Hidden SIMS

Analytical Secondary Ion Mass Spectrometry Products
Introduction to SIMS

Sputter Erosion of the Specimen

Sputtered Neutrals

-ve Molecules

+ve Ions

+ve Molecules

-Ve Ions

Electrons

COLLISION CASCADING
ALTERED LAYER

Sputter Erosion of the Specimen
Introduction to SIMS

Sputter Erosion of the Specimen

Static SIMS

• Very low ion dose (~1E12 ions cm\(^{-2}\)) gives surface specific measurement.
• Ideal for investigation of contamination, oxidation and monolayer coatings.

Dynamic SIMS

• Higher ion dose erodes surface exposing deeper material.
• Monitoring mass resolved ion signals results in depth profile.
• Ideal for investigation of impurities (dopants) and layer structures.
Introduction to SIMS – sputter erosion of the specimen

Scanning the beam across the sample

• Flat bottom crater

• Imaging – collect data as a function of position

• Gating, only collect data when the beam is in the central flat part of the crater for high dynamic range depth profiles.
Introduction to SIMS

Anatomy of a Depth Profile

- Pre-equilibrium region before bombardment chemistry stabilises
- Usually a log scale due to the very high dynamic range of SIMS
- Signal monitored as a function of time
- Matrix signal provides a reference for quantification and helps confirm validity of data
- Dip in matrix combined with rise in impurity indicates impurity is not dilute
- Sharp decay shows good depth resolution / flat crater / adequate gating
The probability of ion emission is affected greatly by the sample chemistry. As the ion beam species becomes incorporated into the specimen it can be used to modify the surface chemistry and enhance probability of ionised emission.

- Oxygen enhances ionisation of electropositive elements
  - many metals and semiconductor matrix species
- Caesium enhances ionisation of electronegative elements
  - halogens, many contamination species, some metals
- Caesium can also be used to collect secondary ion cluster
  - \((MCs^+)\) of most species \((M)\) at lower sensitivity but better linearity at high concentration.
Introduction to SIMS
Relative Ion Yields - Positive SIMS Oxygen Primary Ions

John Wiley & Sons Inc. NY 1989
Introduction to SIMS
Relative Ion Yields - Negative SIMS Caesium Primary Ions

John Wiley & Sons Inc. NY 1989
### Recommended Primary Ions

<table>
<thead>
<tr>
<th>Element</th>
<th>Ip</th>
<th>Ion</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Cs</td>
<td>H-</td>
<td>2H if implant</td>
</tr>
<tr>
<td>He</td>
<td>O2</td>
<td>He+</td>
<td>No for HeCs+</td>
</tr>
<tr>
<td>Li</td>
<td>O2</td>
<td>Li+</td>
<td></td>
</tr>
<tr>
<td>Be</td>
<td>O2</td>
<td>Be+</td>
<td>HMR in AlGaAs (Al3+)</td>
</tr>
<tr>
<td>B</td>
<td>O2</td>
<td>B+</td>
<td>BSi also works</td>
</tr>
<tr>
<td>C</td>
<td>Cs</td>
<td>C-</td>
<td>CM: can give better DL</td>
</tr>
<tr>
<td>N</td>
<td>Cs</td>
<td>N-</td>
<td>use N-15 if implanting</td>
</tr>
<tr>
<td>O</td>
<td>Cs</td>
<td>O-</td>
<td>use O-18 if implanting</td>
</tr>
<tr>
<td>F</td>
<td>Cs</td>
<td>F-</td>
<td></td>
</tr>
<tr>
<td>Ne</td>
<td>O2</td>
<td>Ne+</td>
<td>or NeCs+</td>
</tr>
<tr>
<td>Na</td>
<td>O2</td>
<td>Na+</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>O2</td>
<td>Mg+</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>O2</td>
<td>Al+</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>Cs</td>
<td>Si-</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>Cs</td>
<td>P-</td>
<td>or P+ with O2 (HMR in Si)</td>
</tr>
<tr>
<td>S</td>
<td>Cs</td>
<td>S+</td>
<td>or S- with O2 (HMR in Si)</td>
</tr>
<tr>
<td>Cl</td>
<td>Cs</td>
<td>Cl-</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>O2</td>
<td>Ar+</td>
<td>or ArCs+</td>
</tr>
<tr>
<td>K</td>
<td>O2</td>
<td>K+</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>O2</td>
<td>Ca+</td>
<td></td>
</tr>
<tr>
<td>Sc</td>
<td>O2</td>
<td>Sc+</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>O2</td>
<td>Ti+</td>
<td>or Ti- with Cs</td>
</tr>
<tr>
<td>V</td>
<td>O2</td>
<td>V+</td>
<td>or V- with Cs</td>
</tr>
<tr>
<td>Cr</td>
<td>O2</td>
<td>Cr+</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>O2</td>
<td>Mn+</td>
<td>or Mn- ion</td>
</tr>
<tr>
<td>Fe</td>
<td>O2</td>
<td>Fe+</td>
<td>HMR in Si. Fe54 for implant</td>
</tr>
<tr>
<td>Co</td>
<td>O2</td>
<td>Co+</td>
<td>HMR in Si</td>
</tr>
<tr>
<td>Ni</td>
<td>O2</td>
<td>Ni+</td>
<td>or Ni- with Cs. HMR in Si</td>
</tr>
<tr>
<td>Cu</td>
<td>O2</td>
<td>Cu+</td>
<td>or Cu- with Cs.</td>
</tr>
<tr>
<td>Zn</td>
<td>O2</td>
<td>Zn+</td>
<td>or ZnCs+</td>
</tr>
<tr>
<td>Ga</td>
<td>O2</td>
<td>Ga+</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>Cs</td>
<td>Ge-</td>
<td>or 70Ge+ with O2</td>
</tr>
<tr>
<td>As</td>
<td>Cs</td>
<td>AsM-</td>
<td>or 75As- HMR in Si</td>
</tr>
<tr>
<td>Se</td>
<td>Cs</td>
<td>Se-</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>Cs</td>
<td>Br-</td>
<td></td>
</tr>
</tbody>
</table>

| Kr      | O2 | Kr+       | or KrCs+ with Cs                           |
| Rb      | O2 | Rb+       |                                            |
| Sr      | O2 | Sr+       |                                            |
| Y       | O2 | Y+        |                                            |
| Zr      | O2 | Zr+       |                                            |
| Nb      | O2 | Nb+       |                                            |
| Mo      | O2 | Mo+       |                                            |
| Ru      | O2 | Ru+       | or Ru- with Cs                             |
| Rh      | O2 | Rh+       | or Rh- with Cs                             |
| Pd      | O2 | Pd+       | or Pd- with Cs                             |
| Ag      | O2 | Ag+       | or Ag- with Cs                             |
| Cd      | O2 | Cd+       | or CdCs+. No Cd- ion                      |
| In      | O2 | In+       |                                            |
| Sn      | O2 | Sn+       | or Sn- with Cs                             |
| Sb      | Cs | Sb-       | or SbM or Sb+ with O2                      |
| Te      | Cs | Te-       |                                            |
| I       | Cs | I-        |                                            |
| Xe      | O2 | Xe+       | or XeCs+                                   |
| Cs      | O2 | Cs+       |                                            |
| Ba      | O2 | Ba+       | HMR in GaAs                                |
| La      | O2 | La+       | all L rare earths as La                    |
| Hf      | O2 | Hf+       | no Hf- ion                                 |
| Ta      | O2 | Ta+       |                                            |
| W       | O2 | W+        |                                            |
| Re      | O2 | Re+       |                                            |
| Os      | Cs | Os+       | or Os- with O2                             |
| Ir      | Cs | Ir-       |                                            |
| Pt      | Cs | Pt-       |                                            |
| Au      | Cs | Au+       |                                            |
| Hg      | O2 | Hg+       | or HgCs+. no Hg-ion                       |
| Ti      | O2 | Ti+       | HMR in GaAs                                |
| Pb      | O2 | Pb+       | HMR in GaAs                                |
| Bi      | Cs | Bi-       | or BiM or Bi+ with O2                      |
| Th      | O2 | Th+       |                                            |
| U       | O2 | U+        |                                            |
**IG20 Gas Ion Gun**

- 1-5 keV, 0.5 µA, 100µm (50µm imaging)
- Reliable, long life, electron impact ion source
- Integral bend to remove neutral particles
- May be used with reactive and inert gases (e.g. H, He, O, N, Ar, Xe, air)
- Differential pumping to preserve chamber UHV
- Bakeable to 250°C
- Mounts on CF35
Hiden SIMS Products – Ion Guns

**IG5C Caesium Ion Gun**

- 1-5 keV, 150nA, 80µm (20µm imaging)
- Miniature low power Cs Ion source (~8W), long life, easy replacement.
- Air stable
- Double bend to remove neutral particles
- Differential pumping to preserve chamber UHV
- Bakeable to 250°C
- Mounts on CF35
Hiden SIMS Products – Ion Guns

Ion Gun Control
PC controlled
Settings can be saved and recalled
Automatic ion source warm up / cool down
EHT ramp rate control
Gun diagnostics
Connect via TCP/IP, USB or serial
Upgradeable software and firmware
Hiden SIMS Products – Spectrometers

MAXIM – High Performance SIMS and SNMS

Easy to change filament for SNMS

Off-axis collection
Hiden SIMS Workstation

- 3D imaging
- Depth profiling
- Static SIMS
- SNMS
- MAXIM SIMS/SNMS
- Oxygen Ion Gun
- Cs Ion Gun
- Electron charge compensation gun
- O$_2$ gas jet
- Loadlock degas heater
- Large area near sample cryotrap
- UHV – bakeable
- Large sample holder
- Normal incidence camera
- Single phase 2500 W
- No compressed air
- Air cooled
- Remote backing pump option
- All dry pumps
Hiden SIMS Workstation – sample mounting

- Samples mount from the underside.
- The upper surface is always in the correct plane for analysis.
- Maximum sample thickness 10mm
- Maximum size to load 40 x 40mm
- Easily customisable sample bar
- Spring clip and screws – no adhesive
- Sample bar carries Faraday cup for beam set-up
- Positive bayonet connection and guidance forks make transfer robust and reliable.
Hiden SIMS Workstation – loadlock sample heater

Infra-red sample heating in loadlock

• High purity heater
• Heating from underside (clean top surface)
• Non-contact infra-red
• Uniform heating

• Degas of adsorbed water vapour and volatile compounds.
• Reduced background of hydrogen, oxygen and carbon.
• Preserves UHV environment.
**SIMS Workstation with XPS**

The SIMS workstation is designed to be customisable and has spare ports for the fitting of other techniques or devices.

Here the instrument is configured for SIMS, SNMS and XPS by addition of the Omicron Argus spectrometer with 128 channel detector and DAR400 dual anode X-ray source.

A rotation drive allows the sample to be positioned at the optimum angle for XPS or to make angularly resolved measurements.

**SIMS Workstation family**

The Hiden SIMS Workstation is a modular instrument. All members of the family are based around the same components so it is easily upgradeable from the basic *Foundation* to the fully configured *Plus* version.
Applications – depth profiling GaAs quantum well structure

Negative secondary ions with 5keV Cs primary ion bombardment

- n-GaAs:Si > 10^{19} \sim 0.1 \mu m
- n-AlGaAs:Si > 10^{18} \sim 0.1 \mu m
- p-AlGaAs:C > 5 \times 10^{19} \sim 0.1 \mu m
- GaAs undoped \sim 0.1 \mu m
- InGaAs QW undoped \sim 6 nm
- GaAs undoped \sim 0, 2 \mu m (buffer layer)
- n-GaAs - substrate

Typical Si detection limit in GaAs 1E17 atoms cm^{-3}
Applications – depth profiling – Ion Implanted reference materials

\[1.0 \times 10^{15} \text{ Mg implant into Si}\]

\[5.0 \times 10^{15} \text{ As implant into Si}\]

24 Mg implant in Si, \(10^{15}\) atoms cm\(^{-2}\) analysed using oxygen primary ions from IG20 ion gun on SIMS Workstation with MAXIM spectrometer.

As implant in Si, \(5 \times 10^{15}\) atoms cm\(^{-2}\) analysed using 5keV Cs\(^+\) primary ions from IG5C ion gun on SIMS Workstation with MAXIM spectrometer.
Depth Profiling – detection limits

Detection limit depends on:

- Ion yield
- Volume of analyte; large volume = better statistics, lower DL, but bigger crater or depth increment
- Background or interfering signals – use energy offset to reduce molecular interference, ensure clean surfaces and good ion beam shape, UHV and cold trap to reduce effect of residual gas species (H, O).
- Use 3D data collection to optimise gating

<table>
<thead>
<tr>
<th>Element</th>
<th>Matrix</th>
<th>Detection limit</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>28 Si</td>
<td>GaAs</td>
<td>8E16</td>
<td>Interference signals from AlH in GaAlAs – 5E17 with background subtraction when possible</td>
</tr>
<tr>
<td>11 B</td>
<td>Si</td>
<td>2E16</td>
<td>Surface boron contamination gives rise to background, ultimate shown in clean silicon sample.</td>
</tr>
<tr>
<td>31 P</td>
<td>Si</td>
<td>7E17</td>
<td>Interference from SiH at mass 31- energy offset and loadlock degas for best result</td>
</tr>
<tr>
<td>2 D</td>
<td>Si</td>
<td>1E18</td>
<td>Subtract contribution from natural H for ultimate DL – use cold trap</td>
</tr>
<tr>
<td>2 D</td>
<td>W</td>
<td>2E18</td>
<td>Subtract contribution from natural H for ultimate DL – use cold trap</td>
</tr>
<tr>
<td>24 Mg</td>
<td>Si</td>
<td>5E16</td>
<td></td>
</tr>
<tr>
<td>75 As</td>
<td>Si</td>
<td>8E16</td>
<td></td>
</tr>
<tr>
<td>9 Be</td>
<td>Si</td>
<td>2E17</td>
<td></td>
</tr>
</tbody>
</table>
Applications – depth profiling

Depth Profiling Neutron Mirror – 80x 3.6nm Period

A Si/Fe, 80-period, neutron mirror was analysed using normally incident 1.5keV O$_2^+$ primary ions (100nA) from the IG20 gas gun and detecting secondary ions with the MAXIM SIMS analyser. Although the layers are not fully resolved, the profile shows the thickness to be highly consistent with no loss of depth resolution with depth.
SNMS (sputtered neutral Mass Spectrometry) – Post Ionisation

The generation of ions during sputtering depends very strongly on the chemistry of the sample and primary ion beam and the ion yield can vary non-linearly over orders of magnitude. This ‘matrix effect’ makes quantification of SIMS data difficult when impurities reach high concentration (> 2%) or when the matrix varies. Sputtered Neutral Mass Spectrometry overcomes this problem and permits quantification in this extremely useful range by separating the ionisation from the sputtering.

- Electron impact cell ionises the sputtered neutral material
- Secondary ions deflected from analyser
- Separating the sputter and ionisation events removes most of the SIMS matrix effect
- Easily quantifies large changes in matrix material
- Detection limit typically <0.1 atomic%
- Excellent for alloy multilayers
- No requirement for matrix matched reference materials
- Neutral species are unaffected by surface charging
The MAXIM SIMS/SNMS spectrometer has an electron impact ion source fitted close to its entrance. An external deflector plate removes the secondary ions (which generally constitute less than 1% of the sputtered flux) and allows the neutrals to enter the ioniser. Once ionised, the neutrals follow the same path that SIMS ions would have taken.
The ability to control the electron impact energy enables some mass interferences to be easily overcome using the ion appearance energy.

For example, CO (mass 28) is a common residual gas constituent and could interfere with the detection of the major isotope of silicon. However, careful choice of the electron energy resolves this problem.

Reducing the electron energy to below 19V prevents ionisation of residual CO, confirmed here by noting the lack of signal with the sputter gun off (red) so with the gun on (blue) the detected signal is from silicon only.
SNMS – Magnetic Storage Materials

SNMS depth profile of NiCr/Cu/NiFe disk head layer structure, primary ions 5 keV Ar from IG20 ion gun.
Control of surface topography during sputtering – Oxygen jet

Low energy beams give improved depth resolution but can also induce surface topography.

Fully oxidising the surface using the jet maintains a planar surface and preserves depth resolution.

The jet provides a locally high pressure of pure oxygen over the sample.

2 keV 100nA ion beams at 45°. Target 3.6nm Si/Fe multilayer
After a period of intense engine running, a hard, stain like, deposit was observed on a fuel injector component.

EDX (energy dispersive X-ray) analysis in the SEM was inconclusive as the thin nature of the deposit meant that most of the excited volume was in the underlying metal.
Static SIMS – Contamination on Diesel Injector

$^{56}$Fe SIMS images of the defective region. The right hand image shows detail in the position of the arrow, where something is blocking the iron signal from the steel. The very bright region is caused by ions being directed into the spectrometer by the angled face.
The localised mass spectrum from the defect is dominated by Ca.

The defect is Ca based and it is suggested that this is due to a bio-diesel catalytic production step. This known possible fuel contaminant is limited by EU regulations to 5mg/kg (summed with the Mg content).
New Hiden SIMS Software suite

Philosophy

• Collect all data as images in order to optimise the efficient use of sample material and time by allowing gating and inspection after collection.

• Aim to make it simple, reliable and safe for the inexperienced operator to obtain depth profiles whilst retaining the flexibility that enables expert user develop new protocols and have full control over every aspect of the instrument.
Control of the overall experiment and connection to the mass spectrometer
Mass for analysis is chosen from a periodic table and can include molecules and multiply charged species. Experienced users can also input data directly.
An integral interference calculator identifies possible mass interferences and suggests relative signal intensities.
Global Scan Editor

The image resolution is chosen and any stopping criteria set.

The depth profile can be set to terminate automatically when the set criteria is reached - such as an interface, time or signal level.
Parameters can be set for each mass, typically a target bias offset is used to differentiate molecular and atomic species.

The parameters list has three levels of access and complexity.
The experiment flow shown here has three channels (Si, Ge and B).

Species can be selected or deselected for analysis – this allows a non-expert user to control a range of experiments from a single template.
During analysis the live acquisition window displays the signal so that the progress of the experiment can be monitored and surface features observed.
During analysis the analysis window displays the depth profile, image data and a 3D representation of the distribution. It also controls the electronic gating.
The electronic gate can be optimised independently and interactively for each mass and does not have to be concentric or square.
The video shows the mass resolved aluminium signal arising from aluminium oxide grit particles embedded in the work-piece after a grinding operation. Volume is 800µm square x 35 µm deep.
Case Study – Glass Coating (low-e glass)

Low emissivity glass is installed in buildings to increase energy efficiency. In cold weather it reflects heat back into the building – reducing heating costs; in hot weather it reflects heat from the external environment reducing heat build-up within and lessening required air conditioning capacity.

This is achieved, primarily, through the inclusion of a sputter deposited (typically 10nm thick) metallic silver layer within a sandwich of protective oxides.

Surrounding layers may be chosen to impart a particular colour to the glass but ideally white light should pass through so that colours are rendered correctly within the building.
Case Study – Glass Coating (low-e glass)

Low Emissivity Architectural Glass

- Light is transmitted
- Heat is reflected
- Protective metal oxides
- Total thickness ~100nm
- Silver
Case Study – Glass Coating (low-e glass)

SIMS can provide analysis of glass layers for:

- Failure analysis, identification of defects, impurities and contamination
- Characterisation of processes
- Reverse engineering
Case Study – Glass Coating (low-e glass)

The diagram shows a typical low-e stack where the active silver layer is protected by a mixture of metal oxide layers.
The SIMS depth profile was collected using 5keV Ar ions focused to an 80µm spot and rastered over an area of 400 x 550µm. Positive secondary ions were collected and a 500eV electron flood was employed to prevent surface charging.
Case Study – Glass Coating (low-e glass)

Beginning at the exposed surface, the first layer is extremely thin and is partly consumed by the pre-equilibrium region at the start of the analysis. However, zinc and tin signals are clearly present at the very surface. There is a high silicon signal (rising to a level almost of that in the glass substrate) suggesting that a thin SiO₂ layer may exist in the vicinity of the ZnSnOₓ.

The silicon nitride layer is characterised by a uniform concentration of silicon, however, this layer also contains aluminium, estimated to be ~7% (atomic).

Beneath the SiN layer lies a similar thickness if AlN. Interestingly, throughout this layer the Cr signal is rising, albeit from three orders of magnitude below the eventual peak. SIMS is perfectly suited to the investigation of this type of low concentration feature and for the analysis presented here it was necessary to significantly reduce the sensitivity to ensure that the peak of the Cr signal did not saturate the detector.

The region below the AlN contains the thin silver layer and its associated thin protective barrier layers containing Zn, Al, O Ni and Cr. The design thickness of the NiCrOₓ layer is only 1 nm and there has been some mixing of this into the silver layer during analysis.

Immediately below the silver, the thin Zn and ZnSnO layers are visible, before the final AlN layer and the glass substrate.
Case Study – Glass Coating (low-e glass)

Such a profile is very complex to quantify, however, by comparing similar profiles from different parts of the glass pane it is possible to investigate abnormalities.

Here the silver and oxygen signals from left and right hand sides are overlaid, showing no difference.
When the Cr signals from the left (L), middle (M) and right (R) hand sides are overlaid it becomes immediately apparent that the right hand edge is deficient in Cr.

It should be noted that the NiCr layer is expected to be only about 1 nm thick and so this represents a very sensitive analysis.
Quadrupole Mass Spectrometers for Advanced Science

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