<table>
<thead>
<tr>
<th>Lecture #</th>
<th>Date</th>
<th>Instructor</th>
<th>Lecture Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fri. 25-Jan.</td>
<td>RAB</td>
<td>Introduction to course, why are surfaces interesting, begin surface thermodynamics and surface structure</td>
</tr>
<tr>
<td>2</td>
<td>Mon. 6-Sept.</td>
<td>RAB</td>
<td>Surface Thermodynamics</td>
</tr>
<tr>
<td>3</td>
<td>Fri. 1 Feb. RESCHEDULED: Tues. 29 Jan, 5:00-6:20PM Room: ARC 108</td>
<td>RAB</td>
<td>Surface Structure, Two-dimensional Lattices</td>
</tr>
<tr>
<td>4</td>
<td>Mon. 4-Feb.</td>
<td>RAB</td>
<td>Electron mfp, diffraction methods: LEED, RHEED, Scanning probe</td>
</tr>
<tr>
<td>5</td>
<td>Fri. 8-Feb.</td>
<td>PB</td>
<td>Microscopy: Principles of SEM TEM LEEM</td>
</tr>
<tr>
<td>6</td>
<td>Mon. 11-Feb.</td>
<td>LF</td>
<td>Intro to electron spectroscopy: Analyzers, electron optics</td>
</tr>
<tr>
<td>7</td>
<td>Fri. 15-Feb.</td>
<td>RAB</td>
<td>Surface/Film Composition: XPS</td>
</tr>
<tr>
<td>8</td>
<td>Mon. 18-Feb.</td>
<td>LF</td>
<td>Ion Scattering Methods: RBS (channeling, NRA, ERD)</td>
</tr>
<tr>
<td>9</td>
<td>Fri. 22-Feb.</td>
<td>TG</td>
<td>Ion Scattering II - MEIS (Channeling, Blooming, HighRes RBS)</td>
</tr>
<tr>
<td>10</td>
<td>Mon. 25-Feb.</td>
<td>LW</td>
<td>Lab session: Ion Scattering [Meet in NPL]</td>
</tr>
<tr>
<td>11</td>
<td>Fri. 1-Mar.</td>
<td>RAB</td>
<td>Intro to Electronic Properties [Term Paper Topic Due]</td>
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<tr>
<td>12</td>
<td>Mon. 4-Mar.</td>
<td>DHV</td>
<td>Band Structure: Bulk, Film, Surface</td>
</tr>
<tr>
<td>13</td>
<td>Fri. 8-Mar.</td>
<td>EG</td>
<td>Chemist's approach to electronic structure: From bonds and bands</td>
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<tr>
<td>14</td>
<td>Mon. 11-Mar.</td>
<td>RAB</td>
<td>Measuring electronic structure: UPS, ARUPS, IPS</td>
</tr>
<tr>
<td>15</td>
<td>Fri. 15-Mar.</td>
<td>SR</td>
<td>Lab session: X-ray Photoelectron Spectroscopy [Meet in NPL]</td>
</tr>
<tr>
<td></td>
<td>Mon. 18-Mar.</td>
<td>--</td>
<td>Spring Break [No Classes]</td>
</tr>
<tr>
<td></td>
<td>Fri. 22-Mar.</td>
<td>--</td>
<td>Spring Break [No Classes]</td>
</tr>
<tr>
<td>16</td>
<td>Mon. 25-Mar.</td>
<td>RAB</td>
<td>Quantum Confinement at surfaces</td>
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<tr>
<td>17</td>
<td>Fri. 29-Mar.</td>
<td>RAB</td>
<td>3 Hour Mid-term Exam LOCATION TBA</td>
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<td>18</td>
<td>Mon. 1-Apr.</td>
<td>RAB</td>
<td>Oxide Surfaces</td>
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<td>19</td>
<td>Fri. 5-Apr.</td>
<td>RAB</td>
<td>Vibrational Spectroscopy</td>
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<tr>
<td>20</td>
<td>Mon. 8-Apr.</td>
<td>FC</td>
<td>Lab Session: Transmission Electron Microscopy [Meet in NPL]</td>
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<tr>
<td>21</td>
<td>Fri. 12-Apr.</td>
<td>JH</td>
<td>Adsorption, desorption, diffusion, energy transfer, sticking, atom scattering, etc.</td>
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<tr>
<td>22</td>
<td>Mon. 15-Apr.</td>
<td>SO</td>
<td>Nucleation and growth of nanostructures and films</td>
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<tr>
<td>23</td>
<td>Fri. 19-Apr.</td>
<td>WW</td>
<td>Surface Magnetism</td>
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<tr>
<td>24</td>
<td>Mon. 22-Apr.</td>
<td>FMZ</td>
<td>Photovoltaics</td>
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<td>25</td>
<td>Fri. 26-Apr.</td>
<td>VP</td>
<td>Organic semiconductors/photovoltaics</td>
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<tr>
<td>26</td>
<td>Mon. 29-Apr.</td>
<td>PM</td>
<td>Biomaterial Surfaces and Interfaces</td>
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<tr>
<td>27</td>
<td>Fri. 3-May.</td>
<td>MC</td>
<td>Carbon Nanotubes and graphene</td>
</tr>
<tr>
<td>28</td>
<td>Mon. 6-May.</td>
<td>RAB</td>
<td>Student papers due, oral presentations</td>
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</table>

RAB = Bartynski  PB = Batson  LF = Feldman  EG = Garfunkel  TG = Gustafsson  JH = Hinch  
DV = Vanderbilt  FZ = Zimmermann  MC = Chhowalla  SO = Oh  VP = Podzorov  WW = Wu  
SR = Rangan  FC = Cosandey  LW = Wielunski
ION BEAM ANALYSIS

L. C Feldman
<table>
<thead>
<tr>
<th>Method</th>
<th>Particle Measured</th>
<th>Process</th>
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<td>Scanning Electron Microscopy - Energy Dispersive X-Ray (SEM-EDX)</td>
<td>X-Rays</td>
<td></td>
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<td>None</td>
<td>10000 Å</td>
<td>None</td>
</tr>
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<td>Transmission Electron Microscopy (TEM)</td>
<td>Diffracted Electrons</td>
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<td>-Compound Identification</td>
<td>None</td>
<td>500 Å</td>
<td>None</td>
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<td>X-Ray Photoelectron spectroscopy (APS or ESCA)</td>
<td>Photo Electrons</td>
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<td>-Elements Li-U, Chemical Bonding</td>
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<td></td>
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<td>100 Å</td>
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<td>$10^{-1}$</td>
<td>100 Å - 10000 Å</td>
<td>Via Energy Loss</td>
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</tbody>
</table>
keV electrons and MeV ions interact with matter

- 30 keV $e^-$
- 60 keV $e^-$
- 2 MeV $He^+$

- Restricted to 10 $\mu$m depth, large straggling
- Low beam damage

- Deep probe
- Large damage at end of range

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Introduction

• Ion Beam Analysis
• The Nuclear Microprobe
  – Accelerators: Brightness
  – Focusing MeV ion beams
  – Data Acquisition
  – Imaging modes

Part II: Nuclear microprobe applications
Figure 2.1 (a) Schematic of the experimental setup for Rutherford backscattering. A collimated beam of He ions is incident on a planar sample. Particles scattered to an angle $\theta$ are detected by a solid state nuclear particle detector. All this apparatus must be under vacuum. (b) Schematic representation of an elastic collision between a projectile of mass $M_1$, velocity $v$, and energy $E_0$ and a target mass $M_2$ which is initially at rest. After the collision, the projectile and the target mass have velocities and energies $v_1, E_1$ and $v_2, E_2$, respectively. The angles $\theta$ and $\phi$ are positive as shown. All quantities refer to a laboratory frame of reference.
\[ \frac{1}{2} M_1 v^2 = \frac{1}{2} M_1 v_1^2 + \frac{1}{2} M_2 v_2^2, \quad \text{(2.1)} \]

\[ M_1 v = M_1 v_1 \cos \theta + M_2 v_2 \cos \phi, \quad \text{(2.2)} \]

\[ 0 = M_1 v_1 \sin \theta - M_2 v_2 \sin \phi. \quad \text{(2.3)} \]

Solving \( \phi \) first and then \( v_2 \), one finds the ratio of particle velocities

\[ \frac{v_1}{v} = \frac{\pm (M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{(M_2 + M_1)}. \quad \text{(2.4)} \]

The ratio of the projectile energies for \( M_1 < M_2 \), where the plus sign is

\[ \frac{E_1}{E_0} = \left[ \frac{(M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{M_2 + M_1} \right]^2. \quad \text{(2.5)} \]
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.

For direct backscattering through $180^\circ$, the energy ratio has its lowest value given by

$$\frac{E_1}{E_0} = \left(\frac{M_2 - M_1}{M_2 + M_1}\right)^2,$$

and at $90^\circ$ is given by

$$\frac{E_1}{E_0} = \frac{M_2 - M_1}{M_2 + M_1}.$$

In collisions where $M_1 = M_2$, the incident particle is at rest after the collision with all the energy transferred to the target atom, a feature well known in billiards. For $\theta = 180^\circ$, the energy $E_2$ transferred to the target atom has its maximum value given by

$$\frac{E_2}{E_0} = \frac{4M_1M_2}{(M_1 + M_2)^2}.$$
From Eq. (2.10), the scattering cross section can be expressed as

$$\sigma(\theta) = \frac{-h}{\sin \theta} \frac{db}{d\theta} \quad (2.16)$$

and from the geometrical relations $\sin \theta = 2 \sin(\theta/2) \cos(\theta/2)$ and $d \cot(\theta/2) = -\frac{1}{4} d\theta / \sin^2(\theta/2)$,

$$\sigma(\theta) = \left(\frac{Z_1 Z_2 e^2}{4E}\right)^2 \frac{1}{\sin^2 \theta/2}. \quad (2.17)$$

This is the scattering cross section originally derived by Rutherford. The experiments by Geiger and Marsden in 1911–1913 verified the predictions that the amount of scattering was proportional to $[\sin^2 \theta]^{-1}$ and $E^{-5}$. In addition they found that the number of elementary charges in the center of the atom is equal to roughly half the atomic weight. This observation introduced the concept of the atomic number of an element which describes the positive charge carried by the nucleus of the atom. The very experiments that gave rise to the picture of an atom as a positively charged nucleus surrounded by orbiting electrons has now evolved into an important materials analysis technique.

For Coulomb scattering the distance of closest approach, $d$, of the projectile to the scattering atom is given by equating the incident kinetic energy $E$ to the potential energy at $d$ or

$$d = \frac{Z_1 Z_2 e^2}{E}. \quad (2.18)$$

The scattering cross section can be written as $\sigma(\theta) = (d/4)^2 / \sin^2 \theta / 2$, which gives for 180° scattering $\sigma(180°) = (d/4)^2$. For 2 MeV He ions ($Z_i = 2$) incident on Ag ($Z_a = 47$),

$$d = \frac{(2)(47)(14.4 \text{ eV} \, \text{Å})}{(2 \times 10^6 \text{ eV})} = 6.8 \times 10^{-8} \, \text{Å},$$

a value much smaller than the Bohr radius $a_0 = h^2 / m_e e^2 = 0.53 \, \text{Å}$, and the K shell radius of Ag, $a_0/47 = 10^{-4} \, \text{Å}$. Thus the use of an unscreened cross section is justified. The cross section for scattering to 180° is

$$\sigma(\theta) = (6.8 \times 10^{-8} \, \text{Å})^2 / 16 = 2.89 \times 10^{-8} \, \text{Å}^2,$$

a value of $2.89 \times 10^{-24} \, \text{cm}^2$ or 2.89 barns, where the barn = $10^{-24} \, \text{cm}^2$. 
\[ \frac{d\sigma}{d\Omega} = \left( \frac{\alpha \hbar c}{2mv_0^2} \right)^2 \frac{1}{\sin^4(\theta/2)} \]
ENERGY LOSS:

\[
\Delta E_{\text{in}} \approx \frac{dE}{dx} \cdot t
\]

\[
E_t = E_0 - \Delta E_{\text{in}}
\]

\[
\Delta E_s = (1 - K) E_t
\]

\[
\Delta E_{\text{out}} \approx \frac{dE}{dx} \cdot \frac{t}{\cos \theta}
\]
Stopsing Cross-Section, $\varepsilon$ 
& Energy Loss Rate, $\frac{dE}{dx}$

$\varepsilon = \frac{I \cdot \frac{dE}{dx}}{N}$

$N_{Al} = 6 \times 10^{22}$ atoms/cm$^3$

$\varepsilon_{Al} = \frac{\varepsilon_{He}}{4} E/4$
\[ \Delta p = \frac{2Z_te^2}{bv}, \]  \hspace{1cm} (3.2)

where we have used Eq. (2.15a) with \( \theta \approx 0 \), a small angle approximation. If the electron has not achieved a relativistic velocity, its kinetic energy is given by

\[ \frac{\Delta p^2}{2m} = \frac{2Z^2_te^4}{b^2mv^2} = T, \]  \hspace{1cm} (3.3)

where \( T \) is the energy transfer in the collision.

The differential cross section, \( d\sigma(T) \), for an energy transfer between \( T \) and \( T + dT \) is

\[ d\sigma(T) = -2\pi bdb, \]  \hspace{1cm} (3.4)

and the energy loss per unit path length, \( dE/dx \), is

\[ -\frac{dE}{dx} = n \int_{T_{\text{min}}}^{T_{\text{max}}} T \, d\sigma, \]  \hspace{1cm} (3.5)

where \( n \) is the number of electrons per unit volume. In terms of impact parameter \( b \),

\[ a \quad \text{and} \quad b \]
\[-\frac{dE}{dx} = n \int_{b_{\text{min}}}^{b_{\text{max}}} T\frac{2\pi b}{db}, \]

which reduces to

\[-\frac{dE}{dx} = \frac{4\pi Z^2 e^4 n}{mv^2} \ln \frac{b_{\text{max}}}{b_{\text{min}}}. \tag{3.7}\]

To choose a meaningful value for \(b_{\text{min}}\), we observe that if the heavy particle collided head on with the electron, the maximum velocity transferred to a stationary electron is \(2v\). The corresponding maximum kinetic energy (for a nonrelativistic \(v\)) is \(T_{\text{max}} = \frac{1}{2} m (2v)^2 = 2mv^2\). If this value of \(T_{\text{max}}\) is inserted in Eq. (3.3), the corresponding \(b_{\text{min}}\) becomes

\[b_{\text{min}} = \frac{Z e^2}{mv^2}. \tag{3.8}\]

If \(b_{\text{max}}\) is allowed to become infinite, \(-dE/dx\) goes to infinity because of the contribution of an unlimited number of small energy transfers given to distant electrons. But the smallest energy an atomic electron can accept must be sufficient to raise it to an allowed excited state. If \(I\) represents the average excitation energy of an electron, we choose \(T_{\text{min}} = I\), and find

\[b_{\text{max}} = \frac{2Z e^2}{\sqrt{2mv^2 I}}. \tag{3.9}\]

When Eqs. (3.8) and (3.9) are substituted in Eq. (3.7), we obtain

\[-\frac{dE}{dx} = \frac{2\pi Z^2 e^4 n}{mv^2} \ln \frac{2mv^2}{I}.\]

This calculation is based on direct collisions with electrons in the solid. There is another term of comparable magnitude due to distant resonant energy transfer. The derivation is outside the scope of this book but leads in its simplest form, to a total stopping power twice that shown above, i.e.,

\[-\frac{dE}{dx} = \frac{4\pi Z^2 e^4 n}{mv^2} \ln \frac{2mv^2}{I}, \tag{3.10}\]

or

\[-\frac{dE}{dx} = \frac{2\pi Z^2 e^4}{E} \cdot NZ_e \cdot \left(\frac{M_1}{m}\right) \ln \frac{2mv^2}{I},\]
Rutherford Backscattering

Counts per channel

Vanadium

Graphite

VO₂

1.8-MeV ⁴He⁺

1300 Å

Carbon

Oxygen

RBS data

Simulation

Channel #

50

100

150

200

250

300

350
Figure 2.12: Example of experimental (circles) and simulated (line) RBS spectra for as-deposited vanadium-oxide film on fused-silica (SiO₂) substrate. The VₓOᵧ film was deposited by PLD from a V-metal target in 5 mtorr O₂ background gas—but at a larger target-to-substrate distance than the usual 5–10 cm used for VO₂ precursor films, aiming for pre-anneal stoichiometry x/y as close to 2/3 as possible. The simulation was performed using the SIMNRA program.¹⁰⁴ Analysis: V₂O₃₋₀.₀₁₋₀.₀₀, t ≈ 118 nm.
3.8.1 Grazing Angle Techniques

Equations (3.20a) and (3.28) give the following formula for the depth resolution:

\[
\delta t = \frac{\delta E_1}{K(dE/dx)_{in} + \frac{(dE/dx)_{out}}{|\cos \theta|}}.
\] (3.29)
3.8.2 Straggling

The energy resolution is normally composed of two contributions: detector resolution $\delta E_d$ and energy straggling $\delta E_s$. Assuming the two contributions are independent and satisfy Poisson's statistics, the total resolution, $\delta E_1$ is given by

$$ (\delta E_1)^2 = (\delta E_d)^2 + (\delta E_s)^2. $$  \hspace{1cm} (3.30)
\[ \Delta E = nt \int Td\sigma \]

and

\[ \Omega_B^2 = nt \int T^2 d\sigma. \]  \hspace{1cm} (3.31)

From Eqs. (3.3) and (3.4) we have

\[ d\sigma = \frac{2\pi Z_1^2 e^4}{mv^2T^2} dT \]

so that

\[ \Omega_B^2 = \frac{2\pi Z_1^2 e^4 nt}{mv^2} (T_{\text{max}} - T_{\text{min}}), \]

where \( T_{\text{max}} = 2mv^2 \), and \( T_{\text{min}} = I \). For these swift particles, \( T_{\text{max}} \gg I \)

and \( n = NZ_2 \), giving

\[ \Omega_B^2 = 4\pi Z_1^2 e^4 NZ_2 t, \]  \hspace{1cm} (3.32)
Figure 3.11 The amount of target material $N_t$ (number of atoms/cm$^2$) required to produce 15 keV (FWHM) of energy straggling in a transmission experiment or 21 keV (FWHM) in a backscattering experiment. The projectiles were $^4$He at 2 MeV. [From W. K. Chu et al., Backscattering Spectrometry (Academic Press, New York, 1978).]
ION BEAM ANALYSIS

L. C Feldman
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<td>Auger Electrons</td>
<td><img src="image" alt="Auger Emission" /></td>
<td>Elements Li-U</td>
<td>$10^1$</td>
<td>$20 \text{ Å}$</td>
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<td>Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX)</td>
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<td><img src="image" alt="X-Rays" /></td>
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<td>None</td>
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<td>Compound Identification</td>
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<td><img src="image" alt="Secondary Ion Mass Spectrometry" /></td>
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<td>Rutherford Backscattering Spectrometry (RBS)</td>
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<td><img src="image" alt="Rutherford Backscattering Spectrometry" /></td>
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<tr>
<td>Nuclear Reaction Analysis (NRA)</td>
<td>Light Ion Reaction Product</td>
<td><img src="image" alt="Nuclear Reaction Analysis" /></td>
<td>Light Elements (H, Be, B, C O, F...)</td>
<td>$10^{-3}$</td>
<td>$100 \text{ Å} - 10000 \text{ Å}$</td>
<td>Via Energy Loss</td>
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REVIEW: Lecture of Sept 30 RBS

RBS= Rutherford Back-scattering

Simplest conceptually and most accurate in terms of coverage (atoms/cm²)

Depth resolution (in its simplest form) ~ 2-200 nm
(Can measure surface coverage, cannot define depth well)

Ideal thin film technique for stoichiometry, depth—does not reveal chemical nature/bonding

Spatial resolution – typically 1mm--to-- 1 micron
VARIATIONS ON THE (ION BEAM) THEME

Given an ion beam and the RBS knowledge there are a variety of specialized techniques:

1) Forward recoil scattering—hydrogen detection

2) Channeling—crystallographic information

3) Nuclear reaction analysis—light ion detection

4) PIXE-proton induced x-ray analysis

5) Medium energy ion scattering—high depth resolution (1nm) form of RBS
Main features of RBS

Elements: Be - U
Standard Conditions: 2 MeV 4He beam
Silicon detector: 10 minutes per sample
Precision: Stoichiometry: < 1% relative
Thickness: < 5%
Sensitivity Bulk: 1 % to 10^-4, depending on Z
Surface: 1 to 10^-4 Monolayers
Depth Resolution: 1 to 10 nm
Data analysis: e.g. by RUMP software: http://www.genplot.com/
Remarks: Accessible depth range ~ 1mm
No light elements detectable on heavy substrates
6. Elastic Recoil Detection Analysis & other

ERDA

Sample

Incident Beam - 2 MeV He

Filter

RBS detector

Scanning Transmission Ion Microscopy (STIM)

Sample

Axial STIM Detector

Incident Beam

Off axis STIM Detector

RBS detector
Main features of ERDA

Elements: H – U (Mainly applied for hydrogen)
Standard Conditions: ~100 MeV heavy ion beam
(2 MeV 4He beam for hydrogen detection)
TOF, magnetic, gas ionisation detector, solid state detector
10 minutes per sample
Precision Stoichiometry: 1% relative
Thickness: < 5%
Sensitivity Bulk: % to $10^{-5}$, depending on Z
Depth Resolution: 1 to 10 nm
Remarks: Simultaneous profiles of all elements
Accessible depth range: ~ 1um
Light elements detectable on heavy substrates
Channeling

• Solids have crystal structure
• Therefore the degree of scattering depends on angle

0 degrees (random)
4. Particle Induced X-ray Emission

1: Knock out electron from K-shell (ionization)

2: Decay from L or M shell produces K x-rays

Ion velocity \( \approx \) Electron orbital velocity

\[
E = h \nu = \frac{ke^2}{2a_o} \left( \frac{3}{4} (Z - 1)^2 \right)
\]

Discovered by G. Moseley in

© David N. Jamieson 2005
Main features of PIXE

Elements: C - U
Standard Conditions: 3 MeV proton beam
Si(Li), Ge detector
10 minutes per sample
Precision Stoichiometry: 5% relative
Generally used for trace element analysis
Absolute concentrations: mainly by calibration standards
Sensitivity: 1 to 100 ppm, depending on Z and matrix
Depth Resolution: No depth information
Remarks Probed depth is tens of um
Often used with raster imaging (proton microprobe)
NUCLEAR REACTION ANALYSIS

$^{15}\text{N}$ + $^{1}\text{H}$ → $^{16}\text{O}$ → $^{12}\text{C}^*$ → $^{12}\text{C}$
Table 4
Examples of nuclear reactions suitable for NRA

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{7}\text{Li}(p,\alpha)^4\text{He}$</td>
<td>$E_p \gg 3 \text{ MeV}, \sigma \gg 3 \text{ mb/sr}, Q = 17.3 \text{ MeV}$</td>
</tr>
<tr>
<td>$^{12}\text{C}(d,p)^{13}\text{C}$</td>
<td>$E_d \gg 1-3 \text{ MeV}, Q = 2.7 \text{ MeV}$</td>
</tr>
<tr>
<td>$^{9}\text{Be}(^3\text{He},p)^{11}\text{B}$</td>
<td>$E_{^3\text{He}} \gg 1-5 \text{ MeV}, Q = 10.3 \text{ MeV}$</td>
</tr>
<tr>
<td>$^{31}\text{P}(\alpha,p)^{34}\text{S}$</td>
<td>$E_\alpha \gg 3 \text{ MeV}, Q = 0.63 \text{ MeV}$</td>
</tr>
<tr>
<td>$^{7}\text{Li}(p,n)^{7}\text{Be}$</td>
<td>$E_p \gg 2 \text{ MeV}$</td>
</tr>
<tr>
<td>$^{1}\text{H}(^{15}\text{N},^{12}\text{C})\alpha\gamma$</td>
<td>$E_N = 6.4 \text{ MeV}, \text{resonance}$</td>
</tr>
<tr>
<td>$^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$</td>
<td>$E_p = 340, 484, 872 \text{ keV}, \text{resonances}$</td>
</tr>
<tr>
<td>$^{27}\text{Al}(p,\gamma)^{28}\text{Si}$</td>
<td>$E_p = 991 \text{ keV}, \text{narrow resonance}$</td>
</tr>
</tbody>
</table>

$^{18}\text{O}(p,\alpha)^{15}\text{N}$  
$E_p = 0.73 \text{MeV}, Q = 3.98 \text{MeV}$

$^{2}\text{H}(^{3}\text{He}, p)^{4}\text{He}$
$E_{^3\text{He}} = 0.7 \text{MeV}, Q = 13.0 \text{MeV}$
II. Nuclear Resonance Profiling

- the projectile penetrates the nucleus and induces a nuclear reaction; the reaction product is detected.
Resonant nuclear reactions

\[_{18}^{18}\text{O}(p,\alpha)_{15}^{15}\text{N}\]
Resonant nuclear reactions

$^{18}\text{O}(p,\alpha)^{15}\text{N}$

Energia (keV)

Seção de choque diferencial ($\mu$b/sr)

Resonant nuclear reactions

$E \sim E_r$

$p,\alpha$

raios $\gamma$

detector (BGO)

detector (a)

semicondutor

mylar (13 $\mu$m)
Resonant nuclear reactions

\[ ^{18}\text{O}(p,\alpha)^{15}\text{N} \]
Some low energy nuclear resonances

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Reaction</th>
<th>Resonance energy, keV</th>
<th>Depth resolution</th>
<th>Sensitivity, atoms/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹¹B</td>
<td>¹¹B(p,α)⁸Be*</td>
<td>163</td>
<td>50 nm</td>
<td>10¹³</td>
</tr>
<tr>
<td>¹⁵N</td>
<td>¹⁵N(p,αγ)¹²C</td>
<td>429</td>
<td>&lt; 1 nm</td>
<td>10¹²</td>
</tr>
<tr>
<td>¹⁸O</td>
<td>¹⁸O(p,α)¹⁵N</td>
<td>151</td>
<td>1 nm</td>
<td>10¹³</td>
</tr>
<tr>
<td>¹⁹F</td>
<td>¹⁹F(p, αγ)¹⁶O</td>
<td>340</td>
<td>25 nm</td>
<td>10¹³</td>
</tr>
<tr>
<td>²¹Ne</td>
<td>²¹Ne(p,γ)²²Na</td>
<td>271</td>
<td>&lt; 1 nm</td>
<td>10¹³</td>
</tr>
<tr>
<td>²³Na</td>
<td>²³Na(p,γ)²⁴Mg</td>
<td>309</td>
<td>&lt; 1 nm</td>
<td>10¹³</td>
</tr>
<tr>
<td>²⁴,²⁵,²⁶Mg</td>
<td>Mg(p,γ)Al</td>
<td>223,389,338</td>
<td>&lt; 1 nm</td>
<td>10¹³ - 10¹⁴</td>
</tr>
<tr>
<td>²⁷Al</td>
<td>²⁷Al(p,γ)²⁸Si</td>
<td>327, 405</td>
<td>&lt; 1 nm</td>
<td>10¹⁴</td>
</tr>
<tr>
<td>²⁹Si</td>
<td>²⁹Si(p,γ)³⁰P</td>
<td>324, 417</td>
<td>&lt; 1 nm</td>
<td>10¹⁴</td>
</tr>
</tbody>
</table>

Table 1: Proton induced narrow nuclear resonances in the energy range that can be accessed using the high-energy-resolution 400kV accelerator at Rutgers. As the sensitivity is strongly dependent on the specific experiments (beam dose, measuring time), the numbers given are estimates.
Examples

$^{15}\text{N profile}$

As prepared

Vac annealed

$^{15}\text{N}(p,\alpha\gamma)^{12}\text{C}$

Energia dos Prótons (keV)

Profundidade (nm)

Rendimento (u.a.)

$^{15}\text{N}(10^{19}\text{ cm}^{-3})$
Nuclear resonance depth profiling of Al$_2$O$_3$ on Si(100) (Baumvol et al., Porto Alegre)

Overlapping peaks in MEIS spectrum (M. Copel et al., IBM)
BURIED LAYERS

Nitrogen at the SiC/SiO₂ interface.

~100Å of oxide
Main features of NRA

Elements: H(D) - Al
Standard Conditions: ~ 1 MeV proton beam (15N, 19F, etc. for H-detection)
NaI-, Ge-detector (Si detector for non-g reactions)
15 minutes per measurement
5 hours per profile
Precision Composition: 5% relative
Absolute concentrations: Only by calibration standards
Sensitivity: ppm to % depending on element (ppb to ppt for CPA)
Depth Resolution: 1 to 20 nm
Probed depth ~ um
Examples of nuclear reactions suitable for NRA:

\[ 7\text{Li}(p,a)4\text{He} \quad E_p \gg 3 \text{ MeV}, s \gg 3 \text{ mb/sr}, Q = 17.3 \text{ MeV} \]
\[ 12\text{C}(d,p)13\text{C} \quad E_d \gg 1-3 \text{ MeV}, Q = 2.7 \text{ MeV} \]
\[ 9\text{Be}(3\text{He},p)11\text{B} \quad E_{3\text{He}} \gg 1-5 \text{ MeV}, Q = 10.3 \text{ MeV} \]
\[ 31\text{P}(a,p)34\text{S} \quad E_a \gg 3 \text{ MeV}, Q = 0.63 \text{ MeV} \]
\[ 7\text{Li}(p,n)7\text{Be} \quad E_p \gg 2 \text{ MeV} \]
\[ 1\text{H}(^{15}\text{N},^{12}\text{C})\alpha \quad E_N = 6.4 \text{ MeV}, \text{resonance} \]
\[ 19\text{F}(p,\alpha)16\text{O} \quad E_p = 340, 484, 872 \text{ keV}, \text{resonances} \]
\[ 27\text{Al}(p,\gamma)28\text{Si} \quad E_p = 991 \text{ keV}, \text{narrow resonance} \]
Vanadium oxide undergoes an amazing phase transition at roughly room temperature

Low temperature - semiconductor - high optical transmission, poor conductor

High temperature - metal - low optical transmission, excellent conductor
Properties of vanadium dioxide

- Semiconductor to metal transition
  - $T_c \sim 68 \, ^\circ C$ in the bulk
  - $T < T_c$ semiconducting phase
  - $T > T_c$ metallic phase
  - opt./elec. properties change

Animation by B. Muller http://exploration.vanderbilt.edu

DeNatale et al., J.A.P. 1989
Structural Phase Transition

High temperature phase

Tetragonal (P4$_2$/mn/m)

Low temperature phase

Monoclinic (P2$_1$/c)

- Tetragonal phase: 4.55 Å, 2.88 Å, 4.55 Å
- Monoclinic phase: 4.56 Å, 5.75 Å, 5.38 Å
Rutherford Backscattering

Graphite

1.8-MeV $^4\text{He}^+$

VO$_2$

Counts per channel

Vanadium

Carbon

Oxygen

Counts per channel

Channel #

12x10^3

10

8

6

4

2

0

50

100

150

200

250

300

350

1300 Å

RBS data

Simulation
Figure 2.12: Example of experimental (circles) and simulated (line) RBS spectra for as-deposited vanadium-oxide film on fused-silica (SiO₂) substrate. The VₓOᵧ film was deposited by PLD from a V-metal target in 5 mtorr O₂ background gas—but at a larger target-to-substrate distance than the usual 5–10 cm used for VO₂ precursor films, aiming for pre-anneal stoichiometry x/y as close to 2/3 as possible. The simulation was performed using the SIMNRA program. Analysis: VₓO₃₋₁₋₀.₀₁, t ≈ 118 nm.
\((\text{CH}_3\text{)}_2\text{Cd} + \text{Se:TBPA}\)

isolate CdSe

\((\text{CH}_3\text{CH}_2\text{)}_2\text{Zn} + (\text{TMS})_2\text{S}\)

isolate CdSe/ZnS
CdSe Nanocrystals

Absorption and Emission of CdSe Nanocrystals

Absorbance (OD) vs. Wavelength (nm)

Core absorption
Core emission

CdSe Nanocrystal Model

Hexagonal prism
Polar surfaces
C3v symmetry
Tunable absorption and emission
Tunable Absorption and Emission: Quantum Confinement

Bulk CdSe Nanocrystal

Bulk Bohr Radius

$E_n = \left( \frac{\hbar^2}{8mL^2} \right) n^2$

$\begin{align*}
n &= 1 \\
n &= 2 \\
L &
\end{align*}$
The Function of Nanocrystals is Highly Dependant on the Surface

Efficient transfer of charges from nanocrystal to device

Efficient recombination of charges for maximum fluorescence
Quantum dots are useful in biology because:

- Small size (=> image cellular components)
- Incredibly bright (= enhanced sensitivity, early detection)
- Multiplexed detection (=> multiple simultaneous signals)
- Photostability (= dynamic imaging, sample archive)
- Multivalent Surface (=> enhanced recognition and targeting)

All of these properties originate from the nanometer size of the dots.
Dye vs. Nanocrystal Spectral Characteristics

Dye Molecules (Alexa)

Nanocrystals
Peng et al., JACS, 119, 7019 (1997).
Low power applications require low threshold voltage which demands a near perfect interface (low fixed charge, $Q_f$) and low dopant penetration, $N_A$. 
TEM Sample Preparation

A drop of dilute nanocrystal solution is allowed to dry on an ultra-thin carbon-coated TEM Grid (Ted Pella Inc.)

anti-capillary tweezers

RBS Sample Preparation

The surface of the graphite substrate is coated with the nanocrystal solution. The excess solvent is then wicked off.
Rutherford Backscattering Spectroscopy (RBS): Comparison of TOPO only CdSe vs TOPO/HDA CdSe

- RBS of TOPO only cores shows the existence of excess Cd with a Cd:Se Ratio of 1:2:1

- The addition of HDA to the reaction mixture has changed the Cd:Se ratio to 1:1

- The RBS data combined with Z-STEM data indicates that the excess cadmium existed in the elongated facets not found in the spherical, TOPO/HDA nanocrystals
Comparison of TOPO vs TOPO/Hexadecylamine

The addition of hexadecylamine (HDA) to the surfactant mixture has been known to improve size dispersion in the preparation of CdSe nanocrystals.

- Z-STEM images show elongated growth along c axis in the TOPO only sample.
- The addition of hexadecylamine (HDA) slows growth along C axis creating near-perfect spherical nanocrystals.

* All Z-STEM images have been smoothed to reduce noise.
SECONDARY ION MASS SPECTROSCOPY
SIMS
Figure 4.1 Schematic diagram of two approaches to obtain depth profiles in thin films. With particle energy loss techniques, the thickness of the layer is determined from the energy loss of the energetic particles. With sputter sectioning techniques the amount of material probed is determined by the sputtering yield. The surface composition can be directly analyzed either by electron spectroscopies or the amount of material removed by sputter species detection.
Figure 4.2 (a) Energy dependence of the Ar sputtering yield of Si and (b) incident ion dependence of the Si sputtering yield. The solid line represents the calculations of Sigmund and the data is from Andersen and Bay (1981).
**Figure 4.3** Schematic of the ion–solid interactions and the sputtering process.
Figure 4.4 The screening function $\chi$ in the Molière approximation. At $r = a$, the value of the screening function has dropped to about 0.4 in support of the choice of $a$ as an approximation for the atomic size. Shown also are the screening functions $\chi = a/r$ and $a/2r$. 

Figure 4.6 Factor $\alpha$ occurring in the backward-sputtering yield formula (4.3). (a) Dependence on mass ratio $M_2/M_1$: (——) theoretical, evaluated for elastic scattering only, no surface correction applied; (---) interpolated from experimental sputtering yields for 45 keV ions on Si, Cu, Ag, and Au. (The difference is mainly due to the neglect of the surface correction at large mass ratios.) (b) Dependence on angle of incidence: (——) theoretical for Ar ions on Cu; (---) $(\cos \theta)^{-1}$ dependence, valid mainly in the high-velocity limit. [From Sigmund, 1981.]
Figure 4.7 (a) Schematic of the SIMS apparatus. An incident ion beam results in sputtered ionic species which are passed through an electrostatic energy filter and a mass spectrometer and finally detected by an ion detector. (b) The beam is usually swept across a large area of the sample and the signal detected from the central portion of the sweep. This avoids crater edge effects.
Figure 4.8 Secondary ion cluster spectrum from Ar bombardment of Al. Note that the ordinate is a log scale. The predominant species is $\text{Al}^{+}$ but $\text{Al}_2^{+}$ and $\text{Al}_3^{+}$ are also in abundance. [From Werner, 1978.]
Figure 4.9 Positive (——) and negative (---) ion yields from GaAs bombarded with 5 keV Ar ions. The SIMS spectrum shows the large difference in sensitivity between ionized species for nearly identical sputtering yields of Ga and As from GaAs. [From Magee, Nucl. Instr. Meth. 191, 297 (1981).]
Figure 4.10 SIMS concentration profile of As implanted in Si and redistributed by pulsed laser melting of the outer Si layer. The measured concentration profile extends below levels of $10^{16}$/cm$^3$.[From C. Magee, RCA Laboratories, private communication.]
Figure 4.11 SIMS measurements of hydrogen depth profiles for 5 keV Cs sputtering of a silicon sample implanted at 35 keV with a dose of $1 \times 10^{16}$ H ions/cm$^2$. The effect of the H$_2$O partial pressure in the analysis chamber upon the H dynamic range is evident. [From Magee and Botnick, 1981.]
Figure 4.12 Model of the electronic structure of an ion or atom close to a metallic surface. $E_F =$ Fermi energy; $E_i =$ ionization energy; $RI =$ resonance ionization and $RN =$ resonance neutralization.
Figure 4.13  (a) Comparison of the secondary ion yield of clean and oxygen covered metals sputtered by 3 keV argon ions. (b) Intensity ratios $\Delta I/I_c$ for $\text{Si}^+$ and $\text{Si}^-$ ion yields from oxygen implanted Si versus oxygen concentration for 3 keV Ar sputtered silicon. The oxygen-induced intensity $\Delta I$ is given by $\Delta I = I - I_c$, where $I$ is the measured intensity from oxygen-doped Si and $I_c$ is the ion emission from clean Si. (Both (a) and (b) from Wittmaack, Surface Sci. 112, 168 (1981).]
Figure 4.14 Apparatus for carrying out Secondary Neutral Mass Spectrometry (SNMS) in which neutral sputtered species enter a plasma environment for postionization. The ions are then extracted and detected in the quadruple mass spectrometer system.
Figure 4.15 RBS spectrum of a PtSi film after sputtering with 20 keV Ar ions. The shaded portion in this Pt signal indicates an increase in the concentration of Pt in the near surface region as a result of the enhanced Si sputtering. [From Liau et al., J. Appl. Phys. 49, 5295 (1978).]
Figure 4.16 Dose dependence of the partial sputtering yields of Si and Pt emitted from PtSi for 40 keV Ar bombardment. [From Liau and Mayer, 1980.]
Figure 4.17 Schematic diagram of Ar sputtering of a 1000 Å Pt layer on Si at three different times in the sputtering process. When the Ar range is less than the Pt film thickness, only Pt ions are sputtered. When the Ar ion penetrates through the Pt/Si interface, ion-induced intermixing occurs and a Si signal is found in the sputtering yield. After the initial Pt film has been removed, a Pt signal is still observed due to mixing of Pt into the substrate Si. [From Liau et al., J. Vac. Sci. Technol. 16, 121 (1979).]
**Figure 4.18** (a) Secondary ion mass spectroscopy (SIMS) and (b) Rutherford backscattering spectrometry (RBS) analysis of a tungsten silicide layer sputter deposited on a phosphorus-doped polycrystalline silicon layer on a layer of SiO₂ on silicon. [Data from C. Magee, RCA Research Laboratories, private communication.]