Use of Secondary Ion Mass Spectrometry as a thin film characterization tool

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Eurofins EAG
• EAG founded by Charles Evans 42 years ago
• Purchased by Eurofins almost 2 years ago
• Eurofins
  – Started in 1987 with four people testing wine
  – 45,000 staff and 800 laboratories
  – Eurofins EAG
Overview of talk

• Introduction to Secondary Ion Mass Spectroscopy (SIMS)
  – Instrumentation
  – Fundamental physics
• Introduction to thin film characterization
  – SiON gate oxide
  – ALD thin films
• Why does SIMS characterization add value
• What are the requirements for analysis
• External calibration possibilities
Analytical Resolution vs. Detection Limit
Comparing Analytical Techniques

Depth of Analysis

![Comparison of Analytical Techniques and Depth of Analysis](image-url)
SIMS Key Applications

• Typical applications include
  – Trace element profiles
  – Major element profiles
  – Survey element profiles
  – Layer structure
• Typical Materials analyzed
  – Semiconductors
  – Dielectrics
  – Metals
  – Polymers
SIMS Technique

ION SOURCE — Sample

MASS SPECTROMETER

DETECTOR

Extraction

Mass Spectra

Most Common

Depth Profile

Image
Si cap layer

SiGe ramp: B doped

SiGeC

Si Substrate
Basic Sputter Process in SIMS

Primary ions (~keV)

Sample atoms

Absorbed molecules

Sputtering event

Sputtered atoms

Secondary ions

Desorbed molecular ions

Escape range (~10 Å)

Mixing range (~100 Å)
Gate oxide analysis

Oxide thickness, N areal density, F dopant

N: 9.5E14 atoms/cm²
O: 1.59nm
Thin film depth resolution

Difference between samples on the order of one atom layer

Sample 1: oxide has grown on SiN
Sample 2: oxide has grown below SiN
SIMS Quantification: Effect of Element

- Secondary ion yields can change by 6 orders of magnitude or more!
- We cannot calculate or predict ion yields (many have tried and failed)
- Ion yields depend strongly on the analysis element

Positive Ion Yields in Silicon
SIMS Quantification: Effect of Matrix

- Ion yields depend just as strongly on the sample Matrix.
- Arsenic implanted into silicon shows the familiar implant profile shape.
- The same implant into SiO$_2$ on Si looks dramatically different.
- The reason? The ion yield for arsenic in oxide is MUCH different.
Composition of AlGaAs

Concentrations are within ±5% of the RBS measurement.

Graph showing the composition of AlGaAs with Al and Ga concentrations plotted against depth.
VCSEL active region

- Aperture composition
- Cladding %Al gradient
- Diffused doping in MQW
- Cladding dopant concentration

C, Si CONCENTRATION (atoms/cc)

Al, Ga CONCENTRATION (group III atom fraction)
• Case of dopants in semiconductor we use PCOR-SIMS to calibrate in layers of varying composition. Examples include SiGe, AlGaAs, InGaAs.

• Case of contaminants in metal or dielectric stacks – ion yield changes may not be corrected.

1. Calibrated using XXX standards, calibration in other layers may have 2x error
2. No sputter rate change with composition applied
3. Profile tails may be compromised by morphology / roughness
• Common ALD metallization stack consists of a conductor and barrier layer
• SIMS can measure the composition and distribution within the stack - interdiffusion
• Requirement for SIMS is to measure the effectiveness of barrier layer
• Front-side SIMS can result in artifacts which distort the real profile
• Analysis from back-side can yield improved depth resolution
**Sample structure**

- Ti
- SiO2
- Si

**Backside thinning**

- Ti
- SiO2
- Si

**Graph**

- X-axis: Depth (microns)
- Y-axis: Concentration (atoms/cc)
- YT-axis: Counts Per Second

**Chart**

- Ti (front side)
- Ti (backside)
- O->

**Bar chart**

- Si/Mid-Porous low-K/TiN
• **Cu in SiO$_2$:**
  
  – Diffusion of copper into dielectric (SiO$_2$) can be seen in this backside profile and we know it is real
  
  – No evidence of copper diffusion into the silicon substrate is seen
  
  – A barrier layer is required to prevent copper diffusion into SiO$_2$
- Compare and contrast XPS and SIMS
- Strength and weakness of XPS
- Introduce RBS and an supporting partner to SIMS
XPS Process

X-ray penetration depth (several microns)

Sample

Photoelectrons characteristic of sample surface

Photoelectron escape depth (~100Å or less)
XPS depth profile

X-ray Induced Secondary Electron Image

Sputter rate ~20Å/min

Atomic Concentration (%)

Fe2p3

O1s

Cr2p3

Ni2p3

Sputter Time (min)
SIMS Profile of Thin Oxide Film

Sample 1: oxide has grown on SiN
Sample 2: oxide has grown below SiN
Limitations of XPS Depth Profile

- Cannot quantify hydrogen
- Depth resolution is not as good as SIMS, 3nm versus 0.5nm
- Detection limit is not as good SIMS, 1000ppm versus 1ppm
- Dynamic range is not as good as SIMS, 2 decades versus 5
- Preferential sputtering introduces calibration error
• MeV ions from an electrostatic accelerator are focused on a sample in a vacuum chamber for analysis
• Typically, 2.2 MeV He$^{2+}$ ions are used (α particles)
Accelerator Based Techniques
Scattering Yields and Energies

\[ E = \left( \frac{m - 4}{m + 4} \right)^2 E_{in} \]

\[ \sigma_{rel} = \left( \frac{Z_x}{Z_{Bi}} \right)^2 \]

\( \sigma = \) scattering cross section

\( Z = \) atomic number
Effects of RBS Scattering Geometry

- Atoms scattered directly backwards out of the sample undergo the minimum energy loss versus depth.
- Atoms escaping nearly tangent to the sample surface undergo a much larger energy loss versus depth.
- This difference can be used to optimize RBS depth resolution.
- Can also be used to resolve ambiguities from data acquired at a single angle.
Limitations of RBS

- Films should be greater than 10nm
- Elements with similar Z cannot be separated
- Stack structure should be modeled prior to analysis
- Low Z elements (C, N, O, F) may not be resolved
- Depth resolution not as good as SIMS
- Low Z elements better by SIMS
Conclusion

• XPS analysis of thin films is easy, if not always accurate
• SIMS analysis of thin films is not easy, but adds value because:
  – better depth resolution than many techniques
  – dynamic range and detection sensitivity allow for measurement of composition and contamination
• Calibration from other techniques can enhance SIMS accuracy