Application of TOF-SIMS and LEIS for the Characterization of Ultra-thin Films

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TOF-SIMS Technique

Characteristics

- **General**
  - Detection of elements and molecules → detailed chemical information
  - Parallel detection of all masses

- **Thin film analysis**
  - $O_2$ and Cs sputter depth profiling in dual beam mode
  - Depth resolution < 1 nm
  - Detection limit $1E16$ atoms/cm$^3$

- **Problems in ultra-thin film analysis**
  - Quantification (complex systems)
  - Need for reactive species implantation (transient effects in sputter yield and ionisation over first several nm)
  - Information depth 1 – 3 monolayers
Detection limits at surface

High mass resolution and sensitivity

- Detection of all elements
- High mass resolution: $\Delta M/M > 12,000$
- High sensitivity
  - $< 1$ ppm of 1 ML
  - $5E7$ to $1E9$ atoms/cm$^2$
Shallow implants

Routine analysis with TOF-SIMS

- high dynamic range (> 1E5)
- good detection limits
- high speed analysis
- reliable quantification
- < 0.5 % RSD reproducibility
- high throughput, unattended operation

Very high dose → dilute limit?
Shallow implants

Reproducibility

Example:
- 33 profiles of 1E16 at/cm$^2$ As implanted in Si
- one automated run
Shallow implants

Reproducibility

Example:
- 33 profiles of 1E16 at/cm² As implanted in Si
- one automated run

![Graph showing dose per position and average dose per sample with RSD: 0.09%](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Detection Limit (at/cm³)</th>
<th>Reproducibility (RSD)</th>
<th>Sputter Rate @ 500 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>6E15</td>
<td>&lt; 0.5 %</td>
<td>3.3 nm/min</td>
</tr>
<tr>
<td>P</td>
<td>2E16</td>
<td>&lt; 0.5 %</td>
<td>4.1 nm/min</td>
</tr>
<tr>
<td>As</td>
<td>1E16</td>
<td>&lt; 0.5 %</td>
<td>4.1 nm/min</td>
</tr>
</tbody>
</table>
LEIS Technique

Features of Low Energy Ion Scattering (LEIS)

- Energy of projectiles: 1…8 keV
- Energy of scattered particles yields mass of target atom
- Intensity of scattered ions directly proportional to surface coverage
- Ultra-high surface sensitivity – top atomic layer analysis
- Detection limits:
  - Li - O \( \geq 1 \% \) of 1 ML
  - F - Cl \( 1 \% - 0.05 \% \) of 1 ML
  - K - U \( 500 \) ppm - \( 10 \) ppm of 1 ML

\( ^3\text{He}^+, \, ^4\text{He}^+, \, \text{Ne}^+, \, \text{Ar}^+, \, \text{Kr}^+ \)
In spinels of type $\text{AB}_2\text{O}_4$ the ions of A are in tetrahedral sites below the surface.

- LEIS spectra of ZnO and ZnAl$_2$O$_4$ (spinel)

Zn not detected at the surface, but directly below!
LEIS Technique

Design of LEIS Instrument

- Dedicated high sensitivity LEIS analyzer
  - scattering angle 145 ±1 degrees
  - integration over all azimuths
  - parallel energy detection
- Limitations in conventional LEIS / ISS instruments
  - low sensitivity (destructive technique)
  - mass resolution not sufficient
LEIS Technique

Sputter depth profiling in dual beam mode

- Sputter depth profiling in dual beam mode
  - LEIS analysis while sputtering with low energy noble gas ions (Ar, Xe)

- Static depth profiling
  - scattering energy is specific for sample atom
  - additional energy loss on the way through the sample
    → in-depth distribution visible in spectrum
      under appropriate surface conditions (similar to MEIS and RBS)
LEIS spectra taken after an increasing number of ALD cycles of WN$_x$C$_y$ on silicon
Spectroscopy and Static Depth Profiling

ZrO$_2$ Atomic Layer Deposition on Silicon

- no matrix effect
- easy calibration / quantification for a two component system
Spectroscopy and Static Depth Profiling

Diffusion Study in Mo/Si layers

- 10 nm Mo/1.6 nm B₄C/5 nm Si
- Annealing @ 660°C
- Formation of MoSi₂ by extensive diffusion

![Graph showing intensity vs. energy with peaks labeled for O, Si, and Mo surfaces.]

Spectroscopy and Static Depth Profiling

Diffusion Study in Mo/Si layers

- 10 nm Mo/1.6 nm B\textsubscript{4}C/5 nm Si
- Depth scale from variation of Si layer thickness

![Graph showing intensity vs. energy](image)

Mo surface peak position: 240 eV

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de Rooij-Lohmann et al., 
Spectroscopy and Static Depth Profiling

Diffusion Study in Mo/Si layers

- 10 nm Mo/1.6 nm B₄C/5 nm Si, annealing @ 500 °C
- Diffusion coefficient without B₄C: \((8 \pm 2) \cdot 10^{-20} \text{ m}^2/\text{s}\)
  with 1.6 nm B₄C: \((4 \pm 1) \cdot 10^{-21} \text{ m}^2/\text{s}\)

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ALD Studies

Principle of Atomic Layer Deposition

Atomic Layer Deposition used for
- diffusion barriers
- high-k dielectrics (gate stack, DRAM capacitors)
- new applications are being developed (not only semiconductor!)

Example:
Al$_2$O$_3$ growth using TMAI and H$_2$O

Questions:
- nucleation phase
- growth per cycle
- homogeneity, conformity of films, pinholes
ALD Studies

TOF-SIMS Analysis of Ta (SiN) Film on Si

TOF-SIMS dual beam profiling:
Bi analysis and 500 eV O2 sputtering at 45°
**ALD Studies**

**LEIS Analysis of Ta (SiN) Film on Si**

**LEIS static analysis**

He, 3 keV, 0°

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**Simplified quantification:**

Assume Ta and Si to be the only species at surface

(Ta + Si = 100%)
ALD Studies

LEIS Analysis of Ta (SiN) Film on Si

Separation of surface composition and depth information

Subtraction of sub-monolayer surface peak after appropriate scaling

Scale 1 cycle spectrum to fit high energy side

Subtract 1 cycle spectrum
In-depth signal shows:
- nucleation behaviour
- layer closure
- possible intermixing with substrate
**ALD Studies**

**LEIS Analysis of Ta (SiN) Film on Si**

**In-depth signal shows**
- nucleation behaviour
- layer closure
- possible intermixing with substrate
- initial change in growth rate

![Graph showing thickness vs. number of ALD cycles](image)

- **red line**: minimum thickness
- **blue line**: maximum thickness

Number of ALD cycles: 0 to 30

Thickness (nm): 0 to 12
LEIS depth profiling in static mode combined with sputtering

- Sample with 10 cycle
- Analysis with 3 keV He scattering after each 500 eV Ar sputter cycle
LEIS Analysis of Ta (SiN) Film on Si

**LEIS depth profiling in static mode combined with sputtering**

- Sample after 10 cycles
- Analysis with 3 keV He scattering after each 500 eV Ar sputter cycle
Ultra-Shallow Implants

As Implant Profiling by TOF-SIMS

**Implant technology trend**
- significant reduction of implant energy
- peak concentrations close to the surface
- concentrations above dilute limit
→ quantification near the surface becomes very important

![Graph showing Si, SiAs, and As implant profiles](sample provided by IHP Frankfurt (Oder), Germany)
Ultra-Shallow Implants

As Implant Profiling by TOF-SIMS

Example: As implant 2 keV, 1E15 atoms/cm²
- analysis: 15 keV Bi
- sputtering: 500 eV Cs, 45°

Quantification
Point-to-point normalization

Variety of protocols has been tested by the SIMS community, but:
- depth scale on the first 3 - 5 nm is inaccurate (surface shift > 1 nm)
- concentration near the surface is inaccurate (poor agreement with simulations)
- implant dose for very shallow implants is inaccurate
Ultra-Shallow Implants

As Implant Profiling by TOF-SIMS

Schematic

Ultra-shallow implant with thin oxide

Problems in SIMS quantification
- matrix transition at SiO₂/Si interface (influence of O concentration)
- strong changes of ion yields by Cs (surface transient, interface)
- changes of sputter rate in transient and at interface (surface shift)
- change of concentration of Si (reference for p-to-p normalization)

Transient width $z_{tr} \approx 2 \times$ projected range
Ultra-Shallow Implants

Fundamental Studies by LEIS - Cs sputter depth profiling

**LEIS depth profiling in dual beam mode**
- analysis: 3 keV He
- sputtering: 500 eV Cs, 60°

**Cs sputtering of thin oxides**
- strong variation of Cs concentration in the oxide layer (implantation of Cs)
- significant reduction of the Cs concentration at the interface
- interface width significantly different for As implant sample
Ultra-Shallow Implants

As Implant Profiling by LEIS - sputter depth profiling

**LEIS depth profiling in dual beam mode**
- analysis: 3 keV He
- sputtering: 1 keV Ar, 60°
- sample: 2 keV As implant, 1E15 /cm²

**Results:**
- oxide thickness approx. 1.9 nm
- As concentration at the surface is very low → confirmed by LEIS spectra
- simplified quantification: As + Si = 100 %
Ultra-Shallow Implants

As Implant Profiling by LEIS - sputter depth profiling

**LEIS depth profiling in dual beam mode**
- analysis: 3 keV He
- sputtering: 1 keV Ar, 60°
- sample: 2 keV As implant, 1E15 /cm²

**Results:**
- oxide thickness approx. 1.9 nm
- As concentration at the surface is very low → confirmed by LEIS spectra
- simplified quantification: As + Si = 100 %
- implant maximum approx. 1.3 nm deeper compared to SIMS
TOF-SIMS and LEIS are complementary techniques. Combination of the two techniques is very powerful for the analysis of ultra-thin layers (< 5 nm).

<table>
<thead>
<tr>
<th></th>
<th>LEIS</th>
<th>TOF-SIMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Information Depth</td>
<td>1 monolayer</td>
<td>1 – 3 monolayers (even larger for organics)</td>
</tr>
<tr>
<td>Detection Limit</td>
<td>10 – 1,000 ppm</td>
<td>0.1 – 100 ppm</td>
</tr>
<tr>
<td>Mass Resolution</td>
<td>&lt; 100</td>
<td>10,000</td>
</tr>
<tr>
<td>Type of Information</td>
<td>elemental</td>
<td>elemental, molecular</td>
</tr>
<tr>
<td>Quantification</td>
<td>simple (including major constituents)</td>
<td>difficult (matrix effects, trace constituents only)</td>
</tr>
<tr>
<td>Depth Profiling</td>
<td>static, noble gas sputtering</td>
<td>by sputtering with reactive ions</td>
</tr>
</tbody>
</table>

Thank you very much for your attention!