High resolution ion beam analysis

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Review articles and Books

Ion backscattering for materials analysis: 3 energy regimes

• Low energy ion scattering (~10 keV or less): LEIS
  – Hard to quantify, very surface specific

• Medium energy (~ 50 – 200 keV) MEIS
  – Quantitative, somewhat elaborate equipment, surface specific

• High energy (1 – 2 MeV) RBS
  – Quantitative, simpler equipment
Advantages of ion beams*

- Penetrating (can access buried interfaces!)
- Mass specific
- Known interaction law (cross sections are known)
- Excellent depth resolution

*Mostly high and medium energy beams
Elementary considerations in ion backscattering (1)

Relation between incoming and backscattered ion energies

\[ E_1 = k \times E_0 \]

\( k = \) the kinematic factor

Cross section for backscattering

\[ \frac{d\omega}{d\Omega} = \left( \frac{Z_1 Z_2 e^2}{4E_0} \right)^2 \frac{1}{(\sin \theta/2)^4} \]
Elementary considerations in ion backscattering (2)

Depth profiling

Figure 2.2 Graphic representation of the kinematic factor $K_{M_2}$ [Eq. (2.5)] for a scattering angle $\theta = 170^\circ$ as a function of the target mass $M_2$ for $^1$H, $^4$He, $^{12}$C, $^{20}$Ne, and $^{40}$Ar.

Figure 3.1 Energy loss components for a projectile that scatters from depth $t$. The sequence is: energy lost via electronic stopping on the inward path, $\Delta E_{in}$; energy lost in the elastic scattering process, $\Delta E_s$; and energy lost to electronic stopping on the outward path, $\Delta E_{out}$. Then $E_1 = E_0 - \Delta E_{in} - \Delta E_s - \Delta E_{out}$. 

$\Delta E_{in} \approx \frac{dE}{dx} \cdot t$  
$E_1 = E_0 - \Delta E_{in}$  
$\Delta E_s = (1-K) E_t$  
$\Delta E_{out} \approx \frac{dE}{dx} \cdot \frac{t}{\cos \theta}$
Structural work using Medium Energy Ion Scattering (MEIS)
MEIS lab at Rutgers

- XPS
- ALD
- IR
- MEIS
- NRP
Electrostatic ion detector

- Depth resolution of $\sim 3$ Å near surface
- Angular resolution $0.2^\circ$
- Mass-sensitive: $E = E(M, \vartheta)$
- Quantitative (cross sections are known)
Surface structure and dynamics

Monte Carlo simulation in the binary-encounter approximation

Input:
- individual atomic positions
- anisotropic rms vibration amplitude

Output: \[ R = 100 \cdot \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left( \frac{Y_i^{calc} - Y_i^{exp}}{Y_i^{exp}} \right)^2} \]
FIG. 1. Views of the Cu(110) surface. (a) Top view. The second-layer atoms are shaded. (b) The (111) plane, showing channeling and blocking directions. (c) The (001) plane, showing the two inequivalent scattering planes, one terminating in the top layer, the other in the second layer.
FIG. 2. Blocking dip in the (111) plane in the geometry of Fig. 1(b) for 100 keV protons. The bulk blocking direction is at 60°. A contraction will cause a shift to smaller scattering angles. The solid curve is a Monte Carlo simulation for $\Delta d_{12} = -7.5\%$ and $\Delta d_{23} = +2.5\%$. 
FIG. 4. Blocking dip in the (001) plane in the geometry of Fig. 1(c) for 100 keV protons. In this plane, both the first and second layers of the surface are directly visible to the incident beam. The bulk blocking direction is at 90°. The solid curve is a Monte Carlo simulation for $\Delta d_{12} = -7.5\%$ and $\Delta d_{23} = +2.5\%$. 
An (oversimplified) picture of the origin of the oscillatory relaxation

Fig. 3.1. Electron smoothing at a metal surface (Finnis & Heine, 1974).
Reconstruction of the (110) surface of Au:

Possible structural models consistent with a (1x2) symmetry
FIG. 1. (a) Top view of the Au (110) surface. The scattering planes in later figures are shown with dashed lines. (b) Side view. Arrows show the movements of the atoms in the model described in the text.
FIG. 2. (a) Side view of the (110) zone. This plane cuts perpendicularly across the rows in the surface, and includes the direction in which the surface unit cell is doubled. There is a second inequivalent scattering plane behind the plane, drawn in a lighter shading. Vacancies are shown as unfilled circles. (b) Angular distribution of the surface peak in the (110) zone of Cu(110) for 100-keV protons incident in the [112] channeling direction. The blocking dips are in the [114], [116], and [118] directions. The data have been normalized to the yield of a (1×1) unit cell and the Rutherford cross section. (c) As (b) but for Au(110).
FIG. 3. (a) Side view of the (111) zone. This plane cuts diagonally across the rows in the surface, and includes all atoms in one single scattering plane. (b) Data taken in the (111) zone with 65-keV protons. The simulation for a 18% contracted surface is drawn with a solid line and for a surface with a 40% expansion is dashed. The bulk crystallographic direction is at 60°.
Conclusions:

Missing row structure

Large first layer inwards contraction

Buckling in the lower layers, results in charge density smoothing
Another research example: Surface structure of TiC(001)

Y. Kido et al, PRB 61 1748 (2000)
Sub-nm Depth Resolution from a Materials Perspective:

• Who needs monolayer resolution?
• In this talk, three techniques:
  – Elastic Recoil Detection Analysis (ERDA)
  – Nuclear Resonance Profiling (NRP)
  – Medium Energy Ion Scattering (MEIS)
• Research examples
Motivation for a lot of work in this field today

The SiO$_2$/Si system: interface of choice in microelectronics for 40+ years

Moore’s law says that the gateoxide thickness will soon be too small (~ 1 nm) due to large leakage currents from quantum mechanical tunneling

SiO$_2$ needs to be replaced by a higher dielectric constant material (“high-k”)
Advantages of ion beams

• Penetrating (can access buried interfaces!)
• Mass specific
• Known interaction law (cross sections are known)
• Excellent depth resolution
Medium Energy Ion Scattering (MEIS)

- a low-energy, high resolution version of conventional Rutherford Backscattering (RBS)
A comparison between RBS and MEIS

<table>
<thead>
<tr>
<th></th>
<th>RBS</th>
<th>MEIS</th>
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<tbody>
<tr>
<td>Ion energy</td>
<td>~ 2 MeV</td>
<td>~ 100 keV</td>
</tr>
<tr>
<td>Detector resolution</td>
<td>~ 15 keV</td>
<td>~ 0.15 keV</td>
</tr>
<tr>
<td>Depth resolution</td>
<td>~ 100 Å</td>
<td>~ 3 Å</td>
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</table>

2 basic advantages vs. RBS: Often better dE/dx, superior detection equipment
Energy Dependence of $dE/dx$ for Protons in Silicon

Maximum of $\sim 14$ eV/Å at $\sim 100$ keV!

This helps, but the greater advantage is the use of better ion detection equipment!
<table>
<thead>
<tr>
<th>Magnetic spectrometers</th>
<th>Electrostatic spectrometers</th>
</tr>
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<tbody>
<tr>
<td>Kyoto university (Kimura)</td>
<td>FOM – IBM (Tromp, van der Veen, Saris ..)</td>
</tr>
<tr>
<td>Kobelco</td>
<td>High Voltage Engineering</td>
</tr>
</tbody>
</table>
From the Ion beam analysis laboratory at Kyoto university; note the magnetic spectrometer.
The Kyoto – Kobelco very compact MEIS facility

Footprint:
~ 2.1 x 1.5 m
New development: 3D-MEIS

S. Shimoda and T. Kobayashi

3D-MEIS
- Pulsed ion beam
- Scattered (and/or recoiled) particles are detected

3D detector
position-sensitive and time-resolving MCP detector

incident beam
- Ion: He+
- Energy: 100 keV
- Repetition: 500 kHz

sample
periodic atomic structure

TOF

• 2D blocking pattern
• Flight times of scattered (and/or recoiled) particles

wide solid angle
Structural analysis of an Er-silicide on Si(111) substrate using 3D-MEIS

S. Shimoda and T. Kobayashi

Fig. 1 3D-MEIS images of the intensities of He particles scattered (a) from Er atoms in the Er-silicide film and (b) from Si atoms in the Si substrate.

Fig. 2 TOF spectra obtained from the data detected in regions indicated by A and B in Fig.1.

Fig. 3 Structural model of the ErSi$_2$

Cross section cut by the ErSi$_2$(2110) plane
Early High Resolution Work

K. Kimura et al. (Kyoto)

Sb on Si(100) with caps of varying thickness; some Sb segregates to the surface

Fig. 4. Observed HRBS spectra of Sb-δ-doped Si films prepared by the low-temperature molecular-beam epitaxy. The density of the doped Sb was $5.6 \times 10^{13} \text{ cm}^{-2}$. The Sb δ-layer as well as the surface Sb layer due to the surface segregation are seen.
Recent Very High Resolution Work

Carstanjen et al. (Stuttgart) (to be published)

Note use of N\(^+\) and N\(^{2+}\) ions and charge exchange effects
The Stuttgart high resolution ion analyzer

Fig. 1. Schematic drawing of the electrostatic spectrometer and the scattering chamber set up at the Pelletron accelerator of the Max Planck Institut für Metallforschung, Stuttgart.
Determining interface strain using monolayer resolution ion scattering and blocking (Moon et al.)

Ozone oxide, no strain

Thermally grown oxide, significant strain

FIG. 3. The blocking dips of the Si peaks of (a) an ozone oxide and (b) a thermally grown oxide as a function of scattering angle. The energy of each spectrum was (1) 95.2 keV, (2) 95.0 keV, (3) 94.9 keV, (4) 94.3 keV, (5) 93.9 keV, and (6) 93.7 keV. (c) The shift of the blocking dip positions of the Si peaks for an ozone-formed oxide (triangle) and for a thermally grown oxide (square).
Spectra and information content

- Sensitivity:
  - $\approx 10^{12}$ atoms/cm$^2$ (Hf, Zr)
  - $\approx 10^{14}$ atoms/cm$^2$ (C, N)

- Accuracy for determining total amounts:
  - $\approx 5\%$ absolute (Hf, Zr, O), $\approx 2\%$ relative
  - $\approx 10\%$ absolute (C, N)

- Depth resolution: (need density)
  - $\approx 3$ Å near surface
  - $\approx 8$ Å at depth of 40 Å
Depth resolution and concentration profiling

Depth resolution for \(\approx 100 \text{ keV} \) protons (resolution of the spectrometer \(\approx 150 \text{ eV} \))

- Stopping power \(\text{SiO}_2 \approx 12 \text{ eV/Å} \); \(\text{Si}_3\text{N}_4 \approx 20 \text{ eV/Å} \); \(\text{Ta}_2\text{O}_5 \approx 18 \text{ eV/Å} \)

- "Near surface" depth resolution \(\approx 3-5 \text{ Å} \); worse for deeper layers due to energy straggling

Layer model:

- Areas under each peak corresponds to the concentration of the element in a 3Å slab
- Peak shapes and positions come from energy loss, energy straggling and instrumental resolution.
- The sum of the contributions of the different layers describes the depth profile.
Oxygen Isotope Experiments: SiO$_2$ growth mode

1. O$^{18}$ uptake at the surface!
2. Growth at the interface
3. O$^{16}$ loss at the surface
4. O$^{16}$ movement at the interface!

Gusev, Lu, Gustafsson, Garfunkel, PRB 52, 1759 (1995)
Schematic model

Surface exchange

Growth

SiO$_2$

Transition zone, SiO$_x$

Si (crystalline)

Deal and Grove
Work on high-k films: MEIS spectra of La$_2$SiO$_5$ before and after vacuum anneal

- Annealing up to 800 °C in vacuum shows no significant change in MEIS spectra.
- Surface remains flat by AFM.
La$_2$SiO$_5$ before and after in-air anneal

- stoichiometry and thickness consistent with other analyses
- 400°C anneal leads to minor broadening of the La, O and Si distributions
- 800°C anneal shows significant SiO$_2$ growth at interface
- La diffusion towards the Si substrate
The film disintegrates!
ZrO₂ film re-oxidized in ¹⁸O₂

- Significant interfacial SiO₂ growth for ZrO₂, less for Al₂O₃
- Dramatic oxygen exchange: ¹⁸O incorporation and ¹⁶O removal
- SiO₂ growth rate faster than for O₂ on Si
- Growth faster under ZrO₂ than Al₂O₃
Why GaAs (or Ge)?

- Potentially great advantages over Si-based devices for both high-speed and high-power applications
- The electron mobility of GaAs is 5x that in Si
- Much thinner interfacial oxide
**HfO$_2$ on GaAs: MEIS and TEM comparison**

<table>
<thead>
<tr>
<th></th>
<th>TEM*</th>
<th>MEIS</th>
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<tbody>
<tr>
<td><strong>No etch</strong></td>
<td><img src="image1.png" alt="TEM Image" /></td>
<td><img src="image2.png" alt="MEIS Image" /></td>
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<tr>
<td></td>
<td>a-C</td>
<td>GaAs</td>
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<tr>
<td></td>
<td>HfO$_2$</td>
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<tr>
<td></td>
<td>Ga-rich oxide</td>
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<td><strong>HF etch</strong></td>
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<td></td>
<td>Ga-rich oxide</td>
<td></td>
</tr>
</tbody>
</table>

- TEM and MEIS results are consistent

*Grazul & Muller, Cornell*
TEM of $\text{Al}_2\text{O}_3$ on GaAs

- No etch
- HF etch

(J. Grazul and D. Muller, Cornell)

- no contrast between $\text{Al}_2\text{O}_3$ and $\text{Ga}_x\text{As}_y\text{O}$
MEIS data of $\text{Al}_2\text{O}_3$ on GaAs: one-parameter fitting

Interfacial oxide:
$(\text{Ga}_2\text{O}_3)_{0.37}(\text{Ga}_2\text{O})_{0.63}(\text{As}_2\text{O}_3)_{0.17}$, porous oxide: $\rho = 0.5 \rho_{\text{bulk}}$

<table>
<thead>
<tr>
<th></th>
<th>$n(\text{Ga+As})$, Å$^{-2}$</th>
<th>$n(\text{Al})$, Å$^{-2}$</th>
<th>$n(\text{O})$, Å$^{-2}$</th>
<th>$n(\text{O})/n(\text{Al})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF etch</td>
<td>0.33</td>
<td>1.48</td>
<td>2.23</td>
<td>1.51</td>
</tr>
<tr>
<td>No etch</td>
<td>0.55</td>
<td>1.30</td>
<td>2.22</td>
<td>1.70</td>
</tr>
</tbody>
</table>

- interfacial oxide is much thinner for the HF-etched sample
Epitaxial Oxides

Very versatile materials:

– Small changes in composition $\rightarrow$ big changes in properties (high-$T_c$!)

– Combining two different oxides may give multifunctionality and/or entirely new phenomena.
Metallic LaAlO$_3$/SrTiO$_3$ (LAO/STO) interface

LaAlO$_3$ ($E_g = 5.8$ eV) by PLD or MBE band insulator

SrTiO$_3$ ($E_g = 3.2$ eV) band insulator

2D Electron Gas

• Metallic conductivity

• Superconductivity

• Magnetic order
  Brinkman et al, Nat. Mat. (2007)
Origin of metallic state at the interface

- Polar catastrophe: polar-nonpolar discontinuity

This model assumes an abrupt interface

Important points

Oxygen vacancies – have been shown by many to influence carrier concentrations
Conductivity only observed on TiO$_2$ terminated substrates

Samples

• We have investigated samples from three different labs.
• None of the samples were made at Rutgers.
• All made by PLD on TiO$_2$ terminated substrates.
• Post-annealed in oxygen.
• Most data presented today from samples by Prof. H. Hwang, Tokyo (now Stanford).
He\textsuperscript{+} channeling spectrum of 4-unit-cell LAO/STO(001)

The measured Sr and Ti peaks fall at significantly higher ion energies than those calculated for a sharp interface:

The energies for the Sr and Ti peaks are those of both species present within the outermost u.c. of LAO \( \rightarrow \) outdiffusion of Sr and Ti to the LAO film
H$^+$ channeling spectrum of a 4-unit-cell LAO/STO film
H\(^+\) channeling spectrum of a 4-unit-cell LAO/STO film
Angle dependent XPS shows poor agreement with sharp interface model (Chambers et al.)
Conclusions

The LaAlO$_3$/SrTiO$_3$ interface shows evidence for substantial interdiffusion, a useful result for understanding the origin of the many interesting effects shown by this system.