

# Unravelling the secrets of Cs controlled secondary ion formation: Evidence of the dominance of site specific surface chemistry, alloying and ionic bonding

Klaus Wittmaack

*Helmholtz Zentrum München, Institute of Radiation Protection, D-85758 Neuherberg, Germany*

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## Abstract

Exposure of ion bombarded solids to Cs gives rise to a very strong enhancement of the yields of negatively charged secondary ions and, concurrently, to a lowering of positive ion yields. The phenomena have been explored in a large number of experimental and theoretical studies but attempts to clarify the mechanism of ion formation were not as successful as assumed. This review examines the state of the art in Cs controlled secondary ion mass spectrometry (SIMS) in great detail, with due consideration of low-energy alkali-ion scattering.

In very basic studies on alkali induced secondary ion yield changes, sub-monolayer quantities of Cs or Li were deposited on the sample surface, followed by low-fluence ion bombardment, to avoid significant damage. If SIMS is applied to characterise the composition of solid materials, the simplest approach to achieving sample erosion as well as high negative-ion yields is bombardment with primary ions of Cs. Two other methods of sample loading with Cs provide more flexibility, (i) exposure to a collimated beam of Cs vapour and concurrent bombardment with high-energy non-Cs ions and (ii) the mixed-beam approach involving quasi-simultaneous bombardment with Cs and Xe ions. Both concepts have the advantage that undesirable sample overload with Cs can be avoided. High Cs concentrations reduce the formation probability of target specific molecular ions and lower the yields of all types of positive secondary ions, including  $\text{Cs}^+$ ,  $\text{M}^+$ ,  $\text{X}^+$ ,  $\text{MCs}^+$  and  $\text{XCs}^+$  (M and X denoting matrix and impurity elements). Quantitative SIMS analysis using  $\text{MCs}^+$  and  $\text{XCs}^+$  ions appears feasible, provided the Cs coverage is kept below about 5%.

The semi-classical model of resonant charge transfer, also known as the tunnelling model, has long been considered a solid framework for the interpretation of Cs and Li based SIMS data. The model predicts ionisation probabilities for cases in which, at shallow distances from the surface, the affinity (ionisation) level of the departing atom is shifted below (above) the Fermi level. Ion yields should be controlled by the work function (WF) of the sample,  $\Phi$ , and the normal velocity of the ejected ions. To explore the predicted velocity dependence, the performance characteristics of the employed SIMS instrument need to be known. The Cs induced negative-ion yield enhancement observed with pure metal and alloy targets often exceeded five orders of magnitude, with enhancement factors essentially independent of the emission energy. This absence of a velocity dependence is at variance with the predictions of the tunnelling model.

Previous theoretical attempts to model the  $\Phi$ -dependence and the apparent velocity effect for the overrated case of  $\text{O}^-$  emission from Li and Cs exposed oxidised metal surfaces must be considered a meander. The experimental data, recorded with a quadrupole based instrument of inadequate extraction geometry, may alternatively be rationalised in terms of alkali induced changes in the energy spectrum of sputtered atoms. Another important finding is that secondary ion yield changes do not correlate with the absolute magnitude of the (macroscopic) WF but often with WF changes,  $\Delta\Phi$ . The frequently used method of determining  $\Delta\Phi$  in situ from the shift of the leading edge of secondary ion energy spectra rests on the assumption, taken for granted or not even appreciated, that Cs induced yield changes are independent of the ion's emission velocity. Hence the approach is only applicable if the tunnelling model is not valid. The local character of alkali induced WF changes, which might provide a route to an understanding of previously unexplained phenomena, has been explored using photoemission of adsorbed inert gases, scanning tunneling microscopy and low-energy ion scattering spectrometry.

At room temperature, the Cs coverage is limited to one layer of adatoms. Close similarities are identified between WF changes generated by Cs vapour deposition and by bombardment with Cs ions. This finding implies that sub-monolayer quantities of

*E-mail address:* [wittmaack@helmholtz-muenchen.de](mailto:wittmaack@helmholtz-muenchen.de)

Cs adatoms grow at the surface of Cs bombarded samples. The process has been studied in-situ by medium-energy ion scattering spectrometry. The stationary Cs coverage,  $N_{\text{Cs}}$ , is controlled by the efficiency of active transport of implanted atoms to the surface, the bulk retention properties of the sample and the cross section for sputtering of adatoms. Unearthing immobile implanted Cs atoms by sputter erosion usually provides only a minor contribution to the stationary coverage. Cs adatoms are mobile; the time required for final adatom rearrangement may be on the order of minutes at room temperature. Exposure of Cs bombarded samples to oxygen gives rise to oxidation of the substrate as well as to the formation of oxide layers of complex composition. Intercalation should be taken into account as a possible route of alkali transport into analysed samples. An important aspect ignored in prior work is that the alkali coverage required to produce a certain WF change is five to seven times higher if Li is deposited instead of Cs. Studies involving the use of Li thus provide no advantage compared to Cs. Furthermore, migration of the tiny Li atoms into the sample and metallisation effects aggravate data interpretation.

Literature data for  $\Delta\Phi(N_{\text{Cs}})$ , measured using Cs vapour deposition, can be converted to calibration curves,  $N_{\text{Cs}}(\Delta\Phi)$ , for calculating the coverage established in implantation studies, a method referred to as  $\Delta\Phi \rightarrow N_{\text{Cs}}$  conversion. This concept may be carried even further, as shown convincingly for silicon, the material examined most frequently in basic SIMS studies:  $\text{Si}^-$  ion fractions,  $P(\text{Si}^-)$ , derived from yields measured under vastly different conditions of Cs supply, exhibit essentially the same  $\Delta\Phi$  dependence. Inverting the data one can produce calibration functions for  $\Delta\Phi$  versus  $P(\text{Si}^-)$ , denoted  $P(\text{Si}^-) \rightarrow \Delta\Phi$ , or, more generally,  $P(\text{M}^-) \rightarrow \Delta\Phi$  conversion. On this basis, transient yields measured during Cs implantation can be evaluated as a function of Cs coverage.

The summarised results imply that secondary ions are commonly not formed by charge transfer between an escaping atom and the electronic system of the sample but are already emitted as ions. The probability of ion formation appears to be controlled by the local ionic character of the alkali-target atom bonds, i.e., by the difference in electronegativity between the involved elements as well as by the electron affinity and the ionisation potential of the departing atom. This idea is supported by the finding that  $\text{Si}^-$  yields exhibit the same very strong dependence on Cs coverage as  $\text{Si}^+$  and  $\text{O}^-$  yields on the oxygen fraction in oxygen loaded Si. Most challenging to theoreticians is the finding that the ionisation probability is independent of the emission velocity of sputtered ions. This phenomenon cannot be rationalised along established routes of thinking. Different concepts need to be explored. An old, somewhat exotic idea takes account of the heavy perturbation created for a very short period of time at the site of ion emission (dynamic randomisation). Molecular dynamics simulations are desirable to clarify the issue. Ultimately it may be possible to describe all phenomena of enhanced or suppressed secondary ion formation, produced either by surface loading with alkali atoms or by enforced surface oxidation, on the basis of a single universal model. There is plenty of room for exciting new studies.

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**Keywords:** Secondary ion formation; Cs deposition; Implantation; Adatoms; Yield enhancement; Ion induced electron emission; Tunnelling model; Velocity dependence; Work function; Local potential; Site specific chemistry; Electronegativity

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