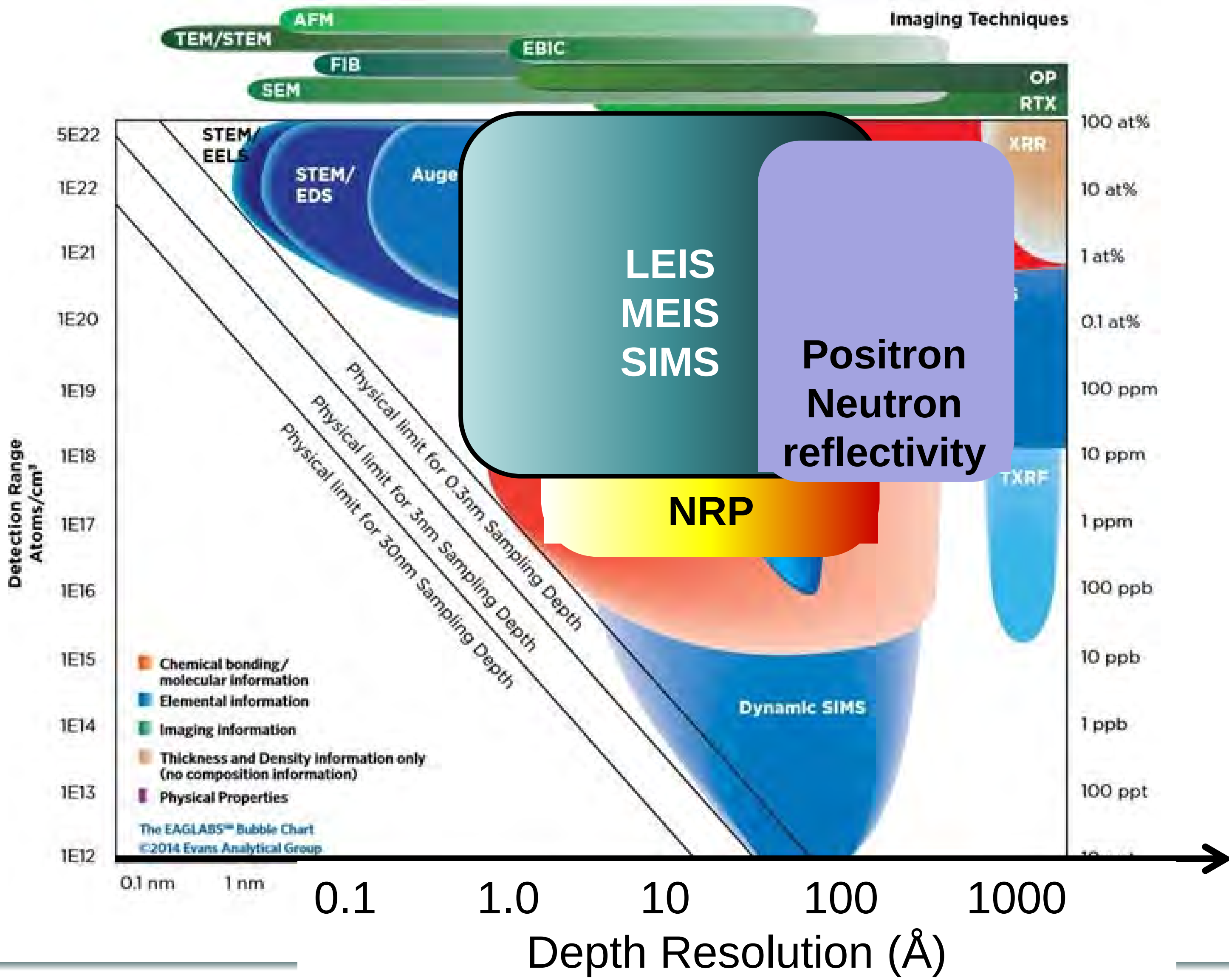
High-resolution depth profiling:
Overview

Lyudmila V. Goncharova

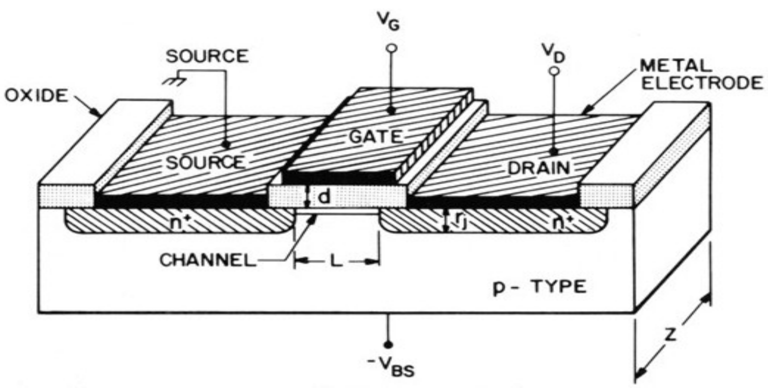
Department of Physics and Astronomy,
University of Western Ontario,
London, Ontario, Canada

Analytical resolution *vs* detection limit



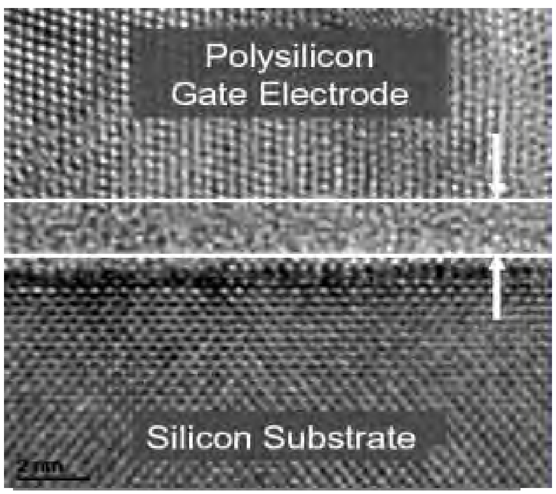
http://www.eag.com

Physical Limits of SiO_2 Gate Dielectrics

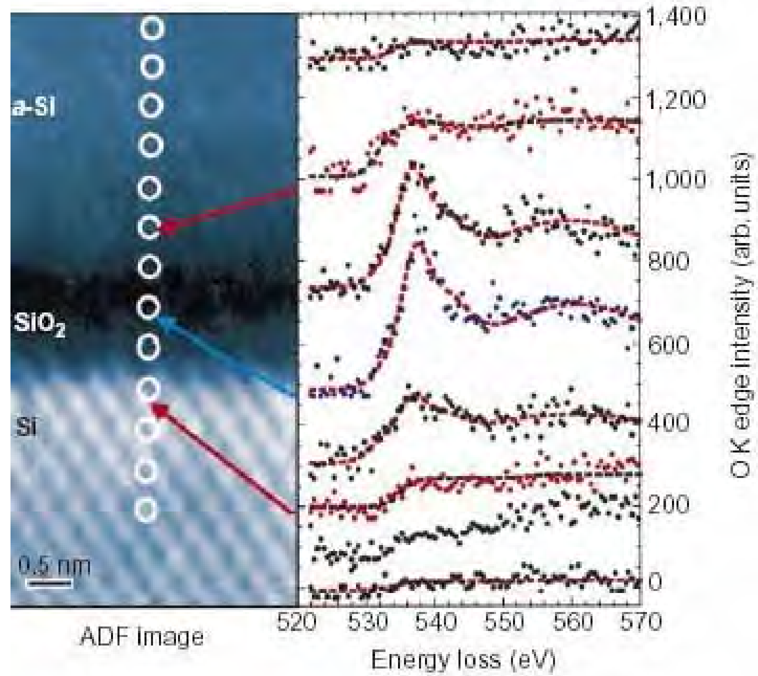


Schematic diagram of MOSFET*

(* from Sze S.M. *Physics of Semiconductor Devices*)



Scanning electron micrograph of cross-sectioned NMOS transistor

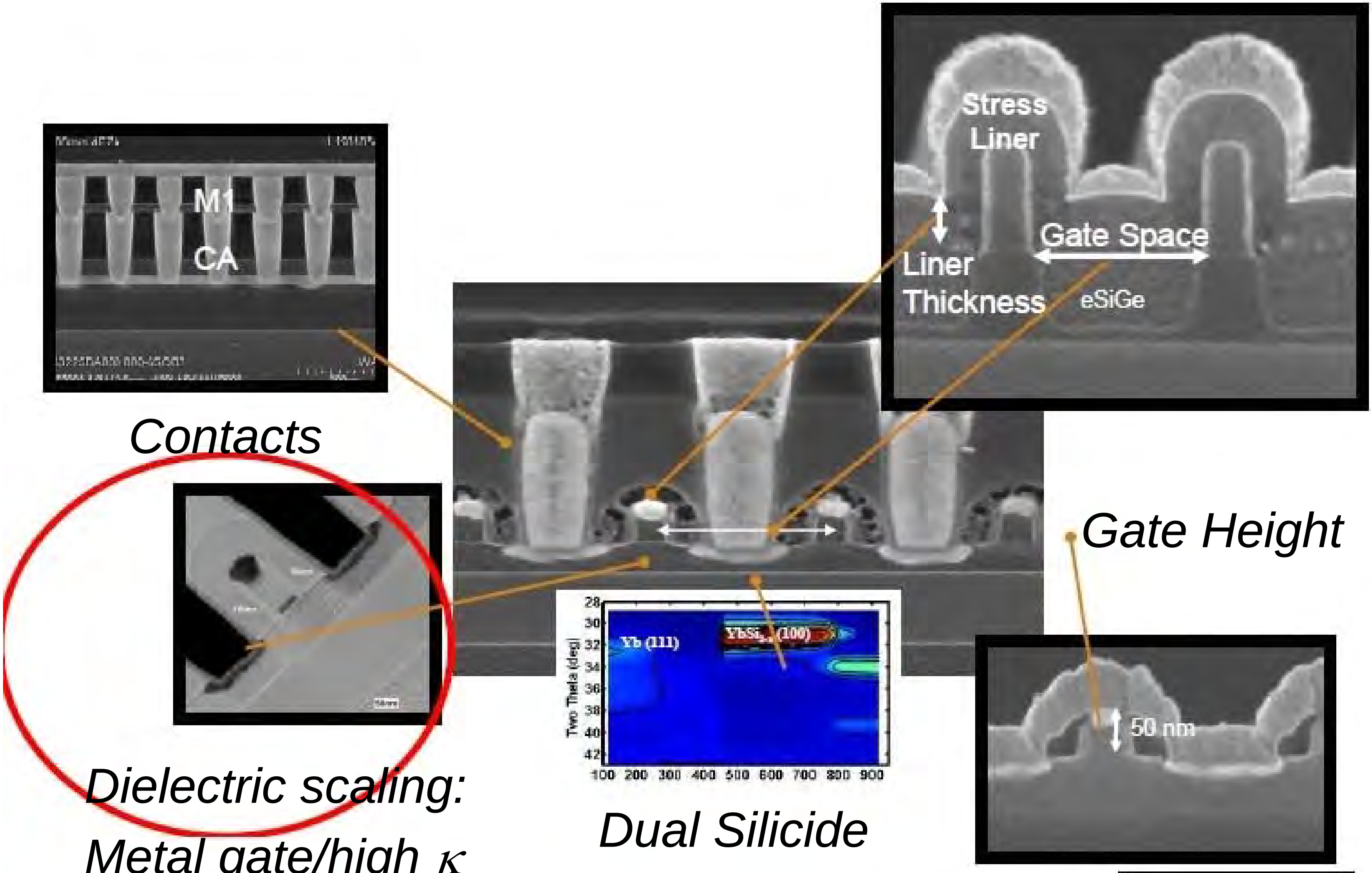


- EELS O-K edge spectra recorded point by point across a gate stack containing a thin gate oxide

D. A. Muller et. al., Nature, ***399****, 758-761 (1999)*

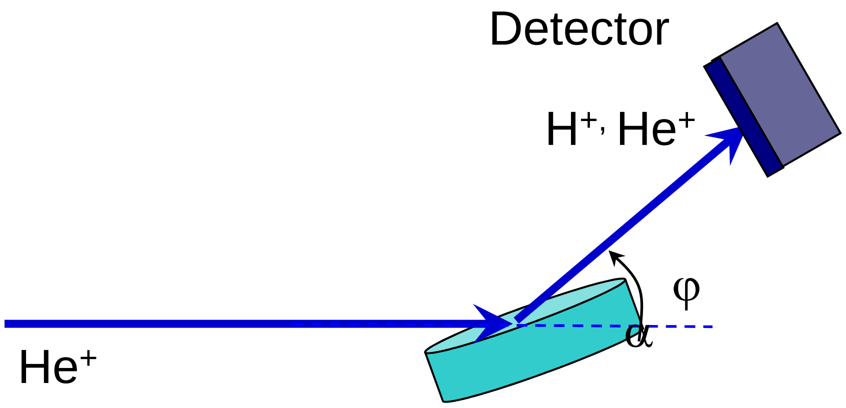
- Bulk SiO_2 properties (e.g. large bandgap) lost for films ≤ 8 Å in thickness

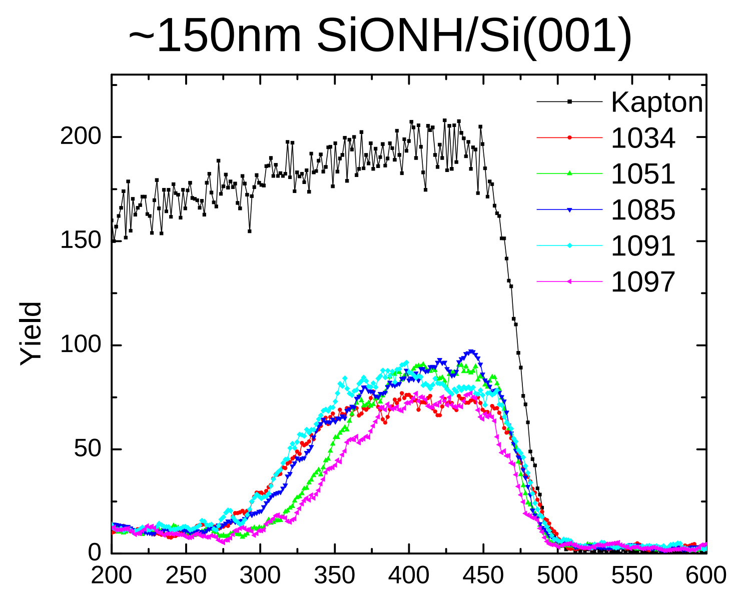
Making things smaller – still the Si way!



J. Sleight *et al.*, *IEMD* 17 (2006) 231.

Missing element from the picture… hydrogen!





Energy conversion

- Novel materials

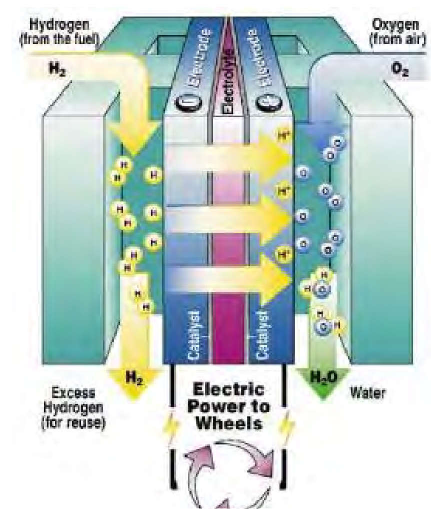
  → Hydrogen storage

- Fuel cells, functional membranes

  → Energy conversion

- Nanoscale catalysis and corrosion

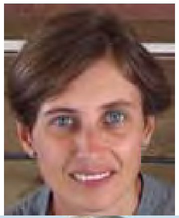
  → Hydrogen diffusion



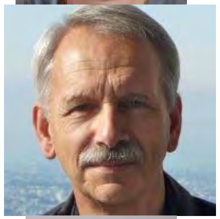
Fuel cell

Methods and presenters today…

- 9:00am **Nuclear reaction analysis and narrow profiling,** *Fernanda Stedile, Universidade Federal do Rio Grande do Sul*



- 10:20am **Medium energy ion scattering,** *Jaap van den Berg, University of Huddersfield*

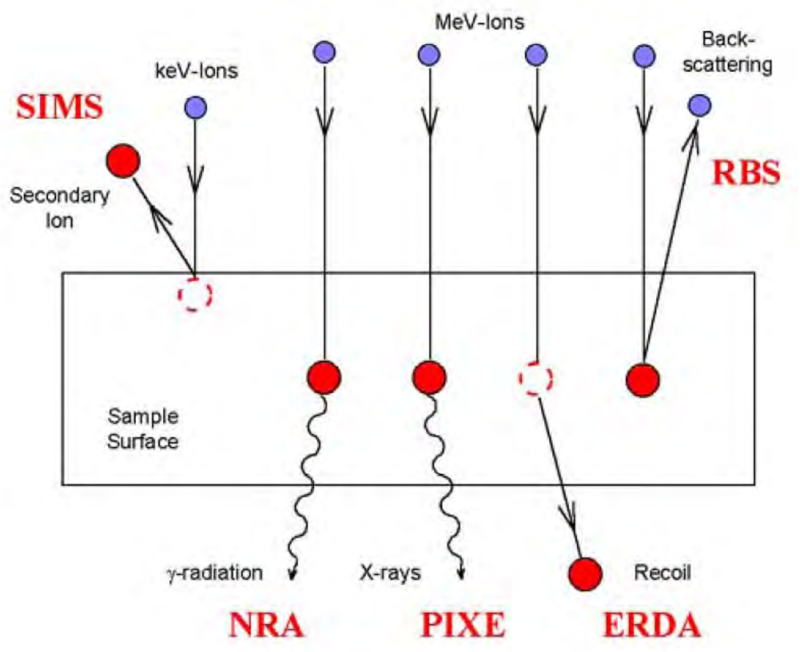


- 11:20am **Secondary ion mass spectrometry applications in materials characterization,** *Stamen Dimov, Surface Science Western*

- 13:20pm **Positron annihilation for defect engineering and analysis for electronic materials,** *Peter Simpson, Western and Andy Knights, McMaster*

- 14:20am **Neutron scattering and reflectivity for depth-profiled information,** *Jamie Noël, Western University*

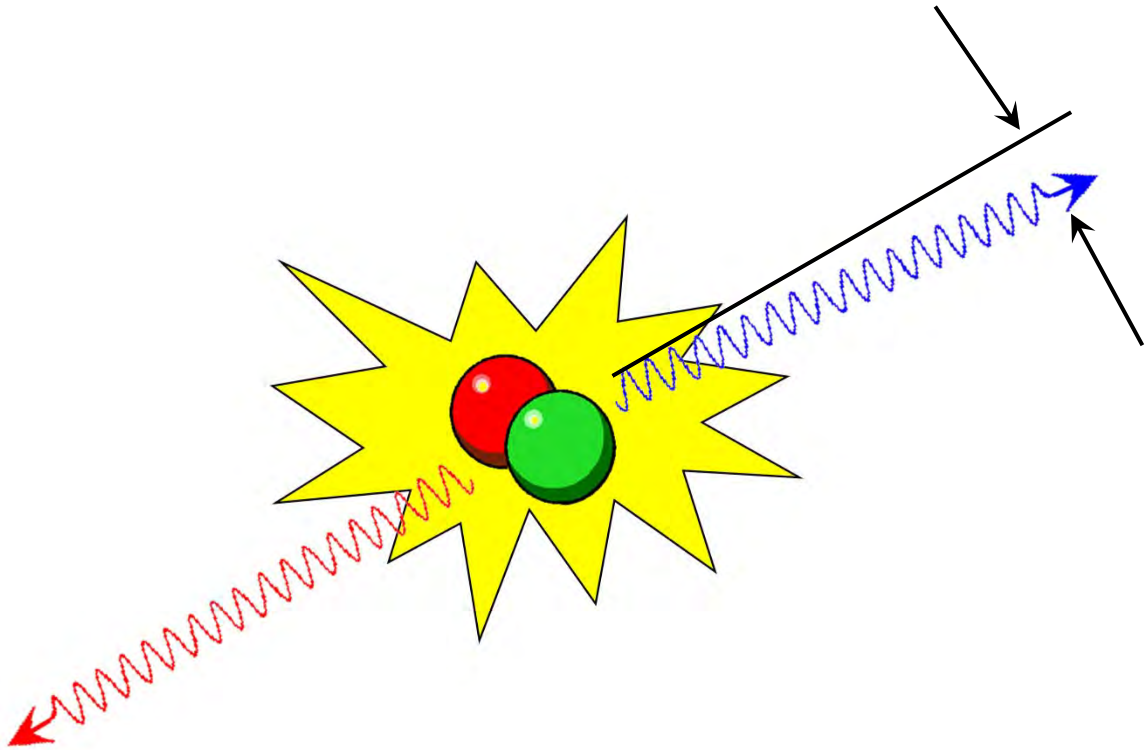
Ion-solid interactions

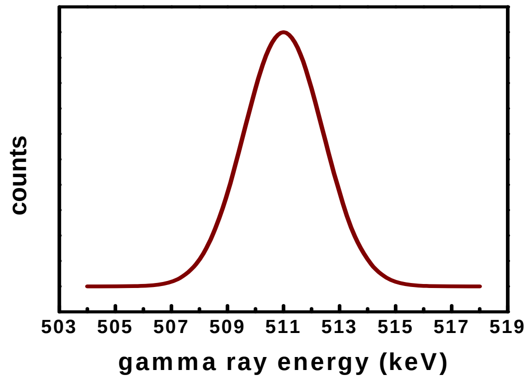


(1) elastic scattering (**RBS, LEIS, MEIS**)
(2) fast recoils arising from elastic scattering
(3) steering effects due to the crystalline structure of target atoms
(4) inelastic processes: energy loss as a function of depth
(5) nuclear reactions (**NRA and NRP**)
(6) interference of elastic scattering and nuclear interaction amplitudes, which leads to so-called resonant scattering

Positron Annihilation

➢ Vacancies present in any material…

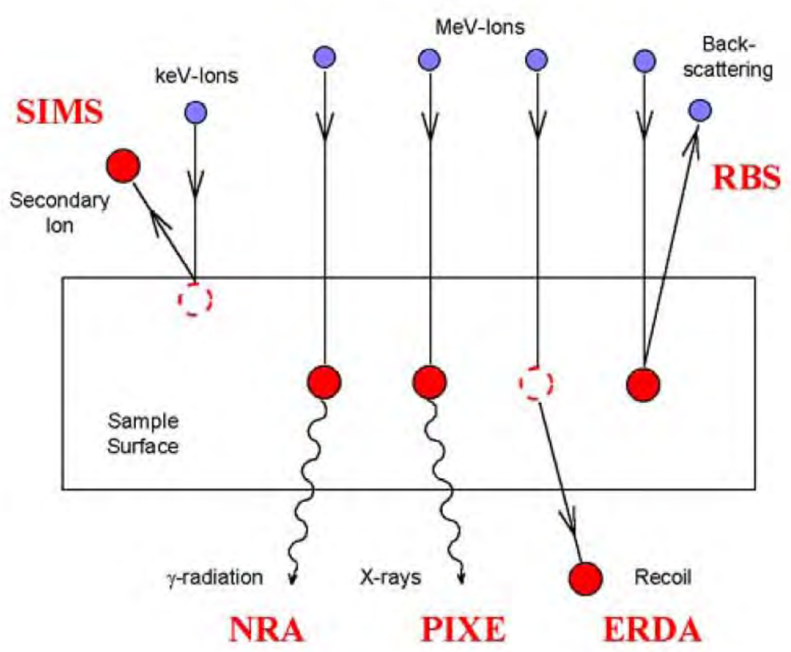




Neutrons and Neutron Reflectometry

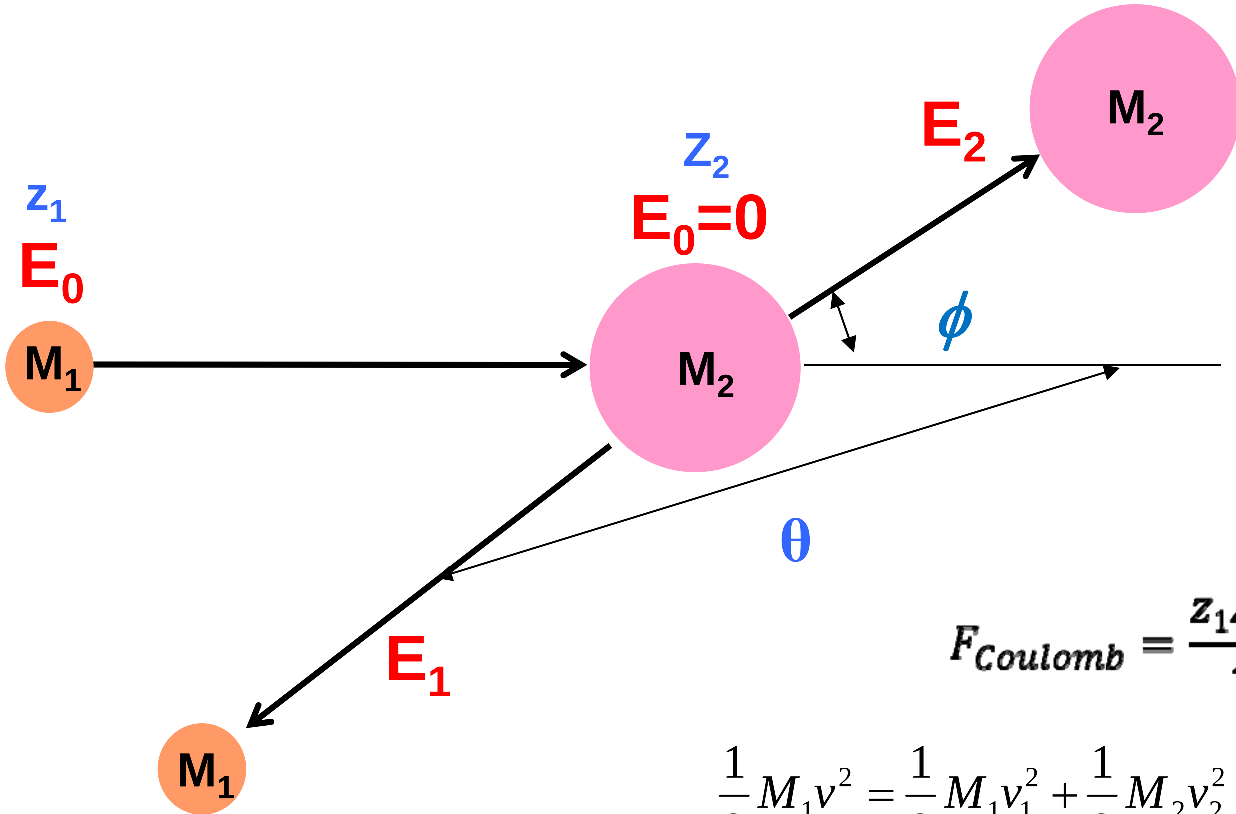
- Interact with atomic nuclei via strong nuclear force
- Thermal neutron energy ~27 meV ($k_B T$)
  - Velocity ~2200 m/s
  - Wavelength ~ few Å
- Interaction strength and direction (attractive or repulsive) are independent of atomic number
  - Different with isotope
  - Coherent bound neutron scattering length

Ion-solid interactions



(1) elastic scattering (**RBS, LEIS, MEIS**)
(2) fast recoils arising from elastic scattering
(3) steering effects due to the crystalline structure of target atoms
(4) inelastic processes: energy loss as a function of depth
(5) nuclear reactions (**NRA and NRP**)
(6) interference of elastic scattering and nuclear interaction amplitudes, which leads to so-called resonant scattering

Elastic Collisions



$$F_{Coulomb} = \frac{z_1 Z_2 e^2}{r^2}$$

$$\frac{1}{2}M_1 v^2 = \frac{1}{2}M_1 v_1^2 + \frac{1}{2}M_2 v_2^2 \qquad \text{(Eq.1)}$$

$$M_1 v = M_1 v_1 \cos\theta + M_2 v_2 \cos\phi \qquad \text{(Eq.2)}$$

$$0 = M_1 v_1 \sin\theta - M_2 v_2 \sin\phi \qquad \text{(Eq.3)}$$

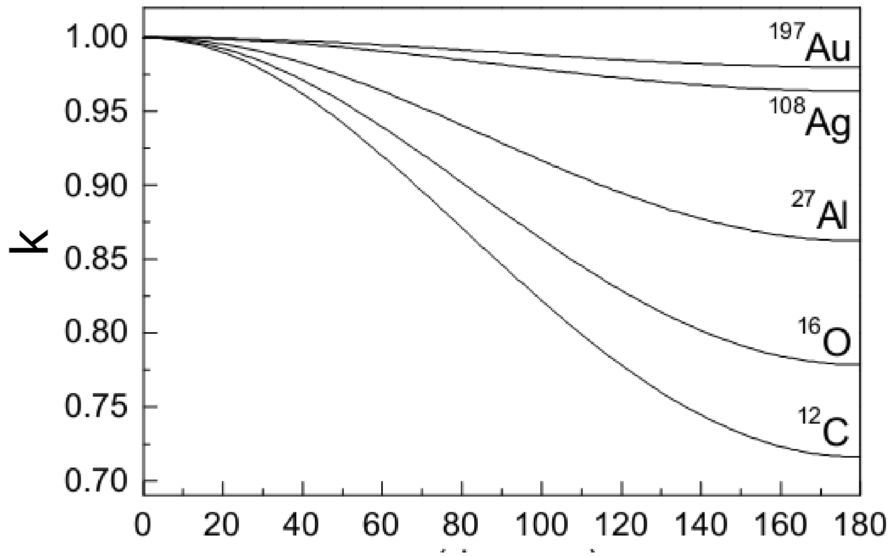
2016 LONDON HRDP 8

Kinematic Factor, k

From Eq. 2 and 3, eliminating ϕ first, then v_2, one finds the ratio of particle velocities, and we can show that the energy of projectile (M_1) after collision can be found by the following relationship:

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

Ratio of E_1 and E_0 is called **kinematic factor**: $k = \frac{E_1}{E_o} = \left[\frac{\left(M_2^2 - M_1^2 \sin^2\theta\right)^{1/2} + M_1 \cos\theta}{M_2 + M_1} \right]^2$



θ

Plot of the kinematic factor, k, vs scattering angle for H^+ scattering from various targets

Advantages of Ion Beams

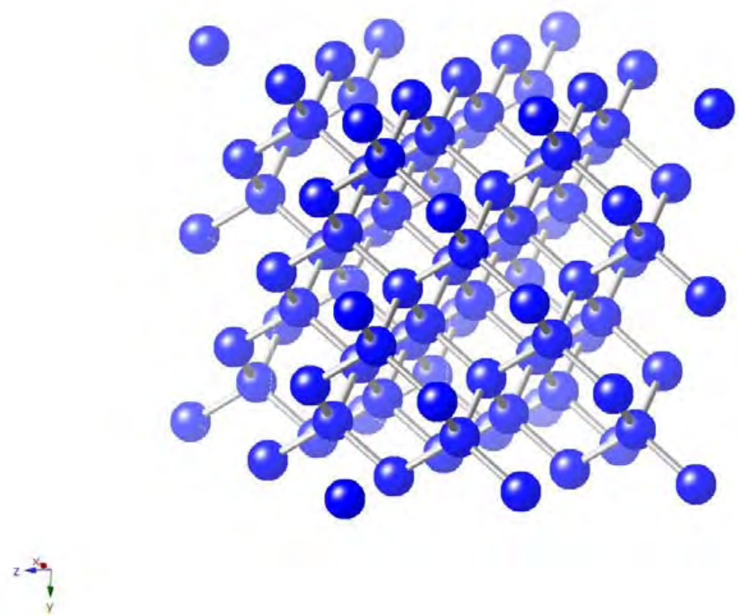
- Can be used for material modification and analysis
- Mass Specific
  - Kinematic factor

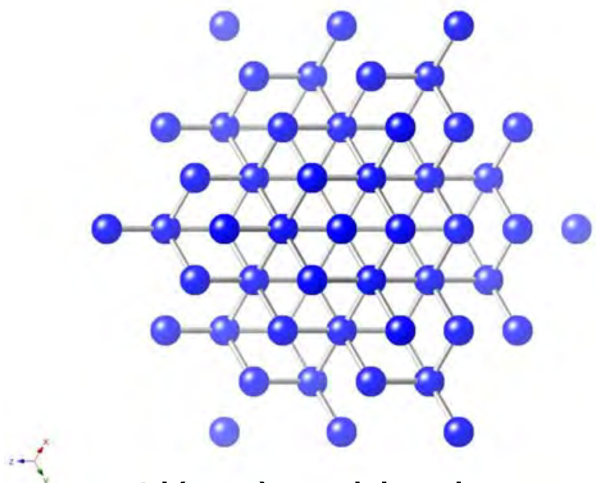
$$E_1 = E_o\left(\frac{\sqrt{M_2^2 - M_1^2\sin^2\theta} + M_1\cos\theta}{M_1 + M_2}\right)^2$$

- Cross sections are very well known
- Good depth resolution
- Penetrating (can access buried interfaces)
- What about substrate?
  - can use channeling and blocking effects

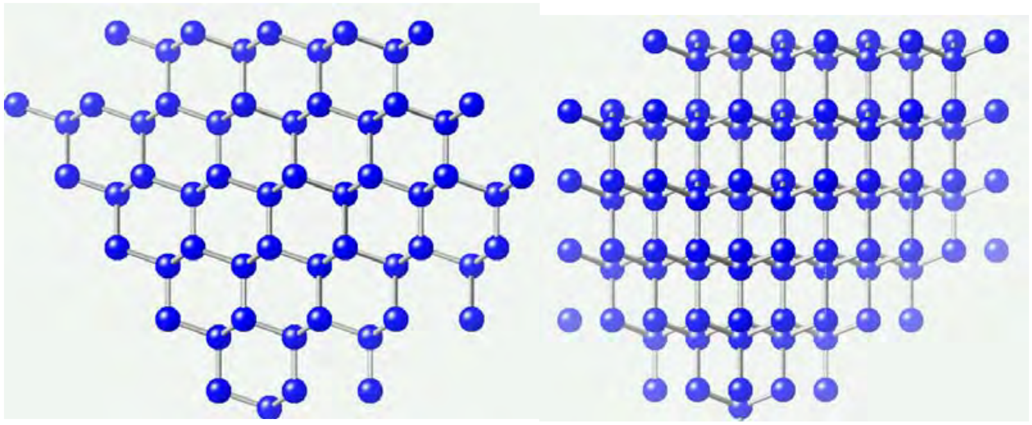
Ion channeling and blocking

Si (diamond structure)



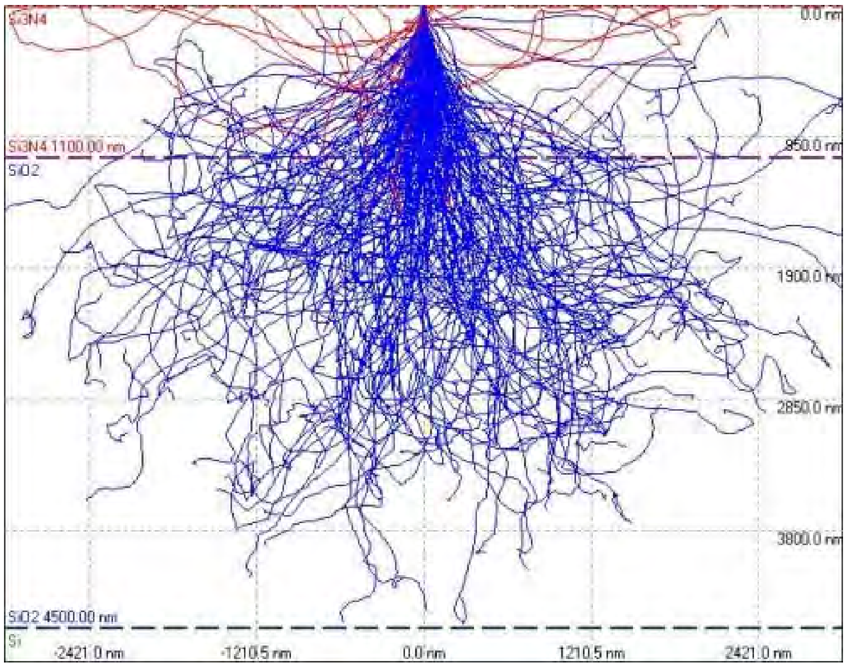


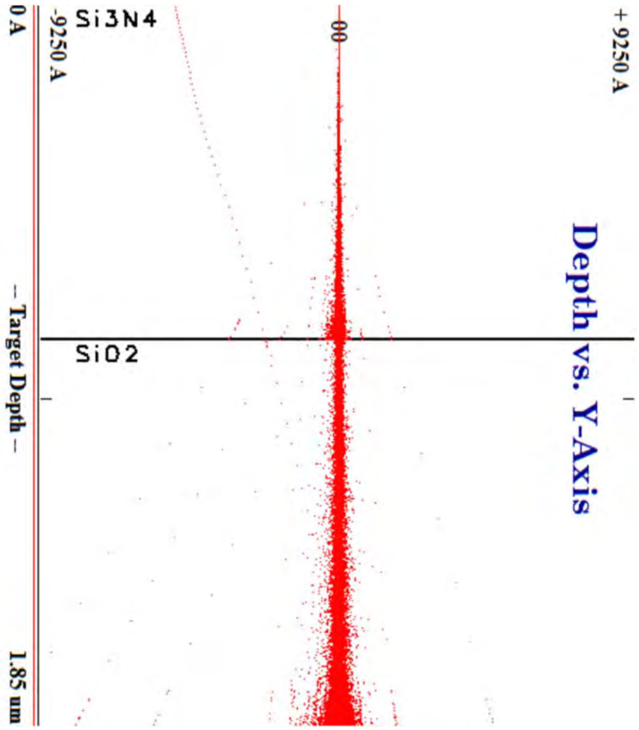
- Si(111) – side view



Electrons vs Ions

When an ion collides with electron clouds in the solid, it does not loose much energy and its direction of motion is hardly change, in a contrast with electrons colliding with electrons

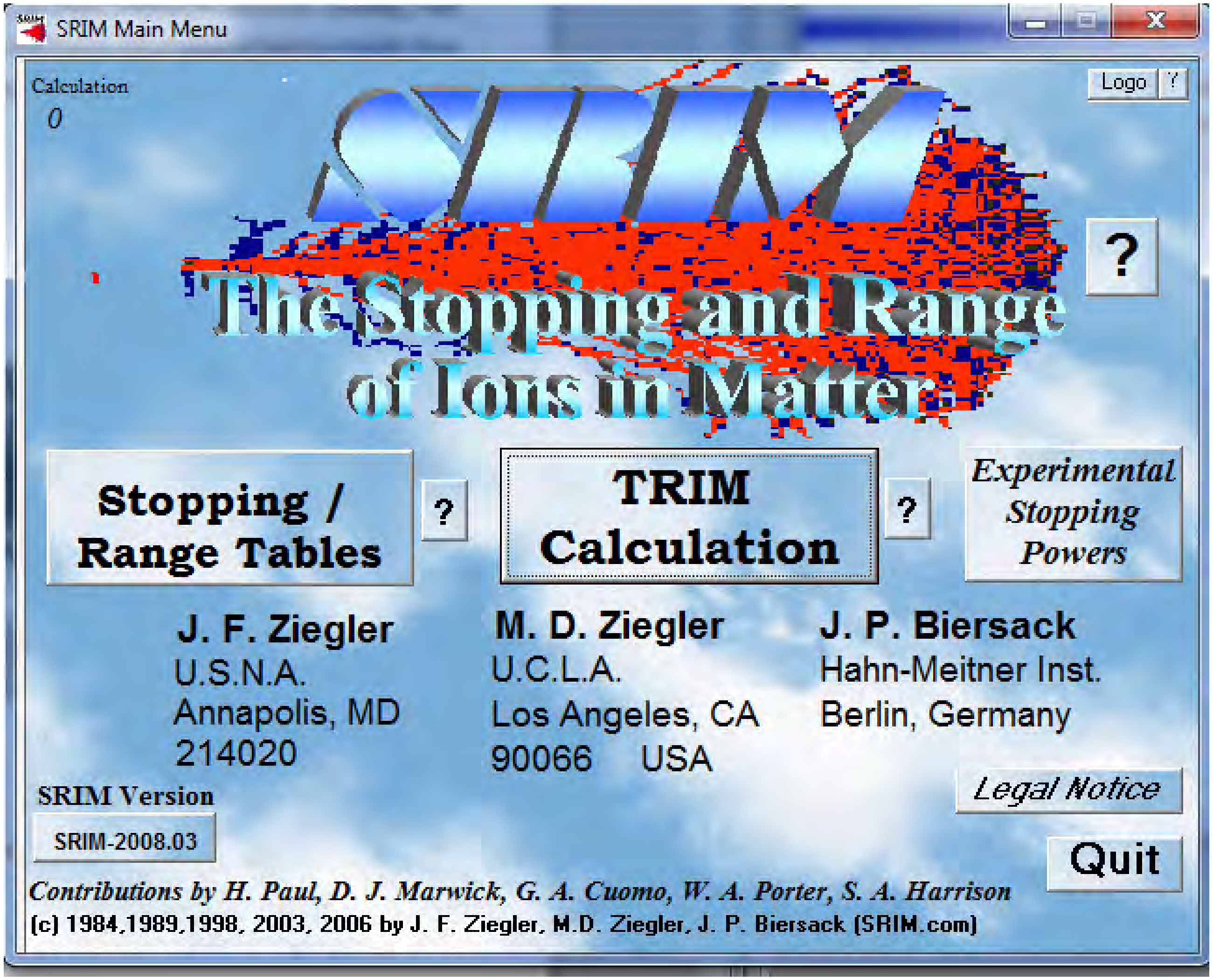




18keV e^- and 18 keV He^+ striking a Si_3N_4 layer with a SiO_2 substrate

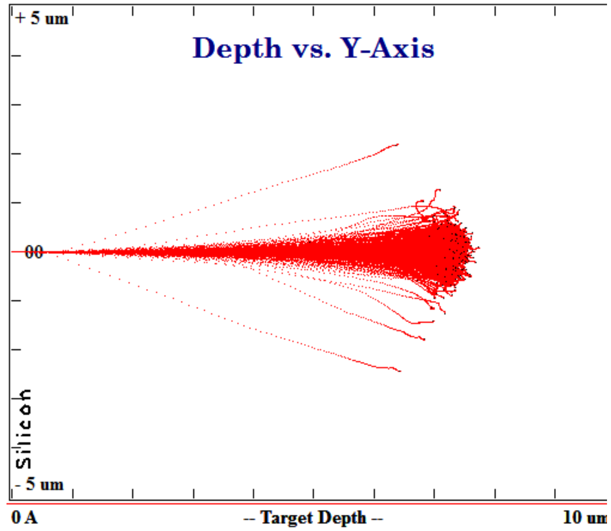
SRIM

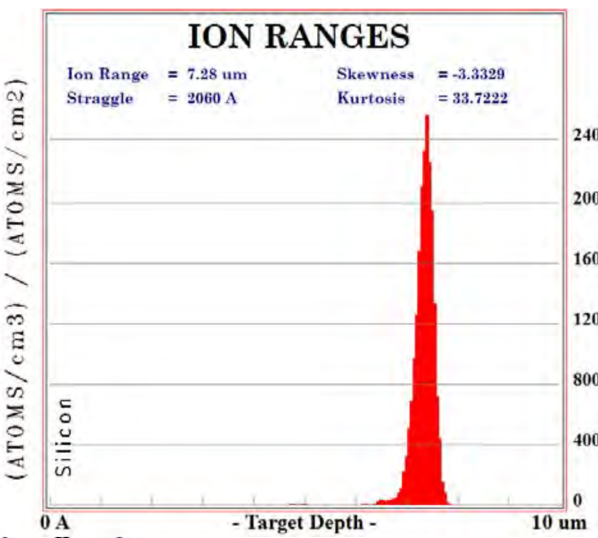
http://www.srim.org/ ⇒**Download SRIM-2013**



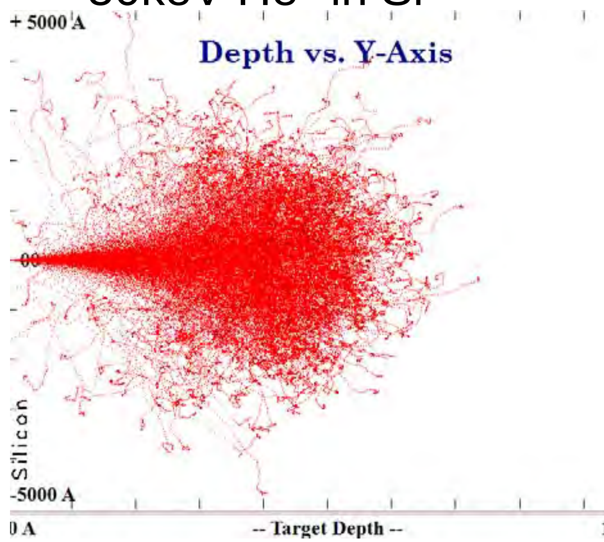
Calculated Ion Trajectories

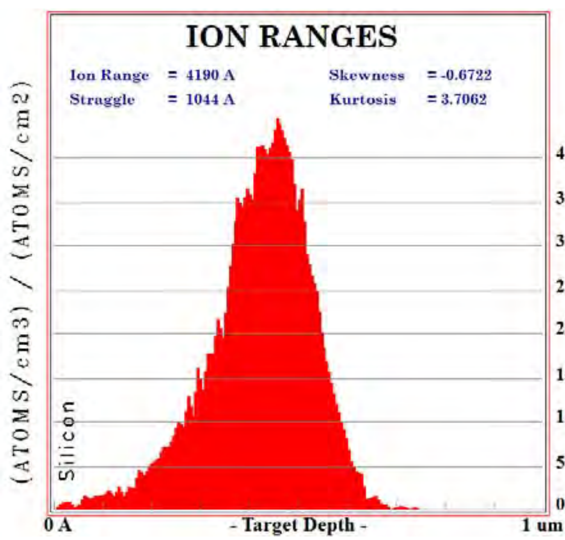
2MeV He^{+} in Si



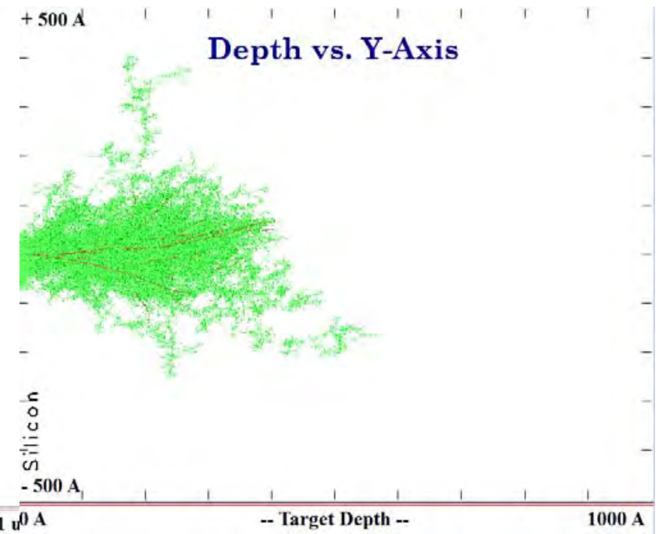


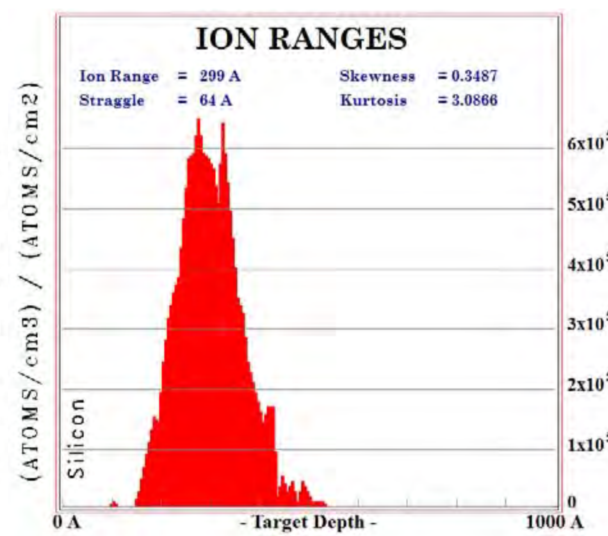
50keV He^{+} in Si



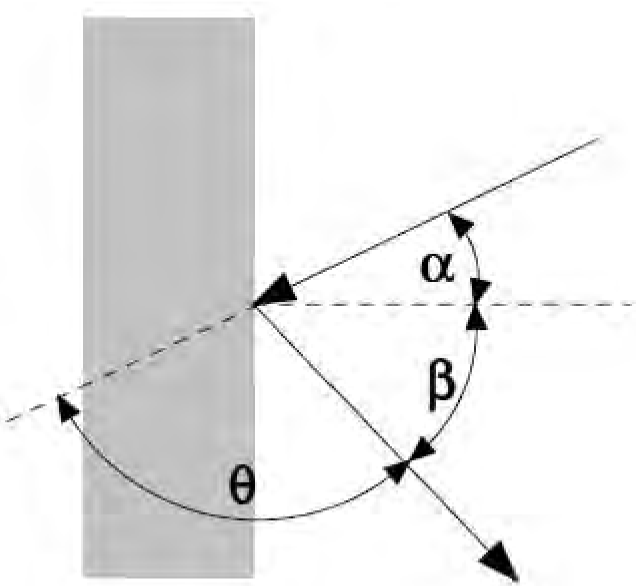


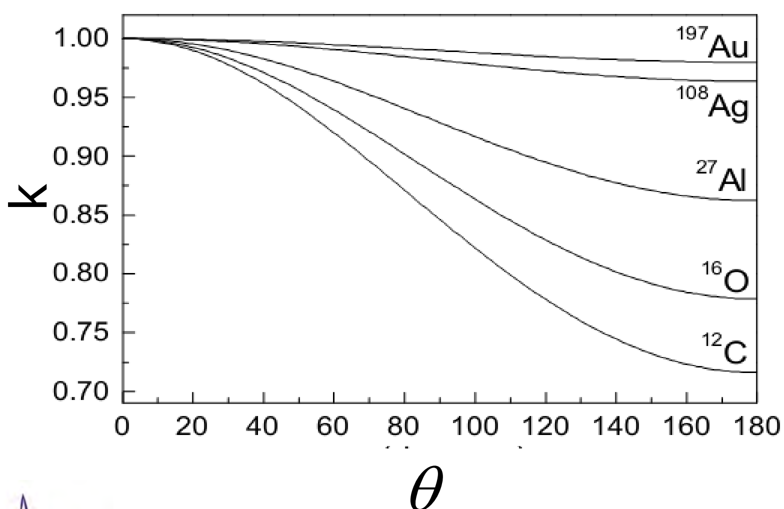
50keV Au^{+} in Si





Rutherford Backscattering: geometry and kinematics





$$E_1 = k\, E_o$$

$$k = \frac{E_1}{E_o} = \left[\frac{\left(M_2^2 - M_1^2 \sin^2\theta\right)^{1/2} + M_1 \cos\theta}{M_2 + M_1} \right]^2$$

α: incident angle

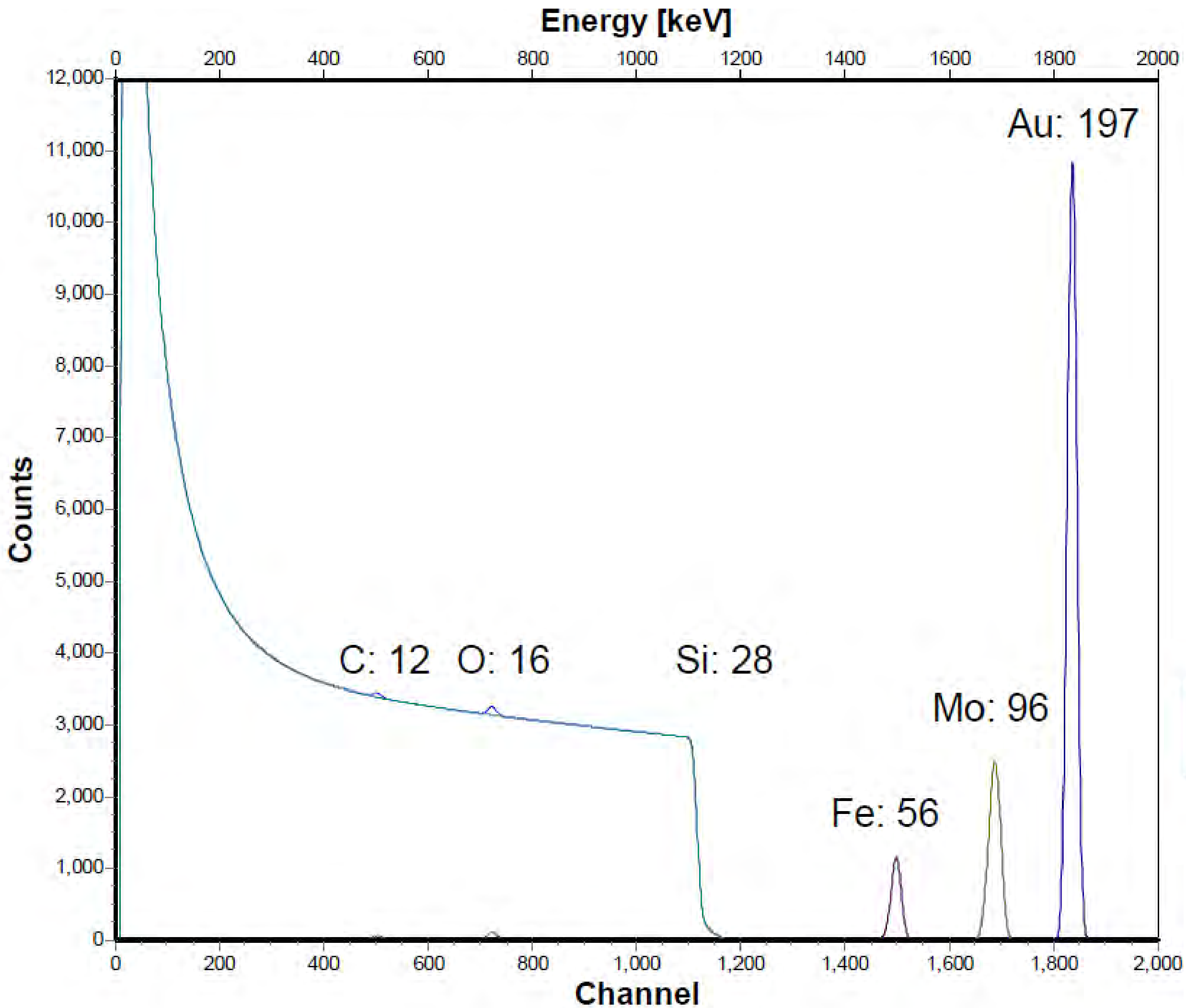
β: exit angle

θ: scattering angle

Optimized mass resolution for:

160º < θ <170º

RBS Scattering kinematics: example 1



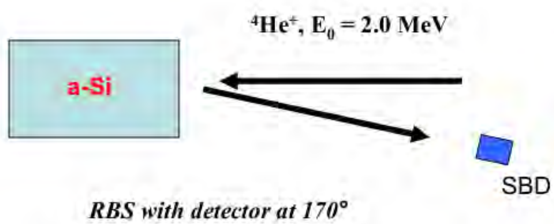
2MeV $^4He^+$, θ=165°

Backscattered from

C, O, Fe, Mo, Au

3×10^{16} atoms/cm^2 each

on Si substrate



Key features of RBS

Ability to quantify depth profile of buried species with a precision of ~ 3%

Qualitative information: **kinematic factor,** k

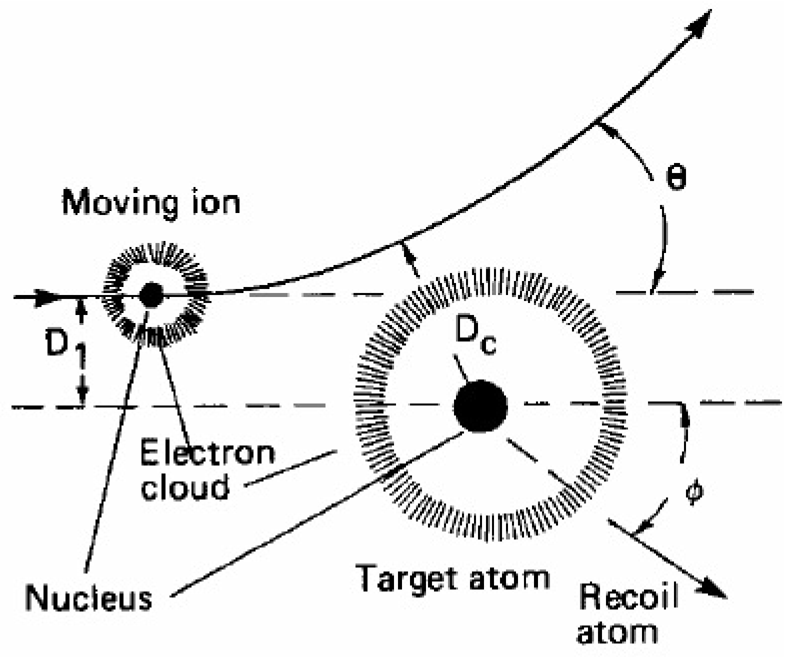
$$k = \frac{E_1}{E_o} = \left[\frac{\left(M_2^2 - M_1^2 \sin^2 \theta\right)^{1/2} + M_1 \cos\theta}{M_2 + M_1} \right]^2$$

Quantitative: **scattering cross section**, σ

$$\frac{d\sigma}{d\Omega} \equiv \sigma(\theta) = \left(\frac{Z_1 Z_2 e^2}{4E \sin^2\left(\frac{\theta}{2}\right)} \right)^2$$

2016 LONDON HRDP 8

Rutherford Cross Section



- Neglecting shielding by electron clouds
- Distance of closest approach large enough that nuclear force is negligible

⇒ Rutherford scattering cross section

$$\frac{d\sigma}{d\Omega} \equiv \sigma(\theta) = \left(\frac{Z_1 Z_2 e^2}{4E \ \sin^2\left(\frac{\theta}{2}\right)} \right)^2$$

Note that sensitivity increases with:

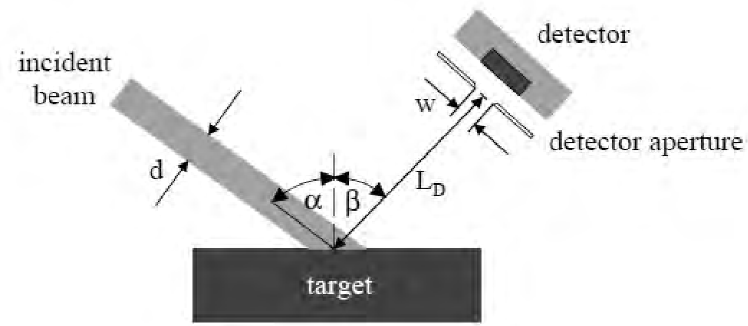
- Increasing Z_1
- Increasing Z_2
- Decreasing E

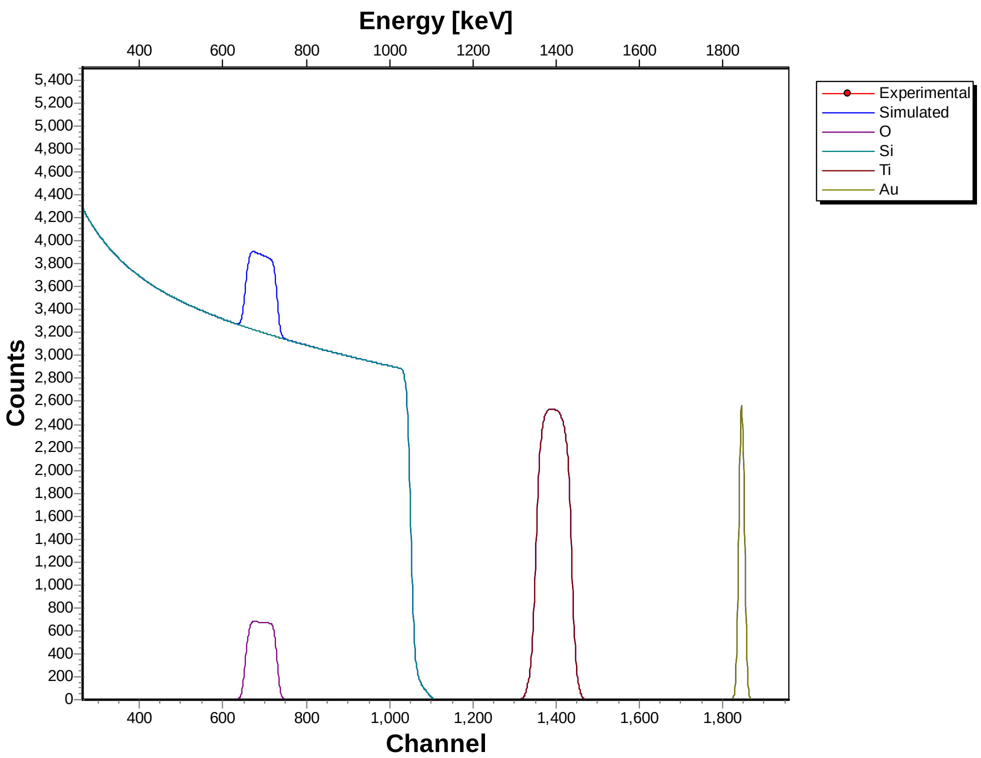
RBS spectra from thin and thick films

The integrated peak count A_i for each element on the surface can be calculated using this equation:

$$A_i = (Nt)_i \times Q \times \Omega \times \frac{\sigma(E,\theta)}{\cos\theta}$$

where
$(Nt)_i$ is areal density, atoms per unit area;
Q – ion beam fluency;
Ω – solid angle of the detector;
$\sigma(E, \theta)/\cos\theta$ – cross section of an element





2016 LONDON HRDP 8

Ion dose (fluency), solid angle, cross section

- **Ion dose (fluency), the number of incident particles (collected charge)**

  - measured by Faradey cup

  - $Q = I \times t$

- **Solid angle, in steradians, sr**

  - stays constant for a particular detector/detector slit

  - need to be verified by the calibration standard measurements

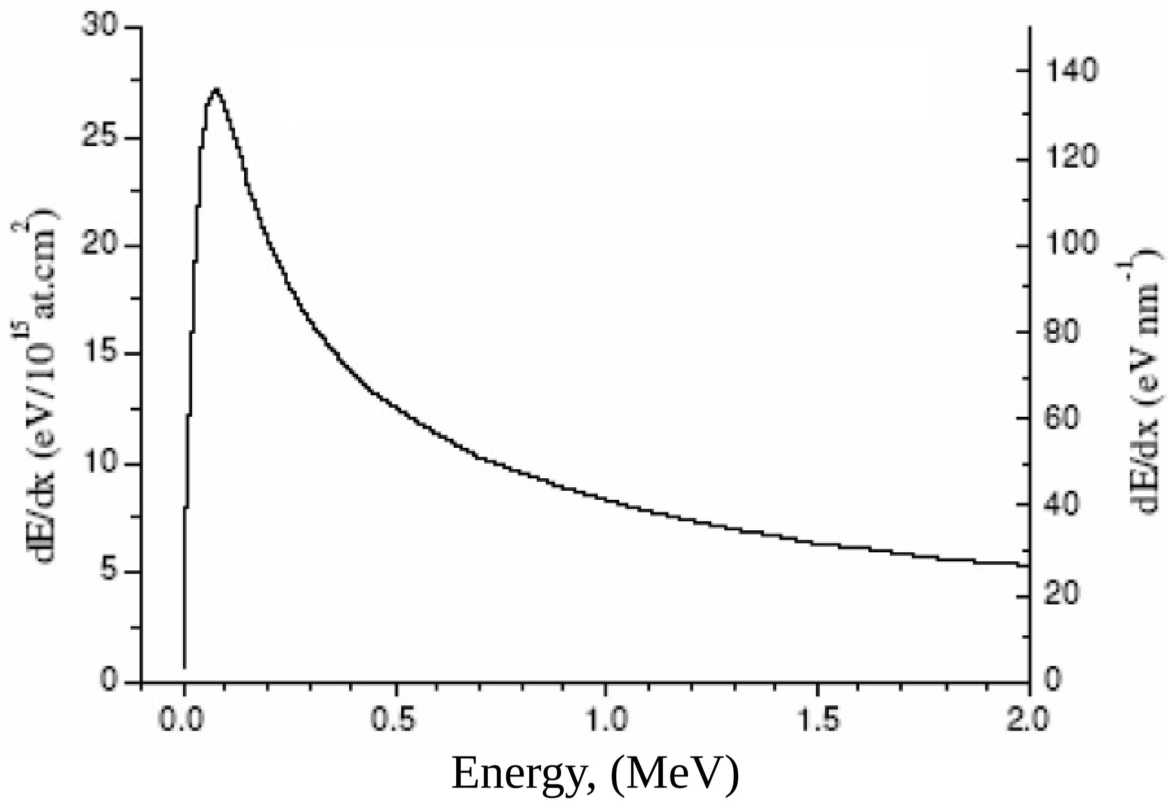
- **Cross section (or differential cross section), in cm^2/sr of the element**

  - well known (tabulated) in Rutherford cross section regime

High-resolution depth profiling parameters

- Energy dependence of dE/dx for H^+ and He^+
- Maximum of ~ 14 eV/Å at ~ 100 keV for Si

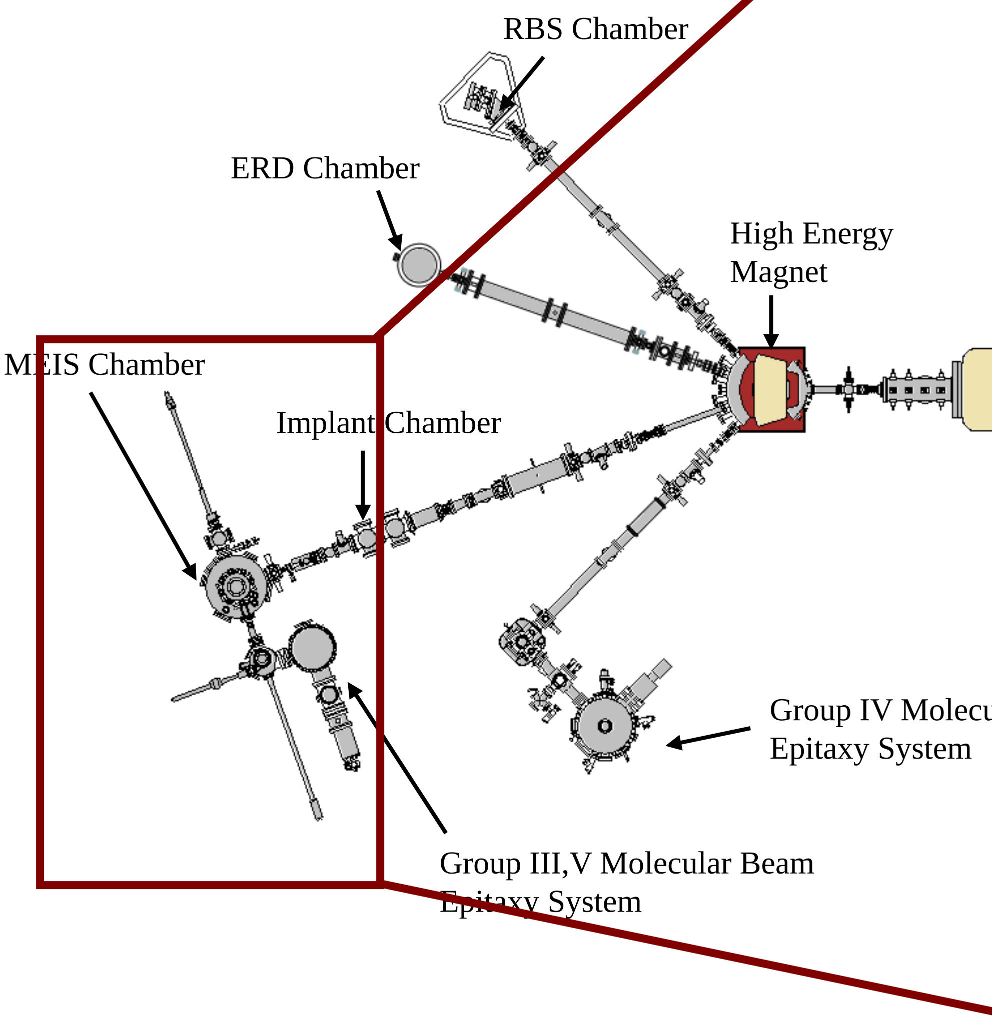
⇒ This helps! Plus use of better ion detection equipment!

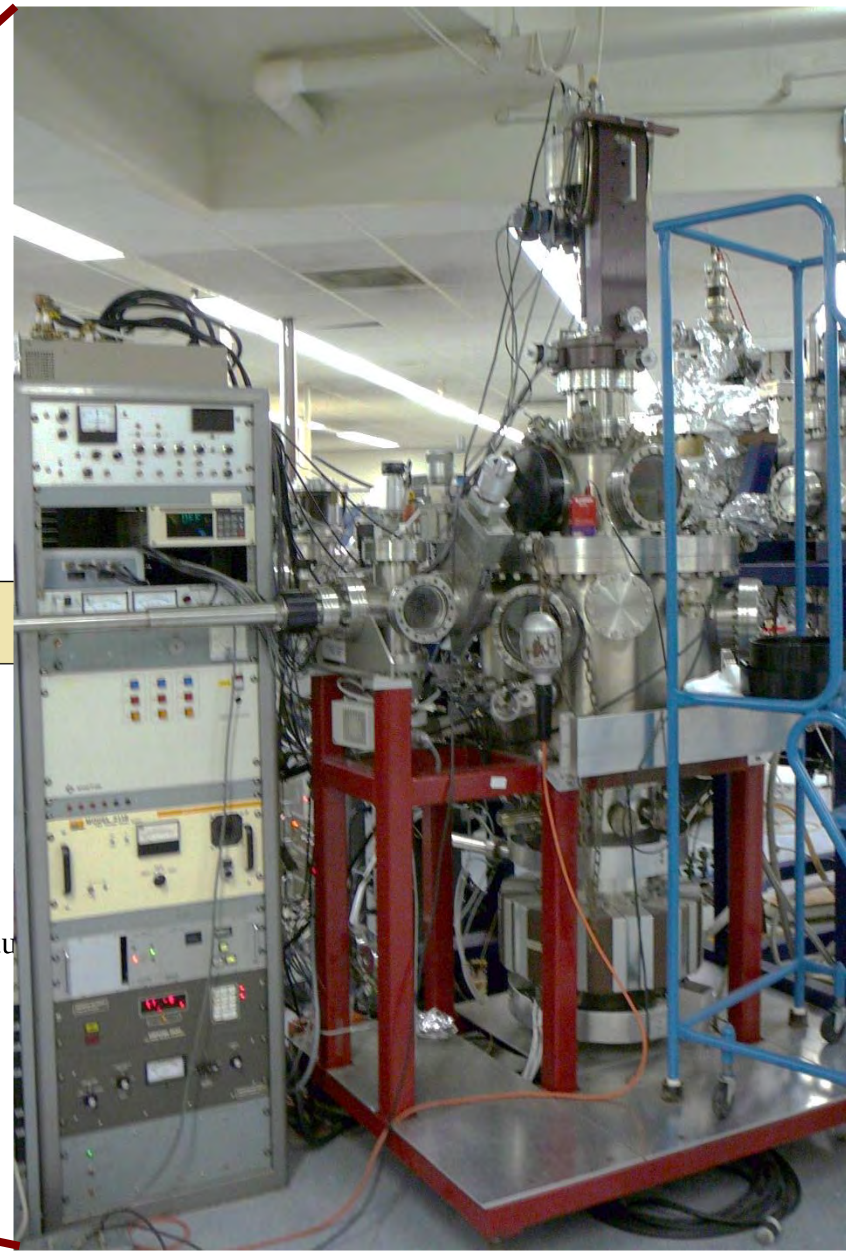


Ion detection equipment

- Detector energy resolution < 1keV
- Magnetic spectrometers
  - Kyoto University (Kimura)
  - Kobelco
- Electrostatic analyzers
  - FOM – IBM (Tromp, van der Veen)
  - High Voltage Engineering
  - Ion-TOF
- TOF detectors

MEIS at Western University



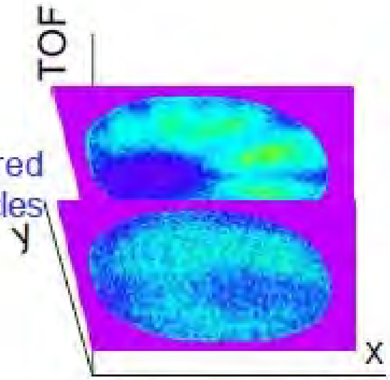


Development of 3D-MEIS

RIKEN S. Shimoda and T. Kobayashi

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

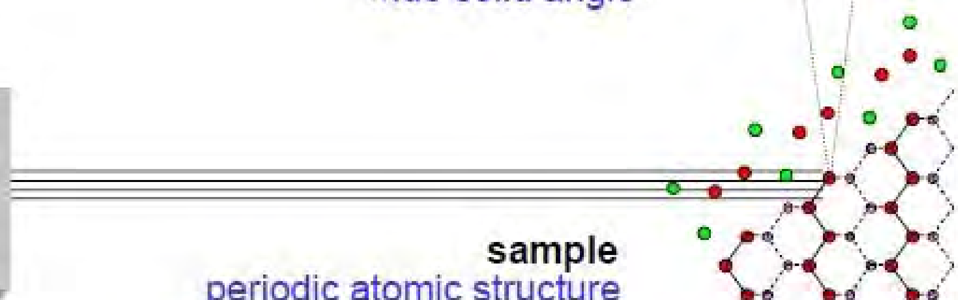
- 2D blocking pattern
- flight times of scattered (and/or recoiled) particles



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

wide solid angle

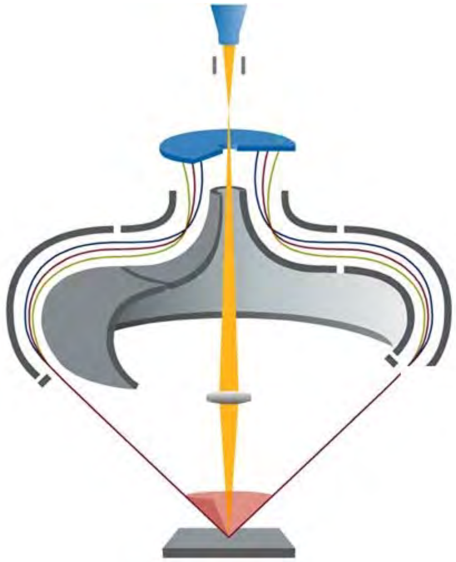
incident beam
- Ion : He+
- Energy : 100 keV
- Repetition : 500 kHz

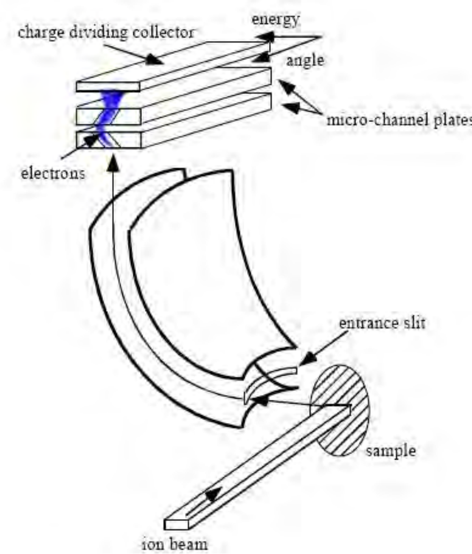


sample
periodic atomic structure

Uncertainties in depth profiling analysis

Issues.	What they affect	Solution
Neutralization ratio for H^+ (He^+, etc.)	Absolute concentrations (relative – ok)	• Measurement by SSD • Reference samples
Energy loss and straggling parameters for H^+ in materials	Scaling of the depth; modeling	• Independent analysis by TEM, XPS • Reference
Non-gaussian energy distribution and non-statistical number of loss events	Peak shape; modeling, especially at the surface	• Not an issue for films >2nm; new basic theory needed
Film thickness, roughness and compositional gradient	May be confused with each other	• Independent measurements by TEM, AFM, XPS, etc.





Electrostatic detectors

$$A_i = (Nt)_i \times Q \times \Omega \times \frac{\sigma(E,\theta)}{\cos\theta} \times f^+$$

Need to detect hydrogen with high sensitivity and high depth resolution…

Some advantages of ERDA: good dynamic range; excellent hydrogen sensitivity; very well suited for analysis of light elements

Some disadvantages: Resolution; Sensitivity to surface contaminations

Method	High Sensitivity	High Resolution	Quantitative
SIMS	+	±	–
ERDA	+	-	+
NRA/NRP	+	±	+
LEIS	+	±	±
ME-ERD	+	+	±

2016 LONDON HRDP 8

Common Pitfalls for ion detection

- **Damage effects are significant $\Rightarrow$ surface needs to be refreshed under the beam**
- **Uniform lateral distribution is assumed**
- **Charge fractions can vary between samples**
- **Accurate background fit is necessary to get quantitative fitting $\Rightarrow$ calculations are necessary!**