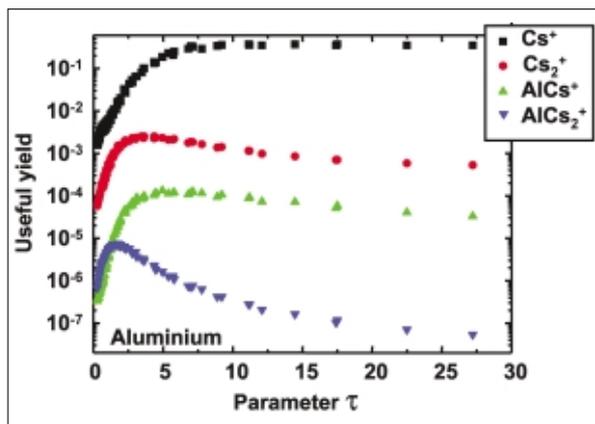


Figure 5. Evolution of Cs_x^+ and MCs_x^+ useful yields with respect to the ratio τ between the erosion and deposition rates for an aluminium sample.

MCs_x^+ useful yields

Our studies performed on various samples and for a large number of different Cs concentrations covering the whole accessible range clearly show (see, for example, Figure 5) that if the Cs concentration is carefully selected it is indeed possible to optimise the MCs_x^+

and Cs_x^+ useful yields on the Cation Mass Spectrometer.

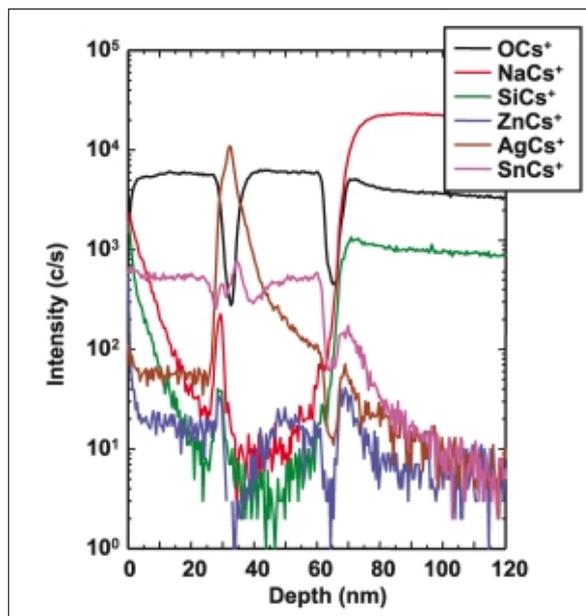


Figure 6. Depth profile obtained in the MCs_x^+ mode of a car front shield covered with various anti-reflecting layers.

The main parameters that govern the intensity of the secondary signals are the

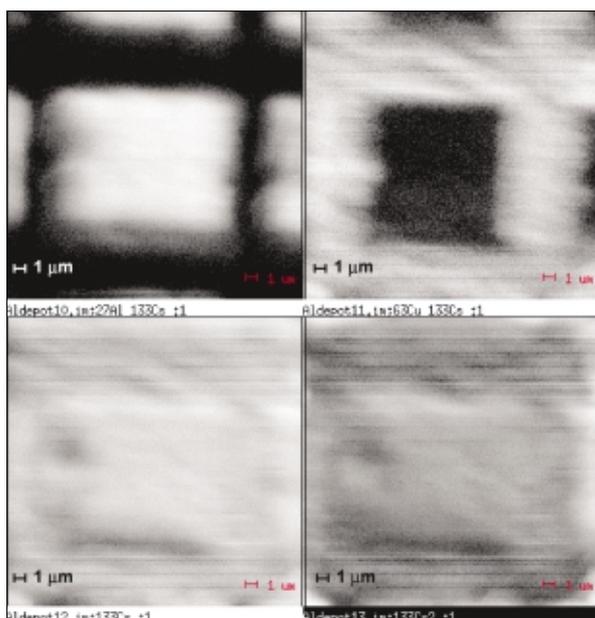


Figure 7. Ion images (AlCs^+ , CuCs^+ , Cs^+ and Cs_2^+ secondary ions) recorded from the same area of an Al/Cu grid. The analysis was performed by rastering a finely focused Ga^+ beam over the sample surface while simultaneously depositing Cs^0 . The images are: top left, AlCs^+ ; top right, CuCs^+ ; bottom left, Cs^+ ; bottom right, Cs_2^+ .

quantity of available Cs atoms to form the respective clusters, the recombination probability between M atoms and Cs^+ ions, which is in particular related to the polarisability of the atom M, and changes in the work function, which cause drastic variations of the ionisation probability of secondary Cs^+ due to the presence of Cs.

For the case of depositing Cs on the sample surface during the analysis by using the Cs^0 column, the value of the Cs concentration and the detected Cs_x^+ and MCs_x^+ signals depend only on the characteristics of the analysed material and the ratio between the erosion and deposition rates, but not on the individual values of these two rates (Figure 5). This is a very important consideration in improving depth resolution by low-energy primary bombardment. In this case the sputtering yield and consequently the erosion rate have very low values; by then lowering the deposition rate to attain optimum values of the erosion to deposition ratio, we can successfully optimise the secondary signals in which we are interested.

To show the benefits resulting from the potential of the Cation Mass Spectrometer for varying the Cs concentration over a large range and thus optimising the important parameter in MCs_x^+ cluster analysis, the same samples were investigated on one of the latest high-performance, commercial conventional SIMS instruments. This study revealed that, depending on the ele-

ment, useful yield enhancements up to a factor of 100 may be achieved on the Cation Mass Spectrometer. This can be explained by the fact that the stationary Cs surface concentrations obtained during analyses on commercial magnetic sector SIMS instruments are too high for most of the samples. As a consequence, the work function is shifted to energies lower than the critical value, which provokes a drastic decrease of the ionisation probability of the necessary Cs^+ ion.

Synopsis of the Cation Mass Spectrometer

- Cs and Ga primary ion guns
- Patented Cs^0 evaporator
- High transmission magnetic sector spectrometer
- Spatial resolution (x, y): 100 nm
- Depth resolution (z): 1–10 nm
- Detection limits: ppb to 100%
- Elemental range: H to U
- Direct quantification by using the MCs_x^+ technique under the optimum conditions
- Depth profiling (Figure 6), elemental mapping (Figure 7), mass spectra (Figure 8)

Unique advantages of the Cation Mass Spectrometer

- Excellent detection limits
- Quantitative analysis

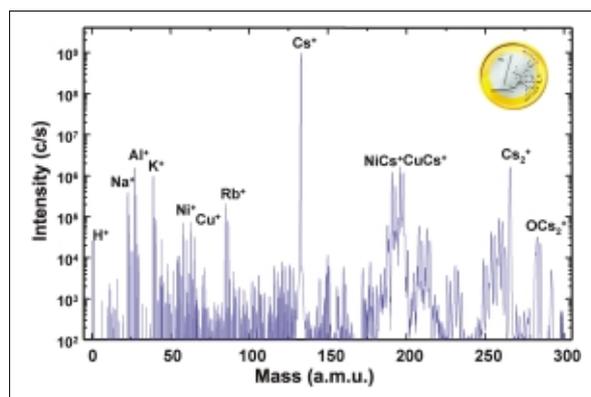


Figure 8. CMS mass spectrum performed on a 1 Euro coin.

- Optimised useful yields in the MCs_x^+ mode due to the Cs^0 evaporator
- Optimised depth resolution
- Rapid ion image acquisition capabilities
- Three-dimensional analysis

Conclusions

The Cation Mass Spectrometer is a powerful instrument for SIMS analyses in the quantitative MCs_x^+ mode. These analyses can be optimised simultaneously with respect to both the obtained useful yields and, due to the successful decoupling of the sputtering and Cs introduction processes realised by using the newly developed Cs^0 column, to the depth resolution. Current and future projects consist mainly in installing a cluster ion gun on the instrument with a view to gaining a significant improvement of the depth resolution capability in order to keep pace with the requirements of upcoming technologies.

References

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