Unique opportunities for new insight in the outer surfaces and interfaces by High Sensitivity Low Energy Ion Scattering (HS-LEIS)

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March 23, 2011
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Outline

- **Introduction**

- **Principles and features of LEIS**
  - 1st atom, In – depth (0 – 10 nm), quantitative

- **Applications**
  - Organics (surface modification, anti-wetting, SAMs)
  - Catalysts (mixed oxides, coke, NP’s, oxid. states)
  - Ceramics (SOFC, membranes)
  - ALD growth (high-k, inter-diffusion)
  - and many more ......
Why High-Sensitivity LEIS?

CONTROL at the ATOMIC LEVEL

requires

QUANTITATIVE ANALYSIS at the ATOMIC LEVEL
Low Energy Ion Scattering

Analytical Capabilities

\[ E_f = f(M_0, M_1, M_2, \theta) \times E_i \]

- Atomic composition of the outermost atomic layer
- Energy 1 – 8 keV
- Lateral resolution 0.01 – 1 mm
- Static in-depth (0 – 10 nm)
- Quantitative !!
- No matrix effects

\begin{itemize}
  \item \( ^3\text{He}^+, \ ^4\text{He}^+, \text{Ne}^+, \text{Ar}^+ \)
  \item \( E_f \) vs. Energy spectrum of an alloy
  \item \( \text{Energy } 1 – 8 \text{ keV} \)
  \item \( \text{Lateral resolution } 0.01 – 1 \text{ mm} \)
  \item \( \text{Static in-depth } (0 – 10 \text{ nm}) \)
  \item \( \text{Quantitative !!} \)
  \item \( \text{No matrix effects} \)
\end{itemize}
Conventional LEIS vs HS - LEIS

Pd / Pt-C (1000 m²/g)

Conventional

4He 10,000 nC

High-Sensitivity LEIS

4He 5.4 nC

Promoters visible, but removed
Qtac : Unique new Analyser
High – Sensitivity LEIS

Energy image:
- parallel energy detection
- only low dose needed

STATIC LEIS

“ Analysis before Damage ”
(Molecular Dynamics simulation)

“ Hit same place only once “

ToF filtering eliminates SIMS ions
HS-LEIS: Principles and Key Features

- Analysis before damage (static)
- 1st Monolayer
- Quantitative (peak concentration / coverage)
- Sensitivity
- Mass resolution
- ToF-filtered LEIS
- Imaging

In-depth: Static (0 – 6 nm) or with sputtering
LEIS and SIMS

Time resolved: LEIS analysis *before* damage!
Quantification

Review:
Quantification

Bromine adsorption on Tungsten

\[ \theta_W + \theta_{Br} = 1 \]

No matrix effect!

1st atom

Simple interpretation!!

\[ \theta = \text{fraction 1st atom layer} \]

\[ \theta_W = 1 \]

\[ \theta_{Br} = 1 \]
Bulk Composition  $\text{Ag}_{80}\text{Al}_{20}$

Surface Composition  $\text{Ag}_{66}\text{Al}_{34}$

( independent of primary energy )

NO matrix effects
Rough silica: 50 – 380 m$^2$/g

HS-LEIS: Insensitive to roughness

LEIS Signals:
rough silica about 77%
of flat silica (quartz)

Monolayer sensitivity

**LEIS** 1st atom and in-depth; quantitative, sensitive

**SIMS** not quantitative for near-surface / interface

**XPS** average over 3 – 10 nm; chemical info
Elemental mapping by LEIS and SE Image
Solder bumps

SE image

100 µm

Ti

Sn

Pb
Depth info for

Ultra thin layers and interfaces
Two possibilities:

1. Static LEIS + sputter depth profiling with dual ion beam
   (advantage of quantification, depth resolution LEIS)

2. Static LEIS
   (analogous to RBS and MEIS, but better depth resolution)
3 keV He$^+$

$\Delta E \approx 160$ eV/nm

Depth resolution better for lower primary E!
1st atom and Static Depth Profile

ZrO$_2$ Atomic Layer Deposition on Silicon

- Closure / quantification pinholes (still present after 70 cycles)
- Thickness distribution ZrO$_2$ layer (160 eV/nm)
- No matrix effect
- Example: calibration / quantification for a 2 component system
In LEIS only backscattered ions are detected

**Peaks:** Ions backscattered from 1\textsuperscript{st} atom. 
(*one well-defined collision*)

**Tails:** Backscattering in deeper layers + reionization 
(Scattering by oxygen atoms: efficient reionization)

**Shape:** $f$ (in-depth distribution Zr)

**Intensity:** $f$ (oxygen concentration in 1\textsuperscript{st} atomic layer)
LEIS Technique
Features of Low Energy Ion Scattering (LEIS)

LEIS Features

Ultra-high surface sensitivity, top atomic layer analysis

Static depth profiling information (up to 10 nm)

Reliable and straight-forward quantification

Detection of all elements > He

Detection limits:

- Li - O ≥ 1 % of 1 ML
- F - Cl 1 % - 0.05 % of 1 ML
- K - U 500 ppm - 10 ppm of 1 ML

He\(^+\), Ne\(^+\), Ar\(^+\), Kr\(^+\)
1 - 8 keV
Sample Treatment
Atom Source for Surface Cleaning

O₂ or H₂

- O atoms remove organics, coke
- Chemical energy: no sputtering

CₓHᵧOᵢ

Sample
Organics

- Surface segregation
  - Dendrimers
- Antiwetting
- Surface modification
- Metal / polymer interface
- SAMs
Polymers, SAMs, ...

- Inter - molecular segregation
  - Segregation impurities, additives (0.1 s - days - ..; up to $10^8$ x !!)

- Intra - molecular segregation (0.1 s - days - ..)
  - Aging plasma oxidized PE

- Anti - wetting layers

- Metal diffusion in polymers

- SAM’s
Acrylonitrile-Butadiene-Styrene (ABS)

Surface segregation of additives
During evaporation of barium on PPV, most of the Ba diffuses into the PPV.

Compare the peak shape of a sub-monolayer of Ba (blue) with the actual peak (red).

Peak shape ↔ depth distribution

**PLED:** higher light output for narrow depth distribution
High-energy edge of SAMs on Au

Fluorinated thiol on dirty Au surface

Fluorinated thiol on clean Au surface

Overlayer thickness

Energy (eV)

Normalised intensity (Cts/nC)
Aging of plasma oxidized HDPE

- Aging (LEIS) faster than aging (XPS)!
- “Straight line” → diffusion process
Selection of examples:

- Pt/Au
- Mixed oxides
- γ-alumina
- Poison (Coke on TWC)
- Poison (oxygen membranes, SOFC)
- Use of probe molecules
- NP’s, core/shell
- Oxidation state 1st atom
The atomic composition of the 1\textsuperscript{st} atom layer controls catalysis.

In a spinel (\(AB_2O_4\)) only the B-cations (octahedral site) are \textit{catalytically active and visible} for LEIS (1\textsuperscript{st} at.).

The A-cations (tetrahedral sites) are in 2\textsuperscript{nd} layer (not active, no LEIS peak).

\[Co_3O_4 = CoCo_2O_4\]

Test reaction:
only Co catalytically active

\[Co \text{ signals:}\]
\[\text{XPS: } 1:2:3\]
\[\text{LEIS: } 0.3:1.9:2.0\]
Fuel Cells and Membranes

Importance of the outer surface

- Performance relies on oxygen transport
- Performance: “Hampered by the surface”
- Why? What is the surface??

For $T > 700 \, ^\circ C$:  No Y, Zr in 1$^{st}$ atom!

XPS: Ca not visible (↔ Zr)

Calcination for 5 hours at 1000$^\circ$C in an oxygen flow of 1.5 bar.

Segregation of monolayer of impurities
Fuel Cells

CaO coverage blocks $^{16}$O – $^{18}$O exchange

Fuel Cells

CaO coverage blocks $^{16}\text{O} - ^{18}\text{O}$ exchange

Cold start: 50% loss of Pt signal — sintering or coke formation?
Room temperature oxidation with atomic oxygen gives complete recovery of Pt signal loss is due to coke.

Detection of C with “any” surface technique.
But: WHERE is the coke?!

LEIS determines which fraction of Pt is covered by coke!

Applications:
- Number of Pt atoms available for catalysis.
  Quality control of catalysts!
- Detection of nucleation site for coke (active phase, support, binder, ...)

TEM:
- excellent catalyst characterisation
- detailed info, but local
- contrast required (high Z cluster on low Z support)

Chemisorption:
- requires known probe / surface interaction

HS - LEIS:
- new technique; any material; clusters: 1 atom - 10 nm

Comparison: Richard A. P. Smith (J&M), ECASIA 2009
Important / unique applications for catalysis

4. Nanoclusters

- Average diameter nanoclusters
- Surface segregation in alloy clusters
- Core/shell particles
  (verification, closure, thickness shell)

**Example:** Three-Way catalyst (exhaust)

Pt clusters on CeO$_2$/ …../ γ-alumina

Loading = 0.004 g Pt / γ-alumina

Cluster diameter: 1.6 nm (average)

Accurate for d < 10 nm

The diameter is derived from the ratio of the bulk loading (volume) to the LEIS signal (surface area)

*This method is possible where TEM fails* (d ≤ 2 nm; high Z support)
Strong Zn(O) segregation
Zn(O) on top of Cu is thermodynamically favorable
Oxidation states Cu and Zn in outer surface?
LEIS + chemical titration!

**XPS:**
Oxidation states, **BUT** averaged over 10 – 20 atomic layers.

**LEIS:**
Elemental composition outer atomic layer, **BUT** no chemical info
Oxidation of metallic Cu, Zn gives shielding by oxygen.
Signal decrease: factor 5 resp. 3.7.

**Chemical titration:**
Information on oxidation states, **BUT** not only the outer surface (?)
Oxidation states Cu and Zn in outer surface?

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**LEIS + Chemical titration:** oxidation states in the outer surface!

- **N₂O** for oxidation
- LEIS for detection increase in shielding after N₂O treatment
Cu / ZnO / SiO₂ - Catalyst

Determination of cluster size and oxidation states by LEIS

Cu/Zn/SiO₂ reduced at 473 K

Outermost atomic layer:
ZnO 0.42
Cu²⁺ 0.54
Zn⁰ 0.02
Cu⁰ 0.02

Subsurface: Cu: Zn = 9

Cu/Zn/SiO₂ reduced at 673 K

Outermost atomic layer:
ZnO 0.77
Cu²⁺ 0.03
Zn⁰ 0.19
Cu⁰ 0.01

Subsurface: Cu: Zn = 9
Atomic Layer Deposition (ALD)

“Growth with Digital Accuracy“
How many cycles for Closure?

ALD cartoons: (often) show closed layer after 1 cycle
In practice: closure after a few up to > 100 cycles!

Typical examples (depending on ALD conditions!):

- 6 cycles CrOx / Al₂O₃
- 6-9 cycles HfO₂ / Si
- ~ 15 cycles ALN / SiO₂
- ~ 40 cycles Al₂O₃ / Si
- ~ 70 cycles Fe₂O₃ / ZrO₂
- ~ 150 cycles TiN / SiO₂
The transient regime determines closure and uniformity.
Characterization of MOCVD vs. ALD HfO$_2$ layer closure and growth mode on Silicon: a new model for preferential deposition

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ALD 2010, June 21 – 23, 2010 Seoul, Korea
HfO₂ layer closure: MOCVD vs ALD

Surface fractions (LEIS) as function of coverage

Earlier layer closure for ALD-HfO₂
LEIS and Growth

- Initial growth; growth mode
- Poisoning, activation
- Closure, pinholes
- Thickness distribution

Conclusion IBM / Global Foundries / ION-TOF / Tascon study:

- Origin of the superior quality of the ALD grown layers revealed by HS-LEIS

( other analytic tools have insufficient depth resolution )
Summary: Why do you need LEIS ?? !!

- Any material, any T
- Quantitative
- 1st atom and high-resolution in-depth !!

Unique applications of High Sensitivity LEIS (NOT’s)

- Segregation, Anti-wetting
- Adhesion: “5% vs 100%“
- Follow ultrathin growth
- Pinholes in ultrathin; Nano pinholes
- Metal / polymer in-depth diffusion
- Catalysis: poison, promoter, probe molecules, core-shell, …..
- Nanoclusters (diameter; outer atoms)
- Inorganics: oxidation states
- Improve cleaning strategies

Complementarity to XPS, ToF-SIMS, ….
Miscellaneous applications

- Microelectronics, polymers, ceramics, catalysis, sensors, .......

But also:

- Pinholes in coatings
- Candy wrappers
- Gold mining
- F 16 Dome
- Bone tissue, implants, stents, .......
- Ageing of Linoleum (“Linowonder”)
- Anti-wetting (watches, .....)
- Floor wax
Complementary Cutting Edge techniques

HS-LEIS + HR-XPS
Qtac¹⁰⁰ Scienta ESCA 300

Lehigh University
Thank you for your attention.