Electron Impact Sputtered Neutral Mass Spectrometry (SNMS) using the Hiden EQS Energy Resolving Quadrupole Mass Spectrometer.

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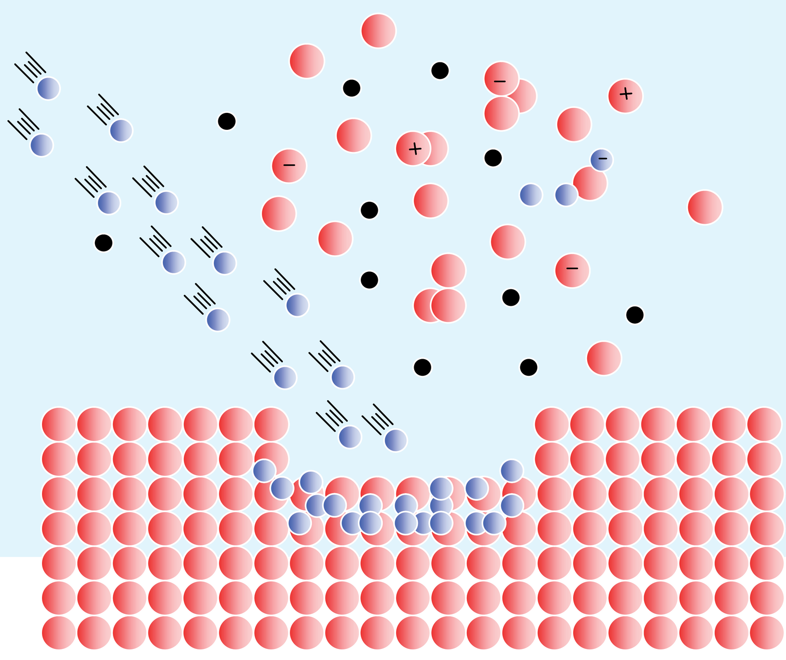
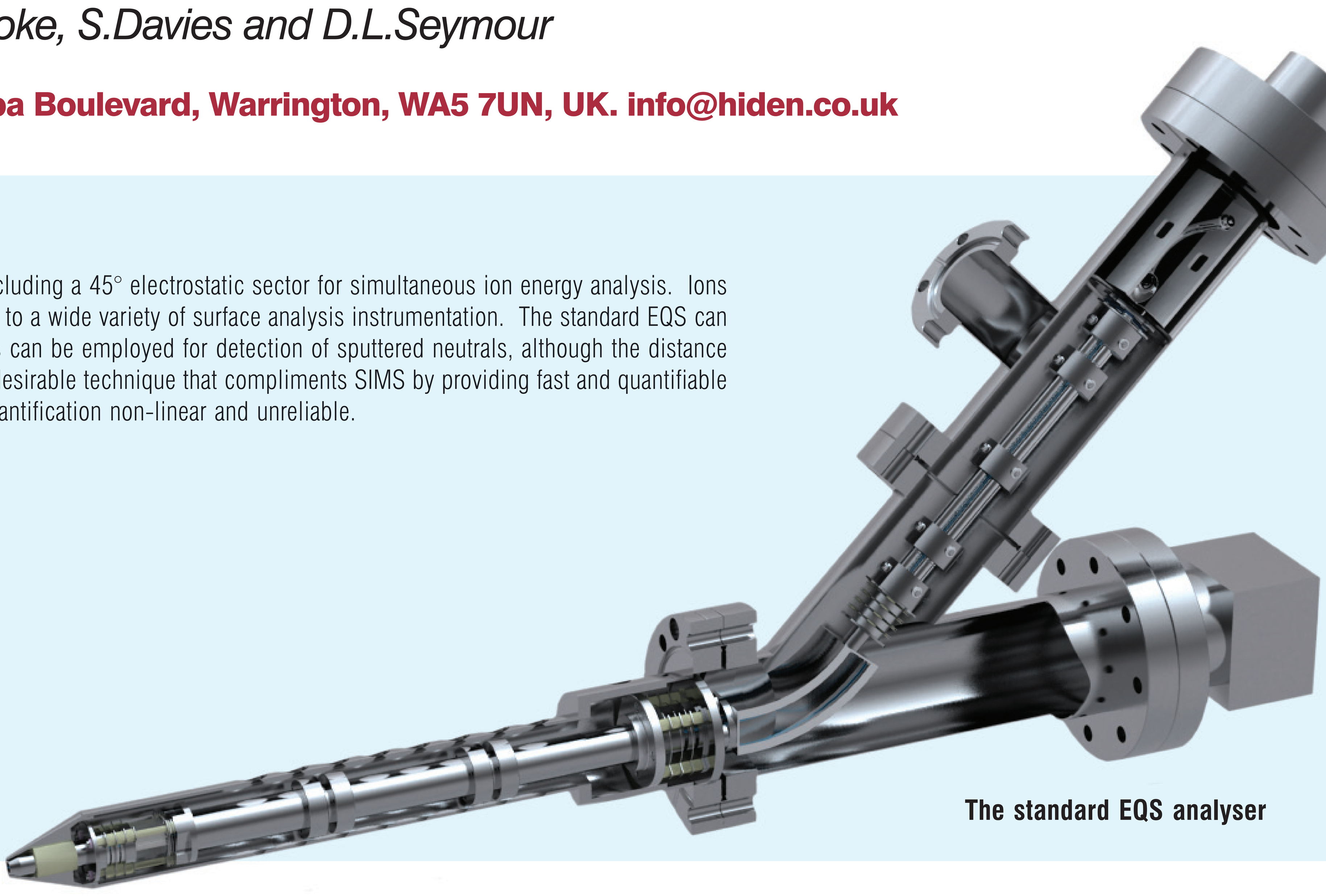
Introduction

The Hiden EQS is a high transmission quadrupole secondary ion mass spectrometry, SIMS, detector including a 45° electrostatic sector for simultaneous ion energy analysis. Ions are collected on the axis of the device which makes it very popular for fitting as an after-market detector to a wide variety of surface analysis instrumentation. The standard EQS can also be used to monitor the residual gas using an electron impact ionizer sited within the device. This can be employed for detection of sputtered neutrals, although the distance from sample to the ionizer leads to a low sensitivity. Sputtered neutral mass spectrometry, SNMS, is a desirable technique that compliments SIMS by providing fast and quantifiable concentration data in the 0.1 to 100 atomic % regime where the matrix effect of SIMS makes direct quantification non-linear and unreliable.

Incident ion beam (blue) sputters the target material with the emission of mainly neutrals with a small fraction of positive and negative ions and many electrons (black).





The standard EQS analyser

SIMS vs SNMS

Both techniques provide mass resolved information for mass spectra, concentration depth profiles and images. SIMS is suited to trace analysis and SNMS to higher concentrations. Combining the techniques provides a very powerful quantitative materials analysis method.

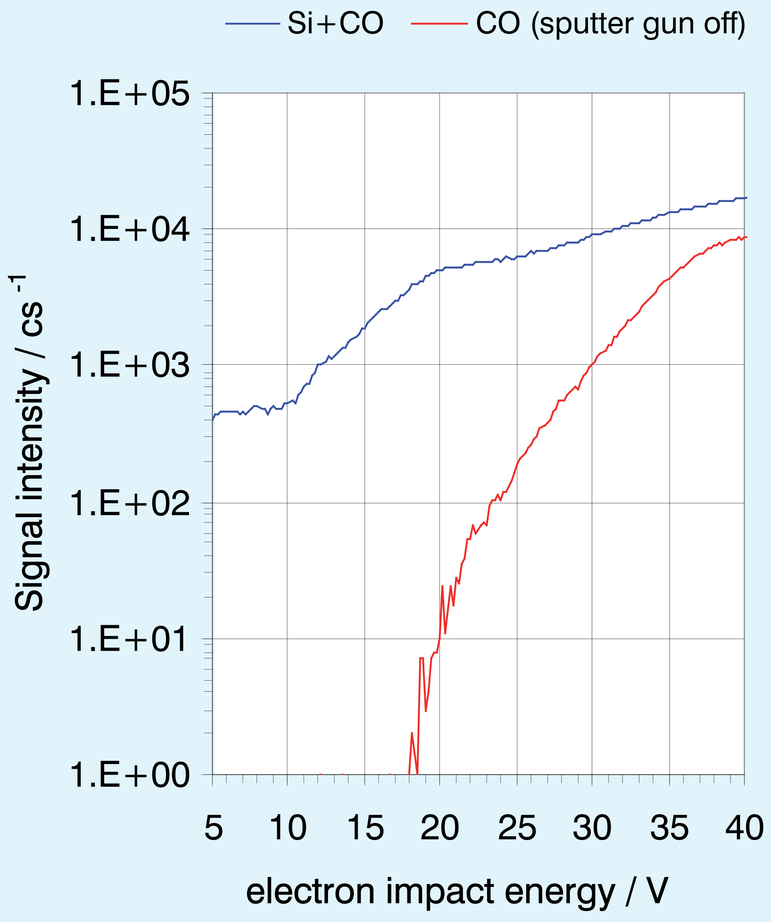
SIMS
- ions created by the sputtering event
- small fraction of all emitted particles
- easily collected by electric field
- ionized fraction depends on surface chemistry
- non-linear when concentration above a few percent
- quantifiable in range ppb to 5 atomic %
- requires reference materials of very similar chemistry

SNMS
- ions created by separate ionizer
- neutrals represent most of the emitted particles
- can only be collected by proximity of the ionizer
- ionized fraction independent of surface chemistry
- near linear in all concentrations (0.1 to 100 atomic %)
- requires reference material containing the element of interest

Mass Interference ^{28}Si and CO – appearance energy selection

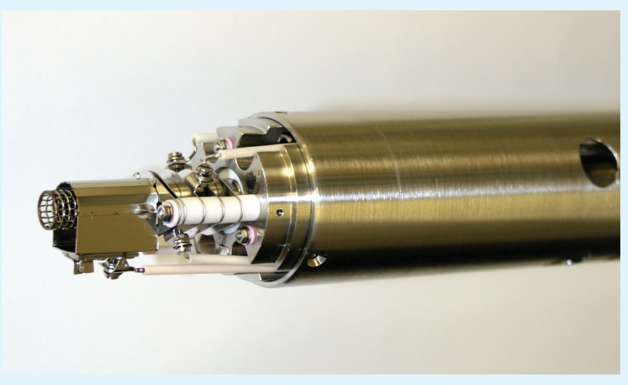
The electron impact source also ionizes CO from the residual gas which can cause a significant mass interference at mass 28. However, use of an electron energy below the appearance energy of CO provides efficient selection of the Si signal.

The red trace shows the signal due only to residual CO in the chamber (the ion gun is turned off) whereas the blue line shows the signal measured during sputter analysis. By choosing an electron voltage below the appearance energy of CO it is possible to get a much higher dynamic range – despite the overall lower signal intensity.



The addition of an SNMS Ionizer

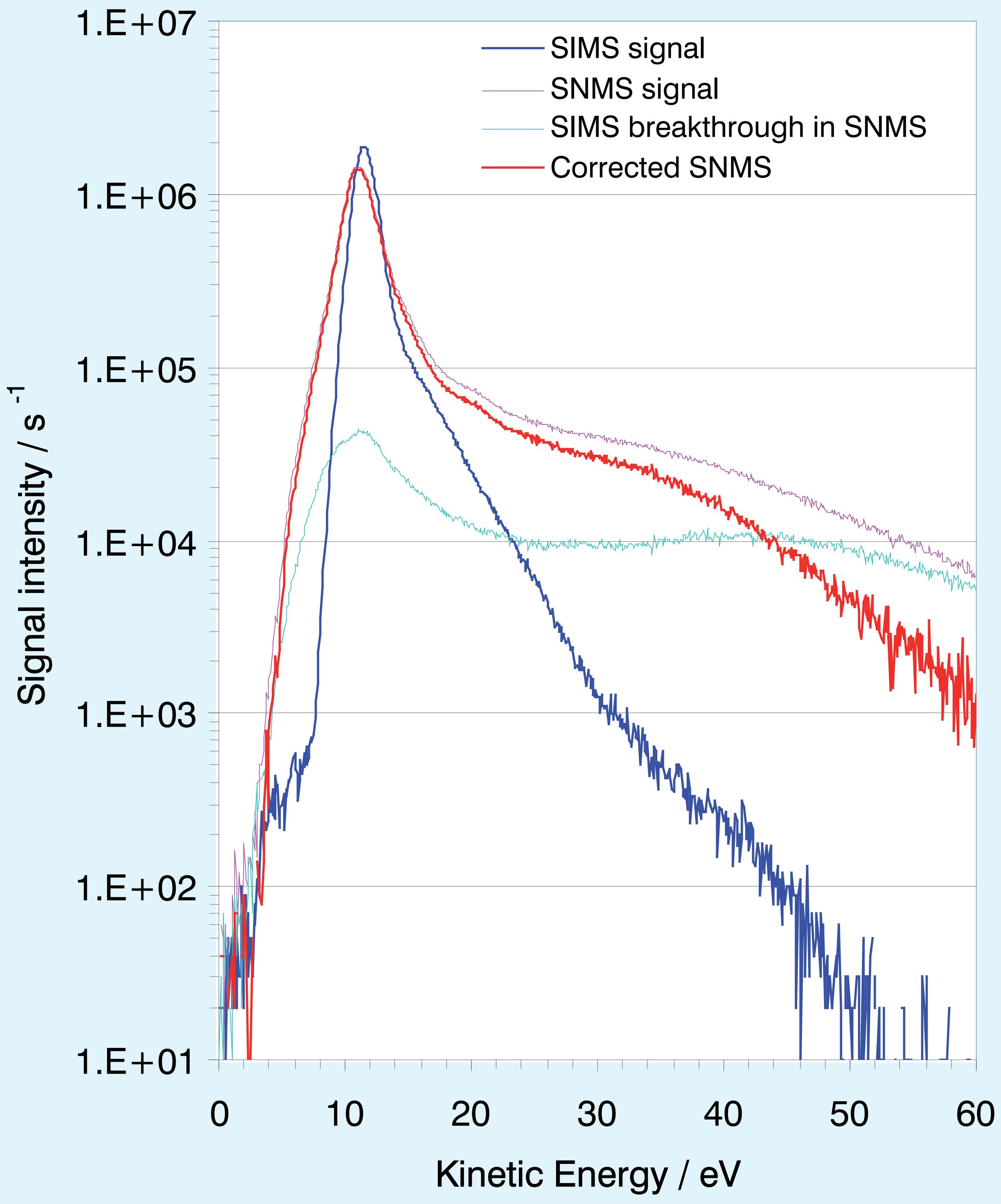
The electron impact ionizer has been relocated to the front of the probe so that it subtends the largest solid angle possible – as the neutrals cannot be directed until they are charged. In SIMS mode the ionizer filament is off and the electrode behaves as an extractor for ions. In SNMS mode the ionizer cage is populated with electrons and neutrals are ionized – these then follow a similar path to that which SIMS ions would have taken. The SIMS signal is deliberately rejected by placing a bias on the target so as to shift the SIMS energy spectrum to a level where it can be filtered by the electrostatic sector.



The filament is housed in the box structure on the underside of the probe and has no line of site to the sample. The electrons, with energy variable between 4 and 150 eV, are directed into the ionization cage visible at the end of the device.

In operation, the optimum sampling distance is between 5 and 10 mm from the end of the probe.

K signals from Microcline



In Use

Turning the filament off, with all other potentials remaining the same, permits detection of "breakthrough" SIMS ions to be monitored. Even in the case of a very high ion yield material, such as potassium, this only represents a few percent.

The data shown are from a natural mineral sample of microcline ($KAlSi_3O_8$) sputtered using 5 keV Ar^+ ions. The ^{39}K signal is detected as a function of kinetic energy – determined by sweeping the transit energy of the ions through the electrostatic analyser.

The sample is insulating and a 500 eV electron flood has been used to provide charge compensation. This is not actually required for the analysis of neutrals but must be provided to ensure the primary ion beam is not affected by high surface potentials.

Conclusions

Modification to the Hiden EQS analyser permits mass and energy analysis of fast neutral species for both materials analysis and basic surface emission studies. Selective measurement with the ionizer filament off enables any breakthrough ions to be detected, thus their contribution to the overall result can be subtracted.

References

[1] Handbook of Surface and interface analysis: methods for problem solving, Eds. J.C.Riviere and Sverre Myhra, CRC Press, 1998.

[2] SIMS: A Practical Handbook for Depth Profiling and Bulk Impurity Analysis, R.G Wilson, F.A.Stevie and C.W.Magee, John Wiley and Sons NY 1989.

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