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Simultaneous SIMS and electron impact SNMS
– a method for rapid and accurate quantification in complex matrices.

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INTRODUCTION

Secondary Ion Mass Spectrometry (SIMS) and Sputtered Neutral Mass Spectrometry (SNMS) are both surface analysis techniques in which the specimen is bombarded by an ion beam and sputtered particles are detected by a mass spectrometer. The critical difference between the techniques is that the SIMS ions are generated directly by the sputtering process, whereas those detected in SNMS are produced by ionisation of neutral particles some time after leaving the surface. The separation of the sputtering and ionisation events results in a near-constant ionisation probability for each element, irrespective of the material from which it originated [1]. This is in contrast to the well known matrix effect of SIMS [2] where the ionisation probability during sputtering can vary by orders of magnitude, depending on the surface chemistry. The SIMS quantification requirement for matrix matched reference materials is absent from SNMS and easily available alloys may be used for calibration.

The techniques are complimentary in the concentrations that they monitor with SNMS covering 100% to 0.01% atomic concentration and SIMS typically providing quantification in the range 3% to ppb levels.

The aim of this work is to demonstrate that SIMS and SNMS data may be recorded from within the same depth profile in a quasi-simultaneous way such that the SNMS may be used to quantify the matrix composition at each point which can in turn be use to provide accurate quantification of the impurity by application of the SIMS RSF relevant to the instantaneous alloy composition.

Hiden SIMS Workstation

SIMS MODE

- Positive or negative ions extracted by extractor and target potential.
- High energy ions and neutrals rejected by electrostatic bend.
- Filament may be turned on but bias prevents electrons from entering ioniser

QUANTIFICATION

- Signals vary non-linearly with matrix composition, often over orders of magnitude
- Accurate quantification when impurity (dopant) is dilute in uniform matrix <3 atomic%.
- Requires reference material with same matrix-impurity combination
- Detection limits to ppm or ppb levels
- Quantification at interfaces not accurate.

Analysis with SNMS ioniser on

MAXIM Spectrometer

IG20 gas Ion Gun

IG-5C Cs Ion Gun

SNMS MODE

- Electrons from filament populate the ioniser cage – user defined energy of 4eV to 100eV.
- Target potential and front deflector plate reject majority of SIMS signal over a wide energy range.
- Electrostatic bend selects sputtered ions with significant energy (10eV) from those formed in the residual gas
- Tuneable electron energy means ionisation (appearance) energy may be used to distinguish RGA and ESD signals

QUANTIFICATION

- Sputtering and ionisation separated – minimal matrix effect.
- Sensitivity is constant and independent of sample chemistry, therefore reference may be any suitable alloy or sample
- Detection range typically 0.1 to 100 atomic%
- SNMS signals vary linearly with composition
- Molecular interference dramatically lower than with SIMS.
- Depth resolution is noticeably better [2], quantification across interfaces is possible.

Mass Interference 28Si 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.

In the analysis shown here, 19V was employed in order to remove the CO interference

Linearity of quantification

A comparison of Ge fraction measured by RBS and SNMS shows SNMS to be linear

Rejection of SIMS Ions

To utilize the high dynamic range of SNMS requires efficient rejection of sputtered ions (which are emitted with an extremely wide energy range). The plot demonstrates that although some ions break through they represent a very small proportion.

Example of SNMS ion detection for ^{107}Ag bombarded by 500nA Ar

A - SNMS signal from ^{107}Ag sample
B – filament off <0.3% of the detected signal is due to secondary ions
C – Ion gun off background signal from residual gas
D – Filament and Ion gun off, no background signals.

Combining SIMS and SNMS in the same analysis

The similarity of instrumentation for SIMS and electron impact SNMS makes simultaneous combination of the two techniques a natural, but rare, development [3]. The Hiden MASsoft spectrometer control software provides an extremely flexible flowchart style control of the relevant voltages permitting SNMS and SIMS conditions to be swapped in approx 500ms and making it realistic to collect both sets of data within the same depth profile analysis. During SNMS analysis, the bias of the ioniser cage is typically 0V (with the filament being suitably biased to achieve the required electron energy). When switching to SIMS mode, the cage becomes negatively biased (reducing the electron population in the ioniser and acting as an extractor for positive ions) but the filament is left on such that thermal stability and filament condition is maintained.

The sample used in this example has a graded SiGe layer of approx 15% Ge peak concentration and includes boron doping. Analysis was undertaken using 500nA, 5 keV oxygen primary ions bombarding at 45° in order to provide a good sensitivity for the boron. The analysed area was an approximately 600μm square with a central electronic gate.

SNMS quantification is essentially very simple as the signals are directly proportional to the composition [1], with a constant of proportionality (sensitivity factor) determined from a single SiGe reference sample (33% Ge).

It should be noted that, as the sum of all signals relates directly to the amount of material sputtered, relative sputter rate may also be determined at every point in the analysis leading to automatic correction of the depth scale.

The boron RSF varies as a function of Ge fraction. Using a curve fitted to the boron RSF as a function of concentration, a point by point quantification may be made across the entire SiGe system. In this case, the RSF was relative to the 30Si SIMS signal, but it can, of course, also be made relative to the SIMS or SNMS signals of Ge or the sum of Si+Ge.

Conclusions

- Combined SNMS and SIMS detection in the same depth profile analysis has been demonstrated on a simple SiGe structure. However, the method is easily applied to other more complex combinations where simultaneous determination of matrix composition and impurity concentration are required, such as across interfaces.
- SNMS can determine the local matrix composition, and erosion rate, so that correct SIMS RSFs can be applied on a point-by-point basis using a mathematical fit to the change in RSF with composition.
- Additionally, SNMS can provide quantification above the dilute limit where the matrix effect prevents accurate application of SIMS.
- Using a sample with a composition across the detection boundary of the two techniques (0.01 to 3%) permits the SIMS RSF to be determined quickly and easily without manufacture of a special reference material. This is especially important in materials development where sample quantity and local uniformity may be an issue.

References

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