

Ion Beam Analysis and Modification for Current Issues in Surface Science

Lyudmila V. Goncharova

*Department of Physics and Astronomy,
Western University, London, Ontario
lgonchar@uwo.ca*

Outline

- Production of Ion Beams
- Basics of Ion-Solid Interactions

I: Ion Beam Analyses

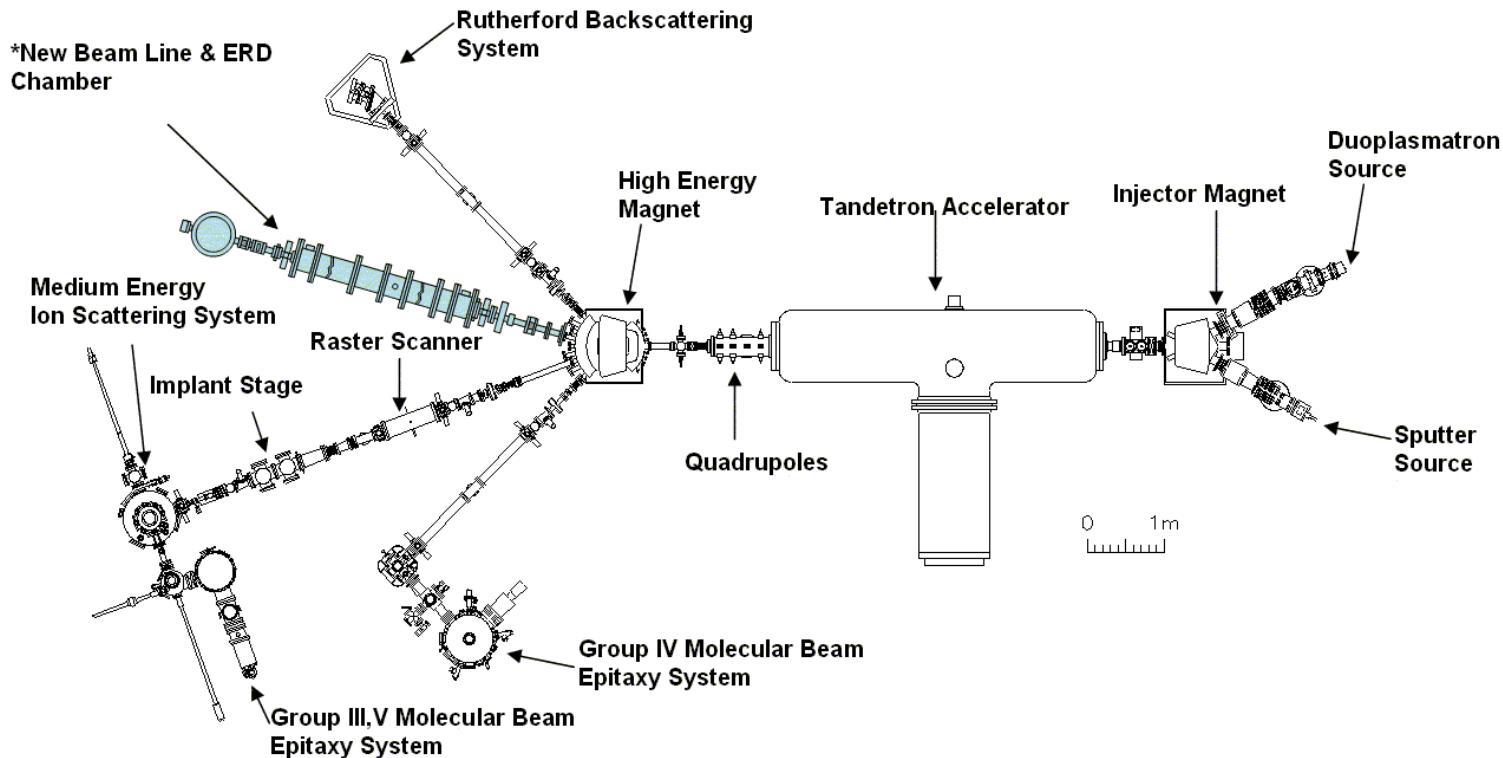
- Rutherford Backscattering Spectrometry
- Elastic Recoil Detection
- Medium Energy Ion Scattering
- Research Examples: interfacial analysis of complex oxide thin film stacks; diffusion and oxidation processes with sub-nm resolution

II: Ion Beam Modification

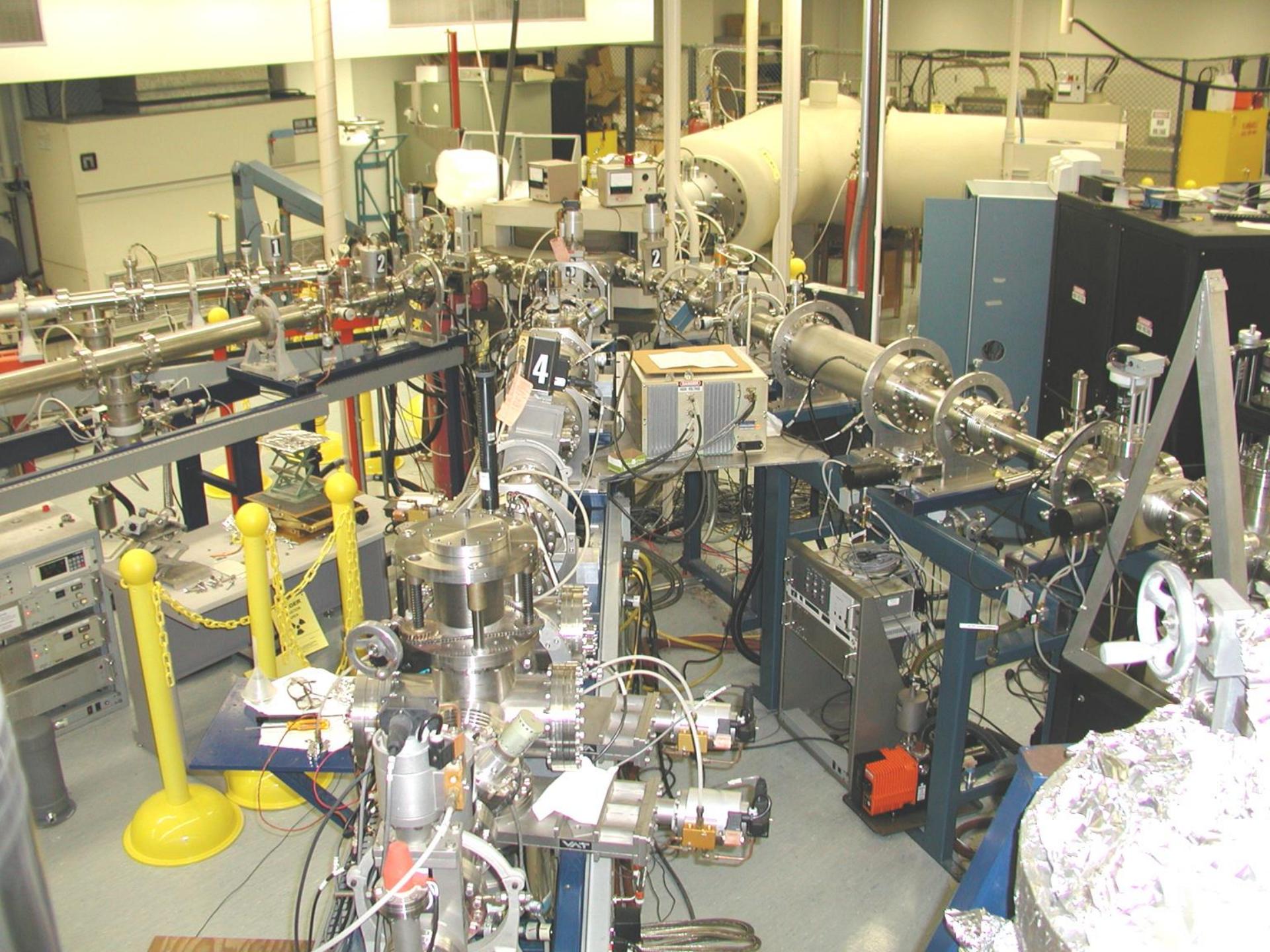
- Implantation
- Research Examples: formation of Si and Ge quantum dots

- Conclusions
- References

Tandetron Ion Scattering facility at UWO



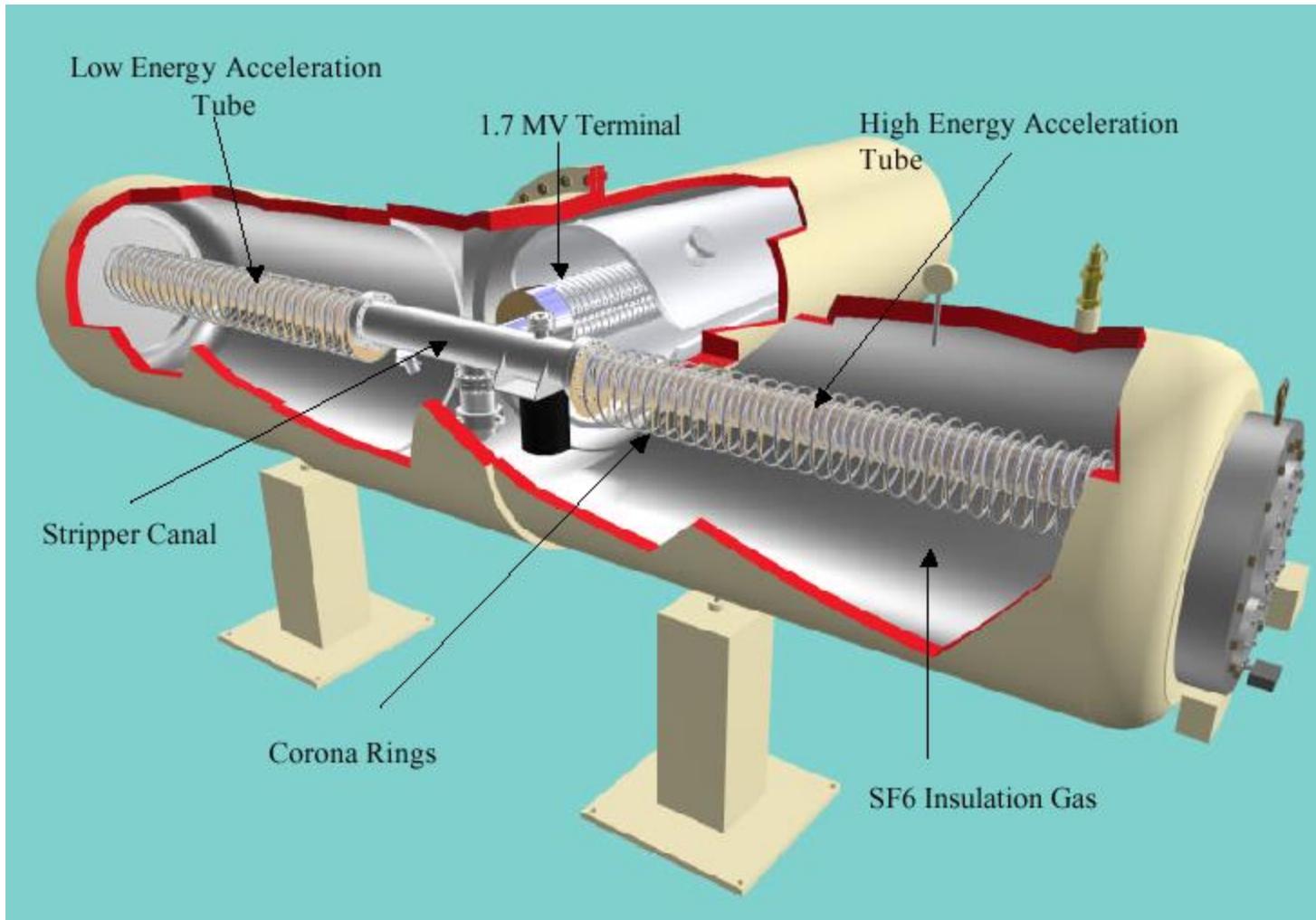
Rutherford Backscattering (RBS) and Medium Energy Ion Scattering (MEIS)
Elastic Recoil Detection (ERD)
Nuclear Reaction Analysis (NRA)
Particle-Induced X-ray Emission (PIXE)
Various implantation capabilities...



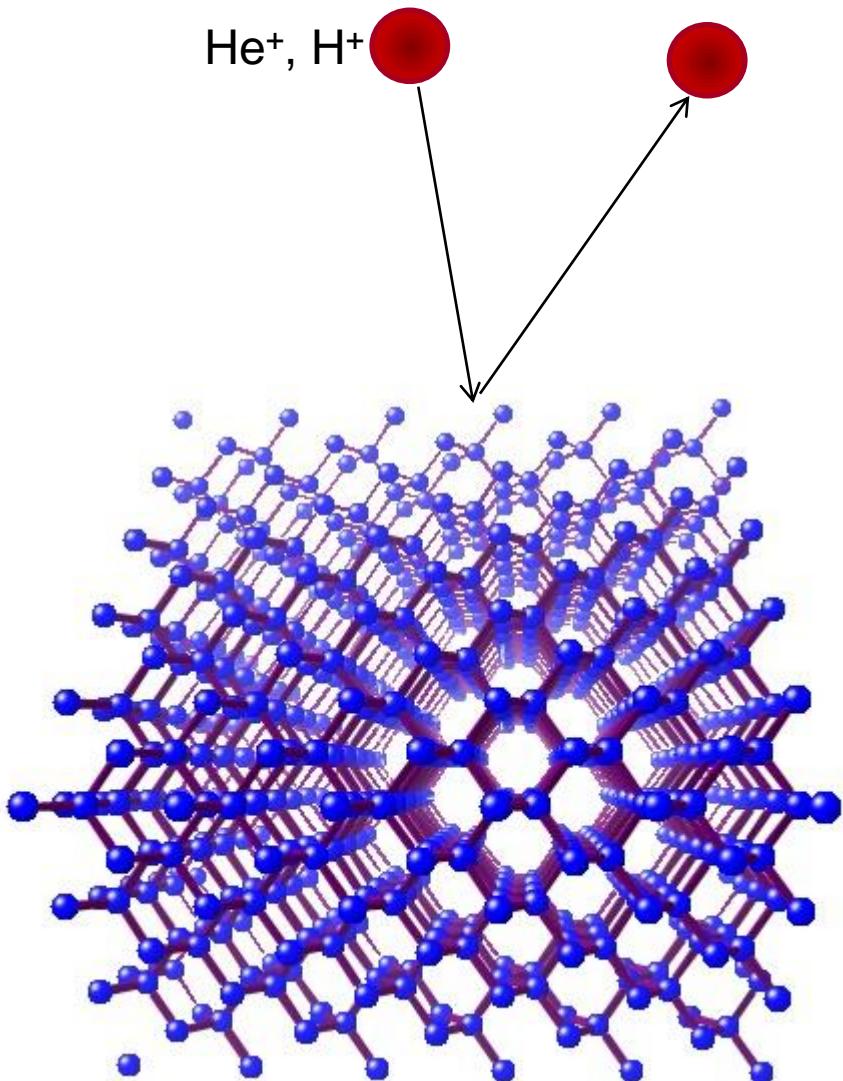
Tandetron operating principle

- (1) Begin with **negative ions** via sputtering for most species
- (2) Accelerate to kinetic energy = qV_t where V_t = terminal voltage (MV)
and $q_i = -1$ so that $E_t \equiv V_t$ [MeV]
- (3) Ions traverse a **stripper gas** at the high voltage terminal to produce a charge state distribution of **positive ions**
- (4) Accel/decel mode is available when the stripper gas is **OFF**: used for $E_{ion} \leq 100$ keV and the incident ions then have $q_i = -1$

Inside Tandetron...



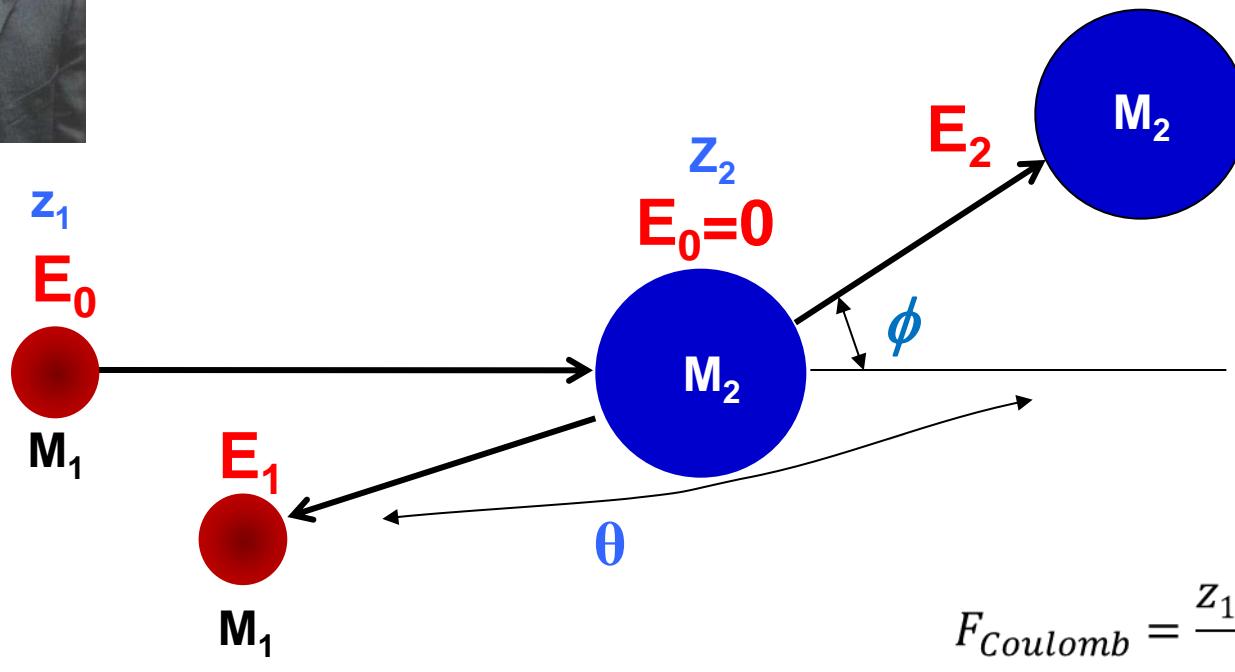
Ion Beam Analysis



- (1) elastic scattering
⇒ Rutherford Backscattering
- (2) fast recoils arising from elastic scattering
⇒ Elastic Recoil Detection
- (3) steering effects due to the crystalline structure of target atoms (channeling)
- (4) inelastic processes: energy loss as a function of depth
- (5) X-ray emission (PIXE) and nuclear reactions (NRA)



Rutherford Backscattering Spectrometry Elastic Collisions!



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

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

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

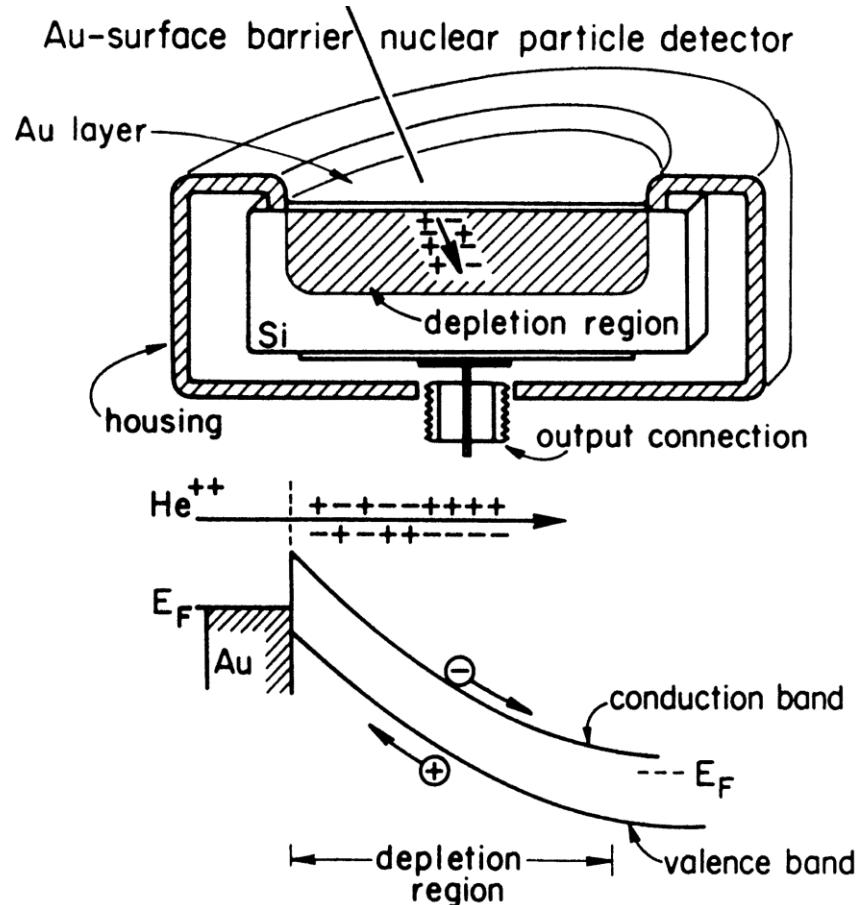
$$0 = M_1 v_1 \sin \theta - M_2 v_2 \sin \phi \quad (\text{Eq.3})$$

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

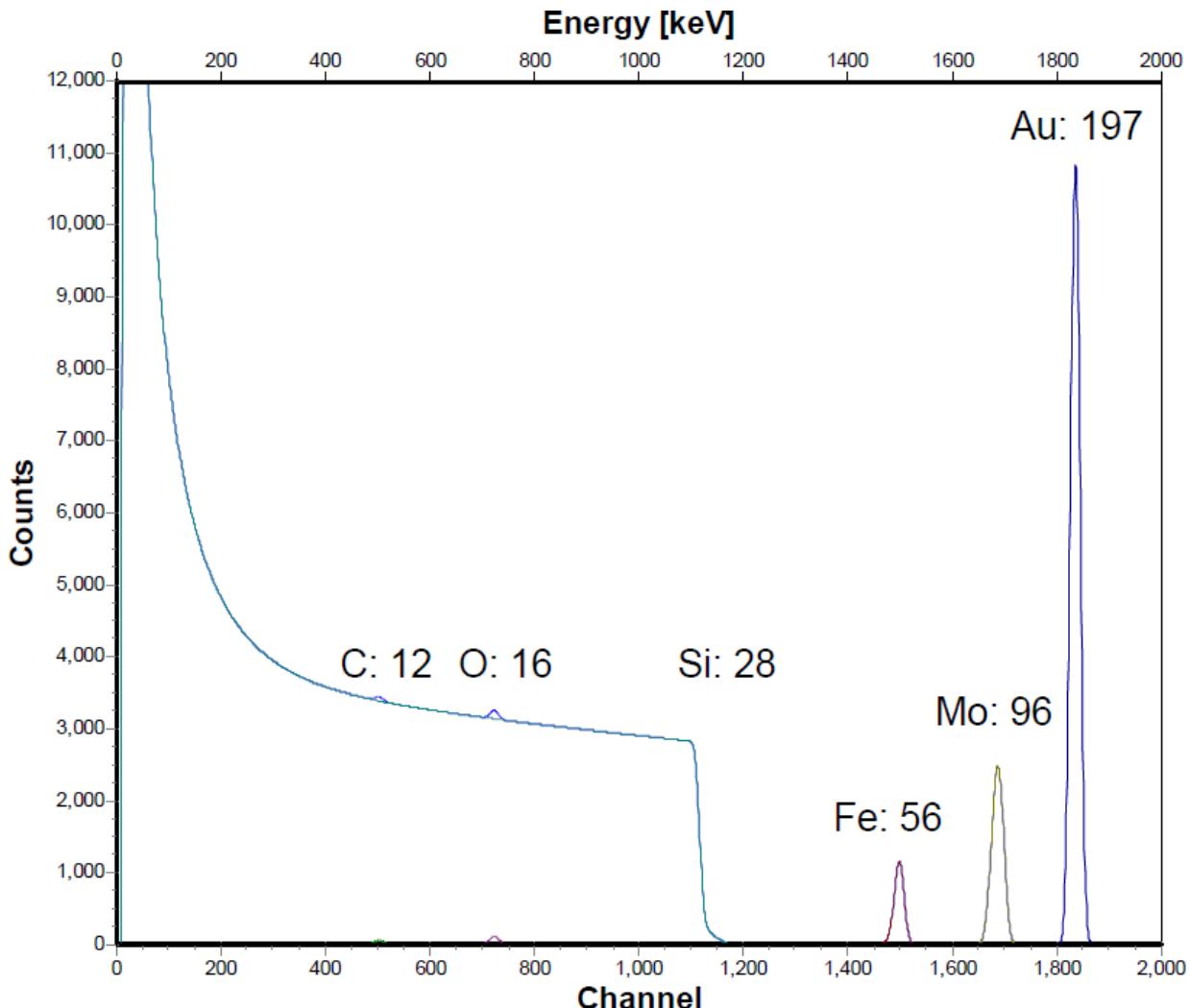
Charged Particle Detectors

Schematic diagram of the operation of a surface barrier detector (SBD)

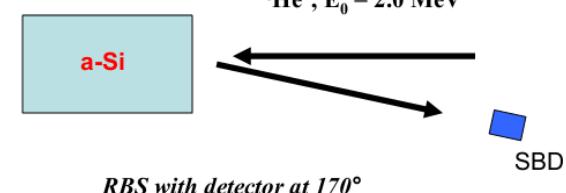
- Silicon disc with gold film mounted in the detector housing
-
- He⁺⁺ particle is forming holes and electrons over its penetration path.
- The energy band diagram of a reverse biased detector (positive polarity on n-type silicon) shows the electrons and holes swept apart by the high electric field within the depletion region.



Scattering kinematics: example 1



2MeV ${}^4\text{He}^+$, $\theta=165^\circ$
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%

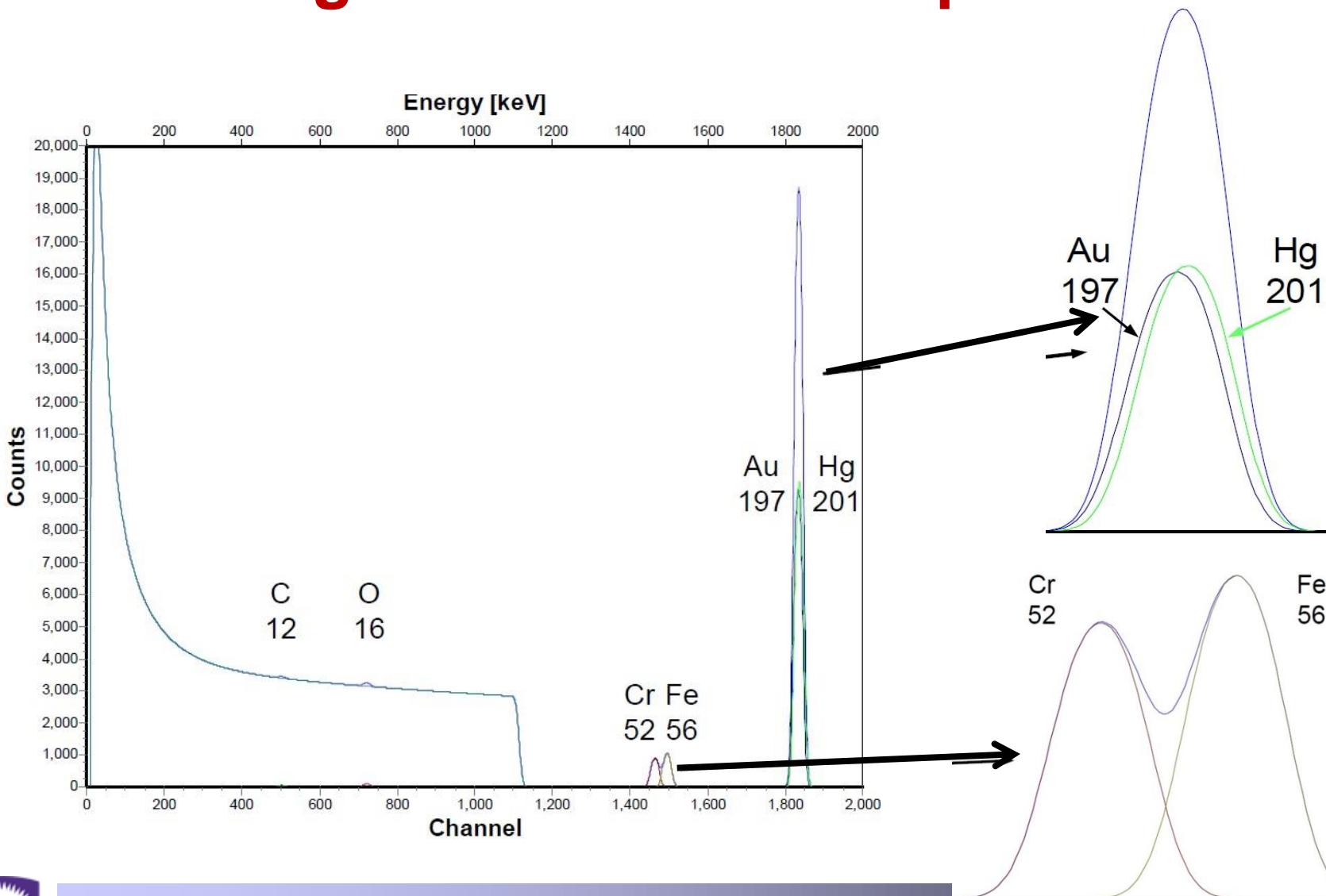
Qualitative information: **kinematic factor, k**

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

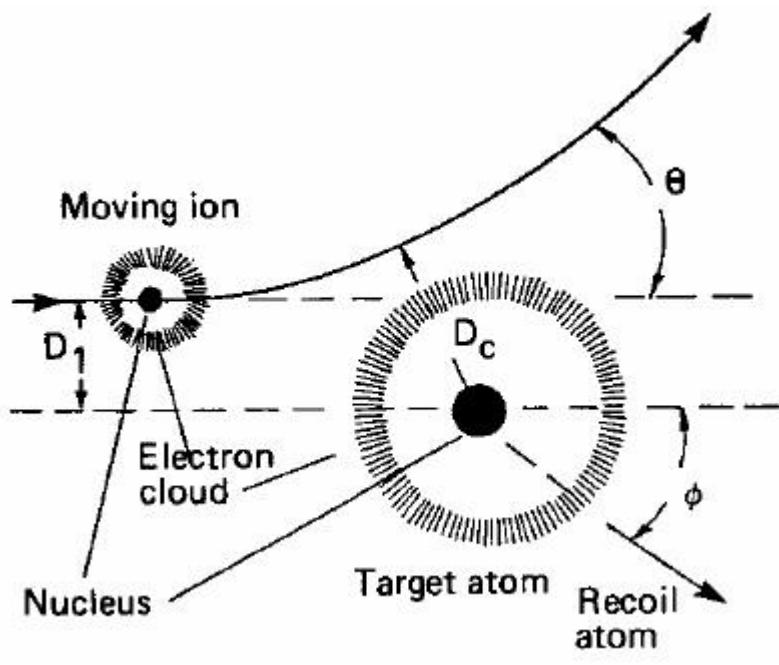
Quantitative: **scattering cross section, σ**

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

Scattering kinematics: example 2



Rutherford Cross Section



- Neglecting shielding by electron clouds
 - Distance of closest approach large enough that nuclear force is negligible
- ⇒ Rutherford scattering cross section

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

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:

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

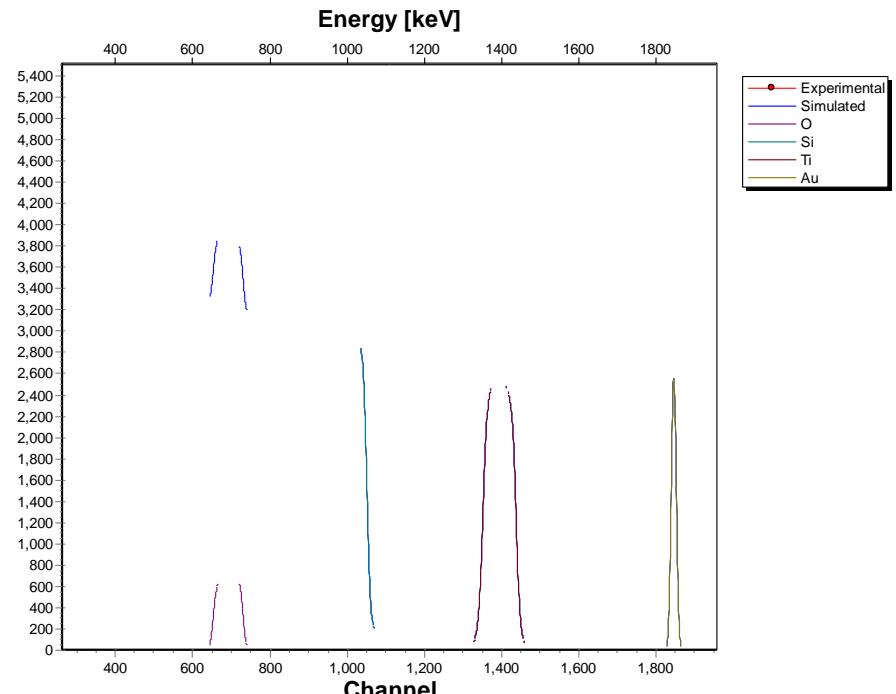
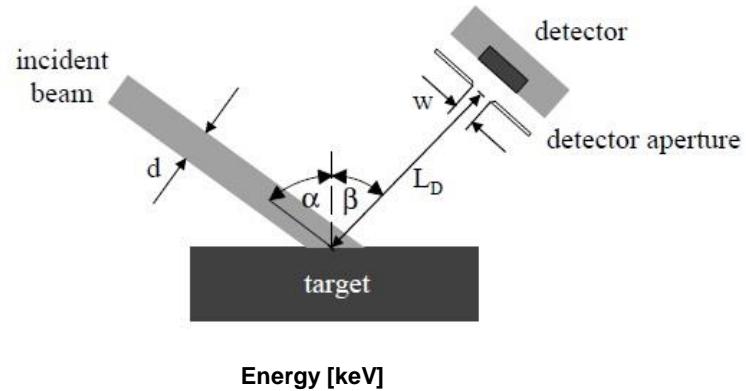
where

$(Nt)_i$ 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



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

Areal density: note about units

Areal density = ρt [g/cm²],

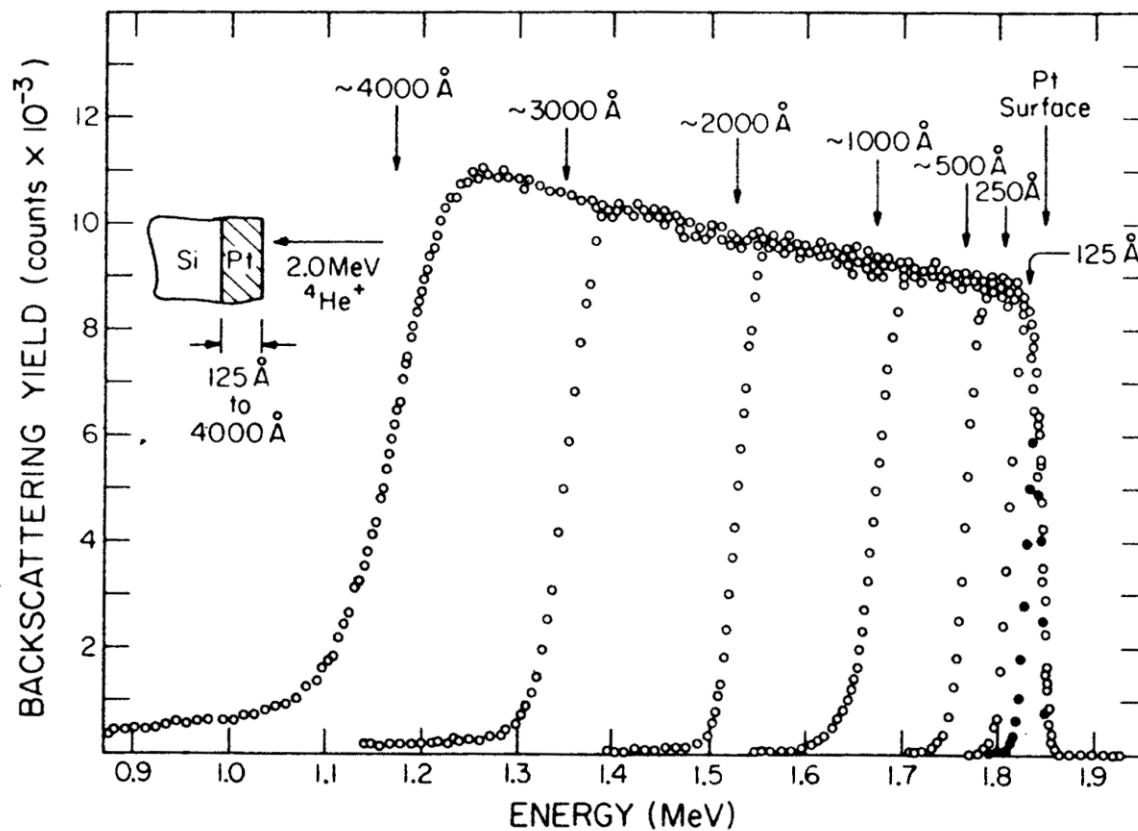
where ρ = g/cm³, t = cm


$$\frac{N_0 \rho t}{M} \text{ [at./cm}^2\text{]}$$

where M = atomic mass [amu], N_0 = Avogadro's number

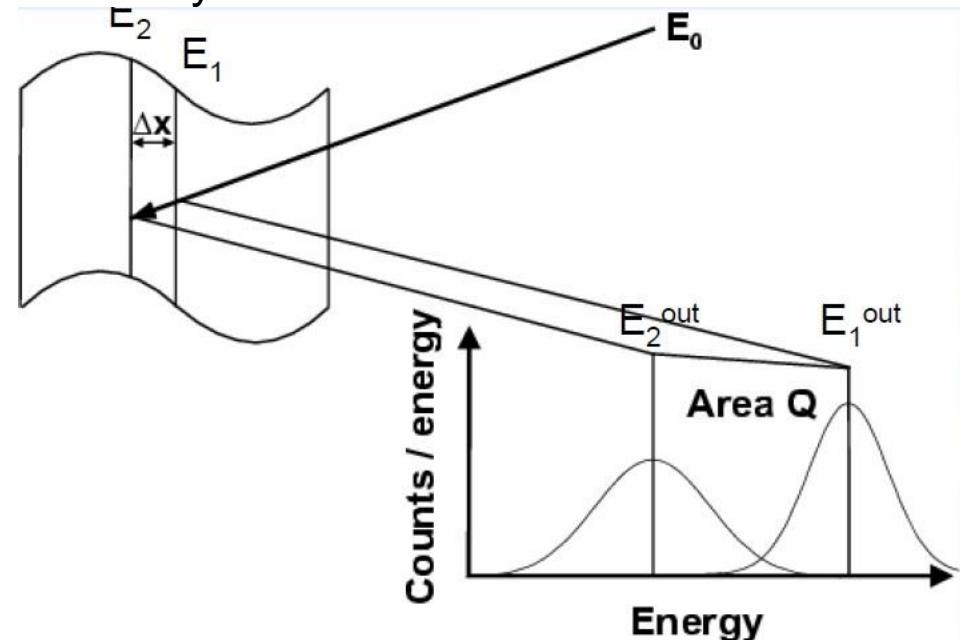
In absolute numbers – close to thickness in Å

Thickness measurement



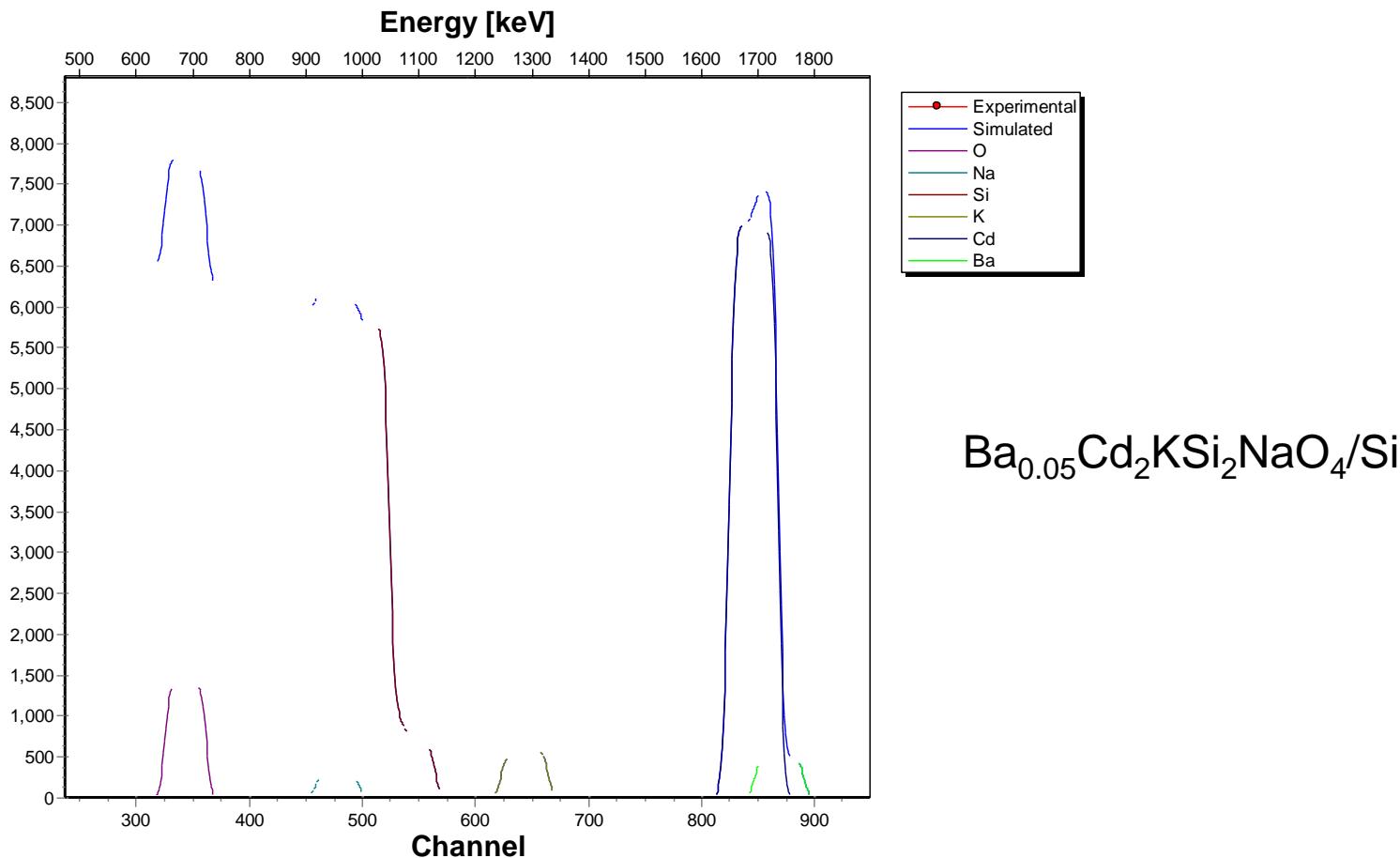
RBS Spectrum of a thick film

- Target is divided into thin sublayers (“slabs”)
- Calculate backscattering from front and back side of each sublayer taking energy loss into account
- For each isotope of each element in sublayer



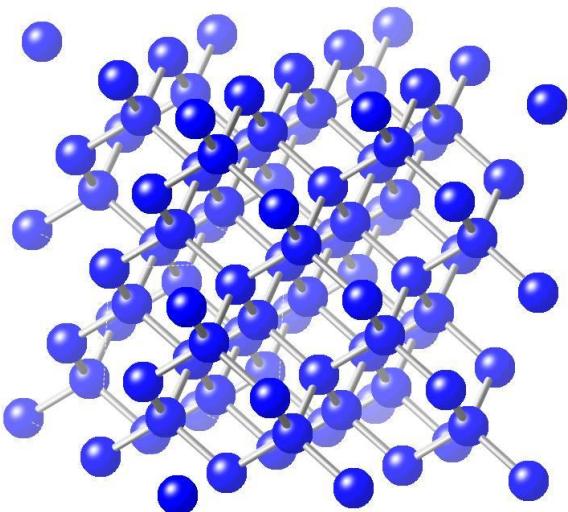
Stoichiometry

2MeV ${}^4\text{He}^+$, backscattered from ceramic films on Si substrate



Ion channeling and blocking

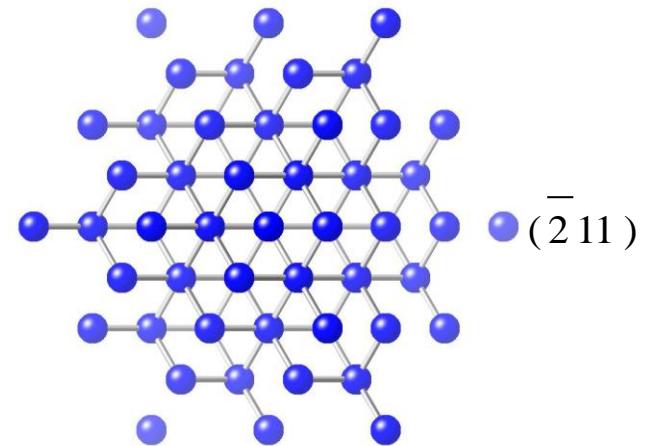
Si (diamond structure)



x
y
z

• Si(111)

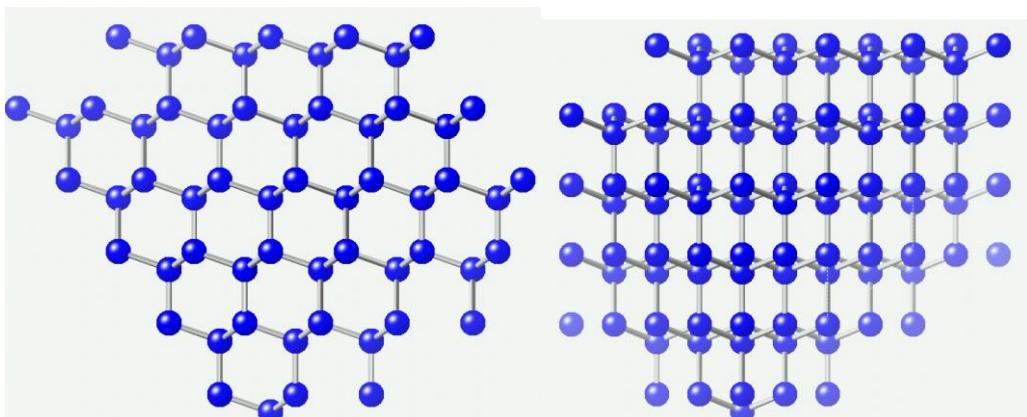
(0 $\bar{1}$ 1)



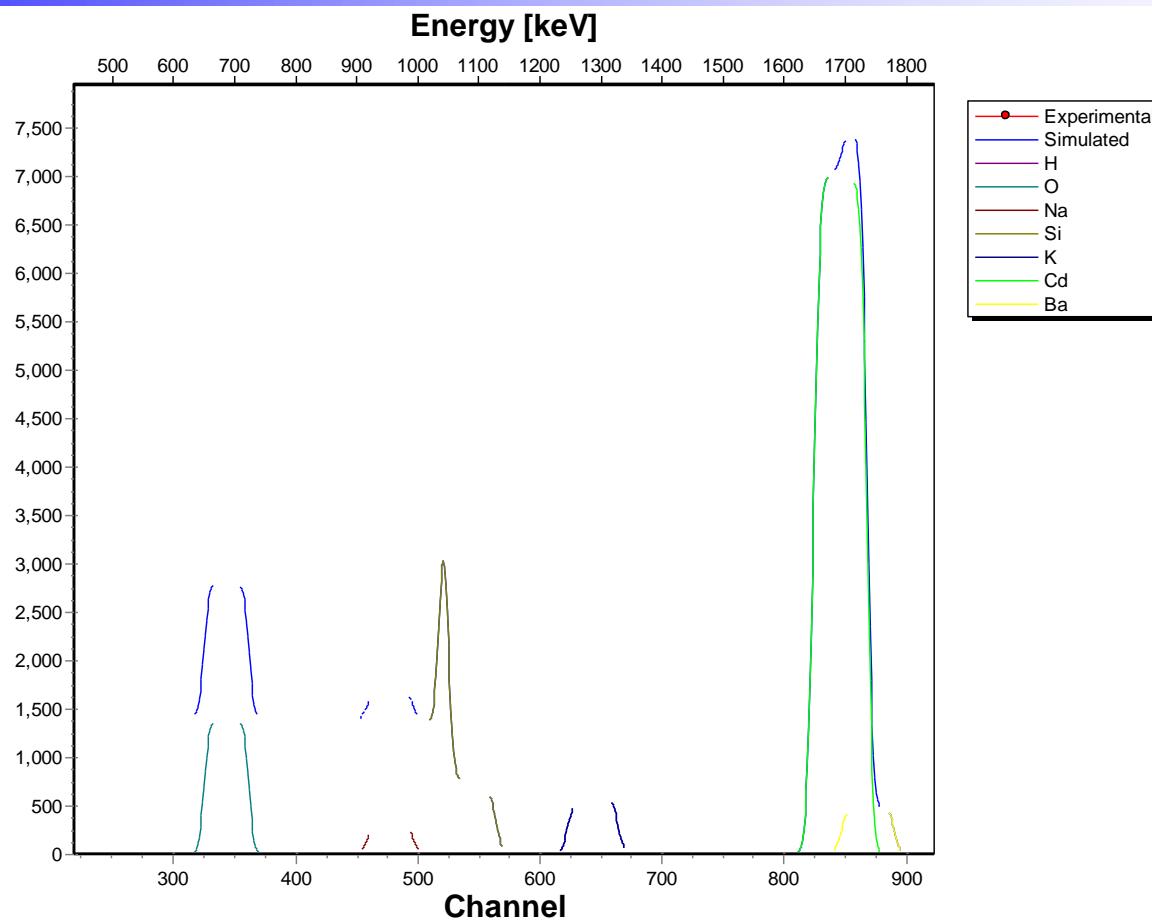
• Si(111) – side view

(0 $\bar{1}$ 1)

($\bar{2}$ 1 1)



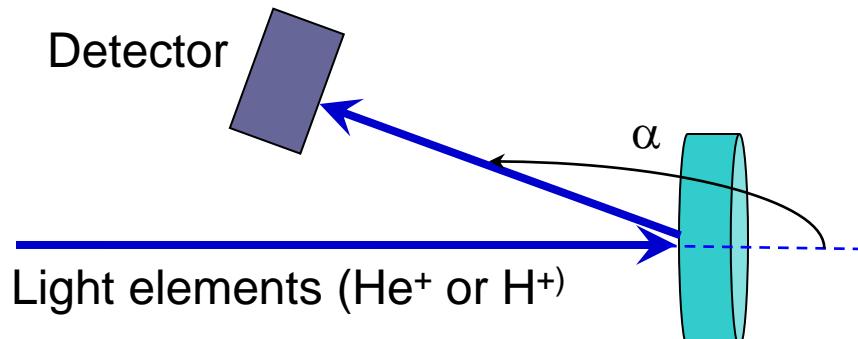
Use crystal structure of the substrate



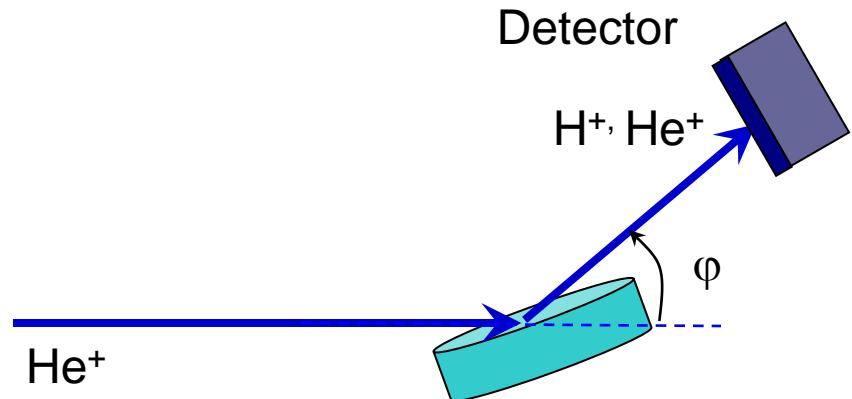
- Substrate can be aligned to a major crystallographic direction to minimize background signal in some cases

Elastic Recoil Detection (ERD)

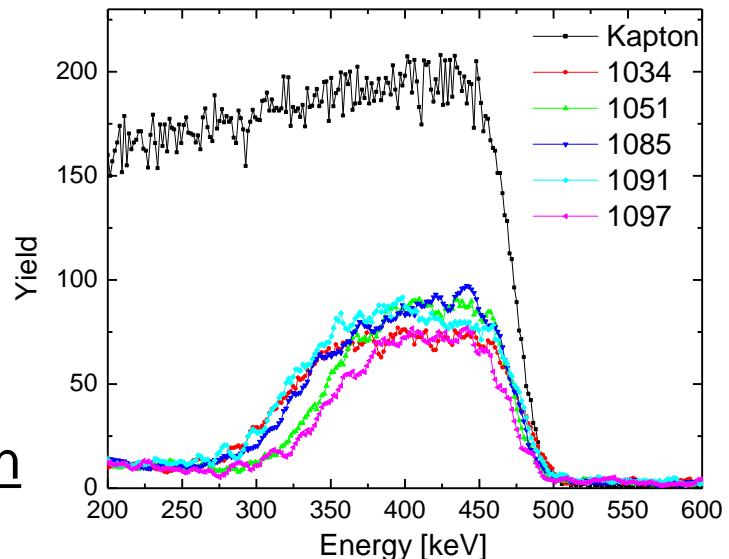
Heavy Elements by MEIS or RBS



Light Elements by Elastic Recoil Detection



~150nm SiONH/Si(001)



“Classical” ERD

Incident energy = 1.6MeV He⁺

Incident angle = 75°

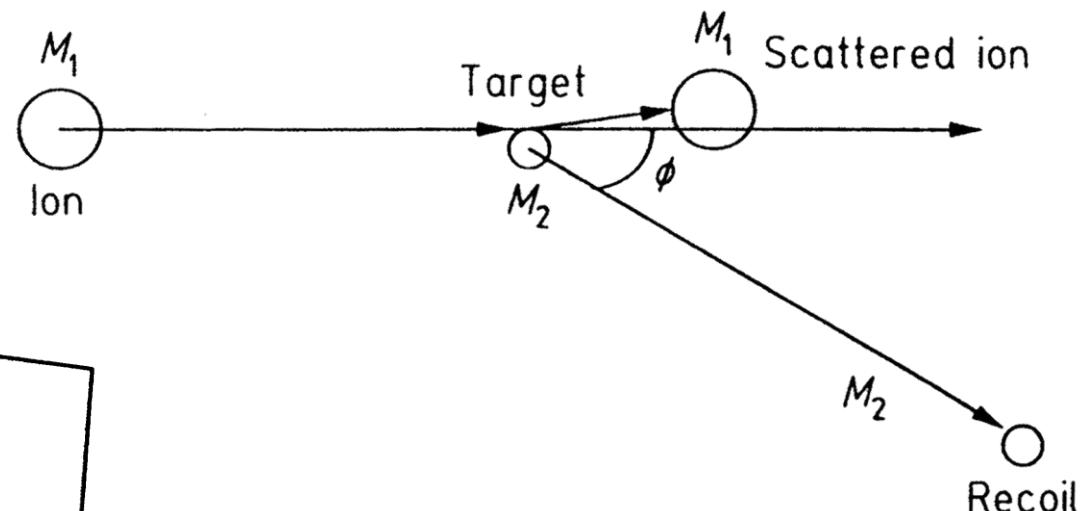
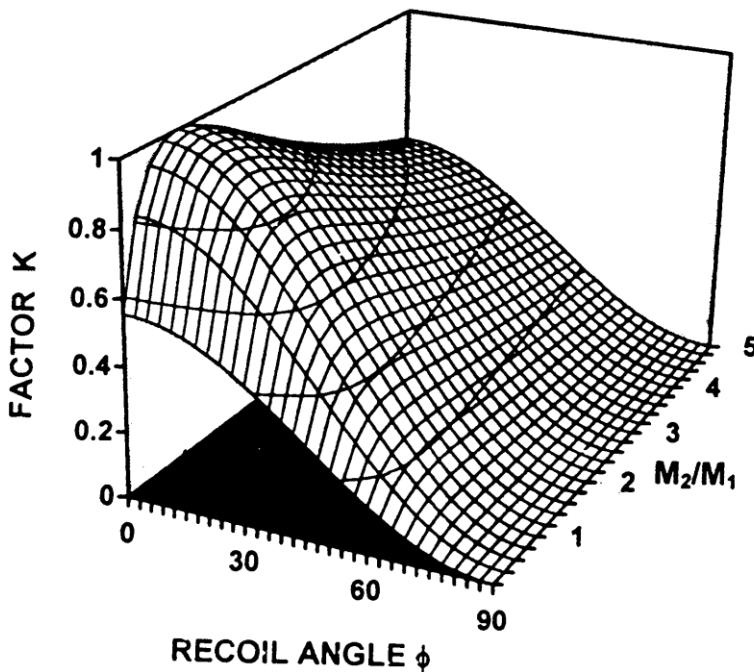
Recoil Angle = 30°

Al-mylar (range foil)

ERD Principles and Limitations

$$E_2 = k E_0$$

$$k = \frac{4 M_1 M_2}{(M_1 + M_2)^2} \cos^2 \phi$$



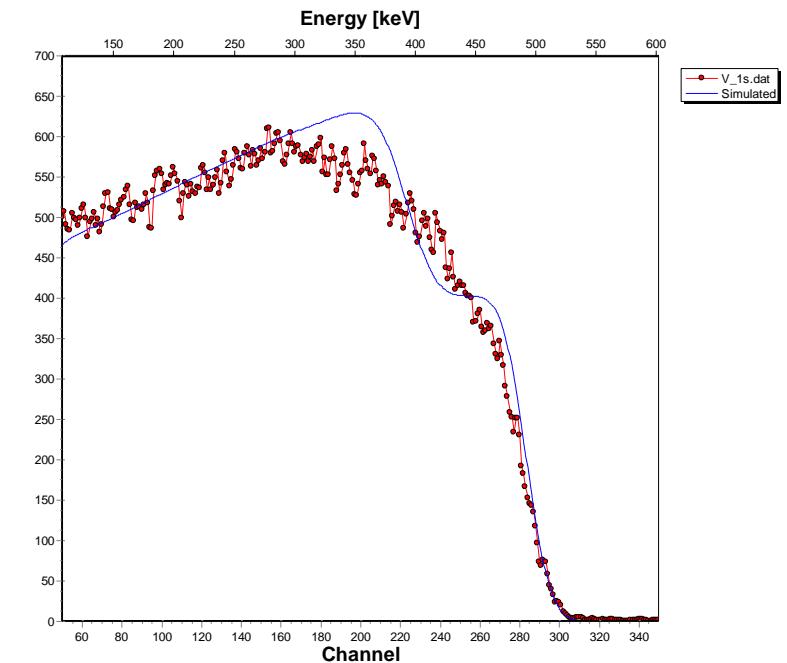
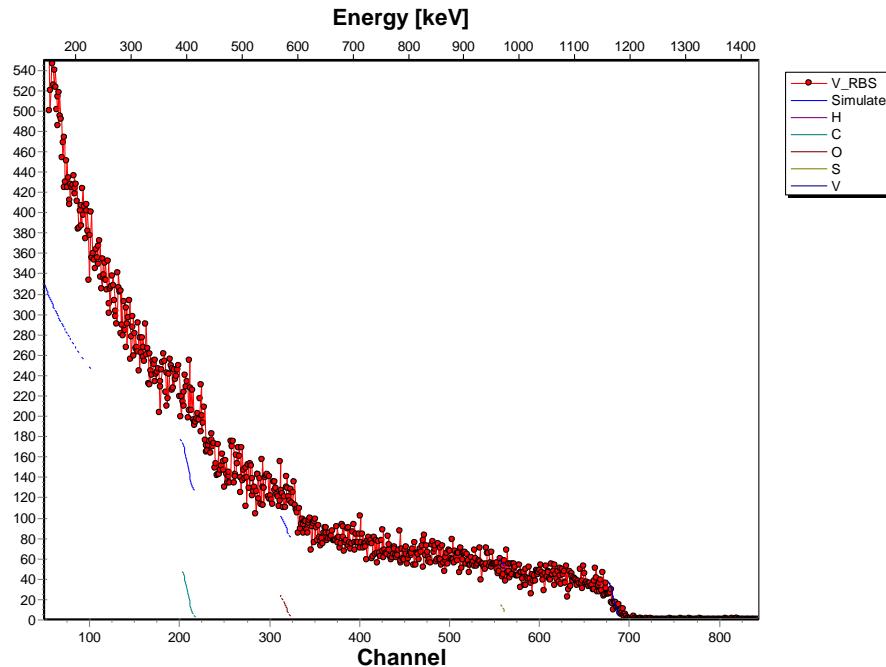
Some advantages of ERD:

- good dynamic range;
- excellent hydrogen sensitivity;
- very well suited for analysis of light elements

Some disadvantages:

- Resolution (limited by detector, ~10-15keV);
- sensitivity to surface contamination

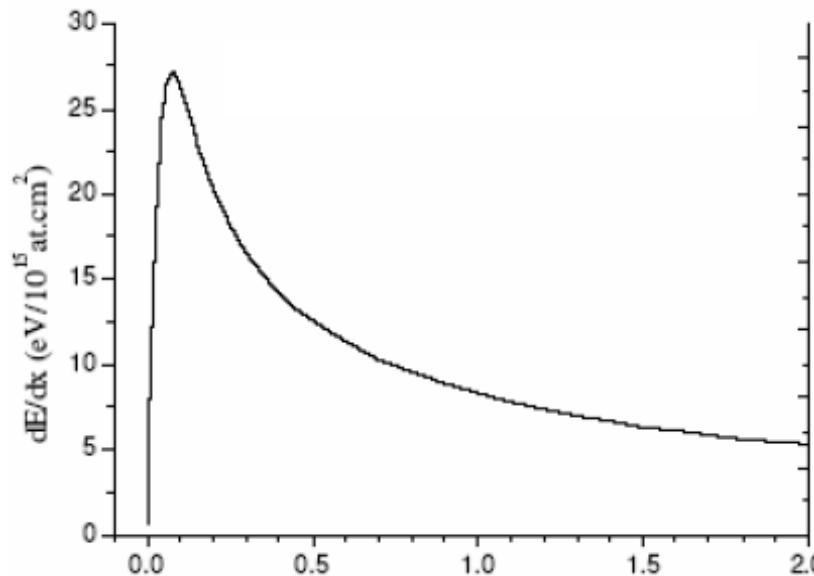
RBS plus ERD \Rightarrow Full Stoichiometry!!!



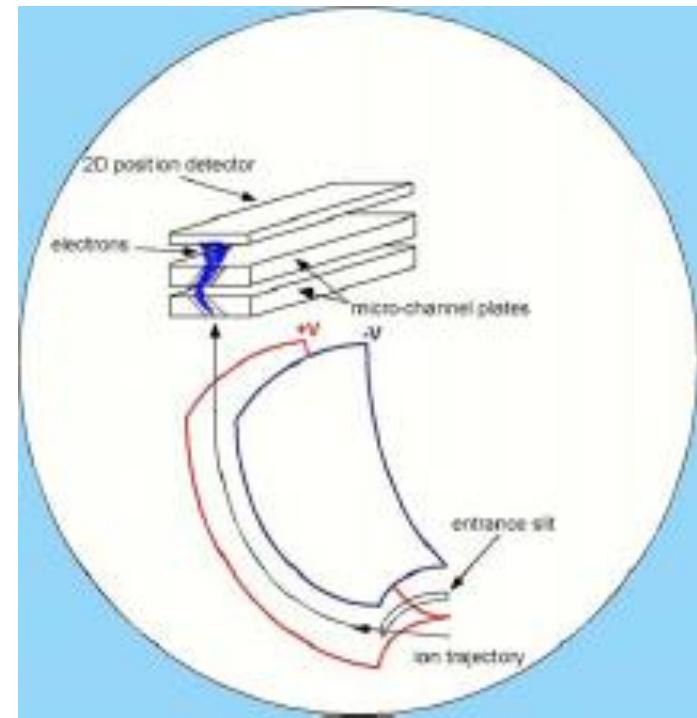
RBS and ERD results for $\text{VS}_x\text{O}_y\text{C}_z:\text{H}$

Assumption: $\sim 900\text{\AA}$ $\text{V}_{0.03}\text{S}_{0.03}\text{O}_{0.25}\text{C}_{0.44}\text{H}_{0.25}/(\text{bulk}) \text{V}_{0.03}\text{S}_{0.03}\text{O}_{0.13}\text{C}_{0.44}\text{H}_{0.37}$

A comparison between RBS and MEIS



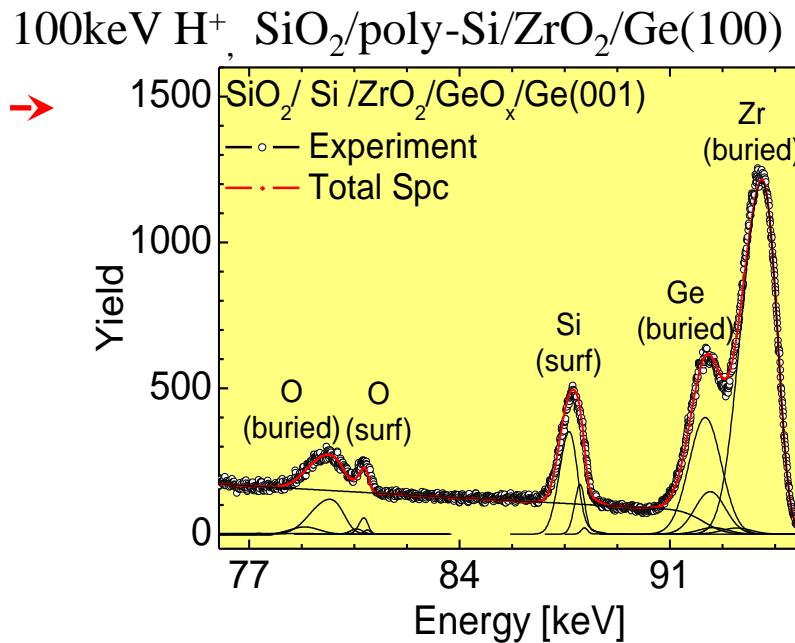
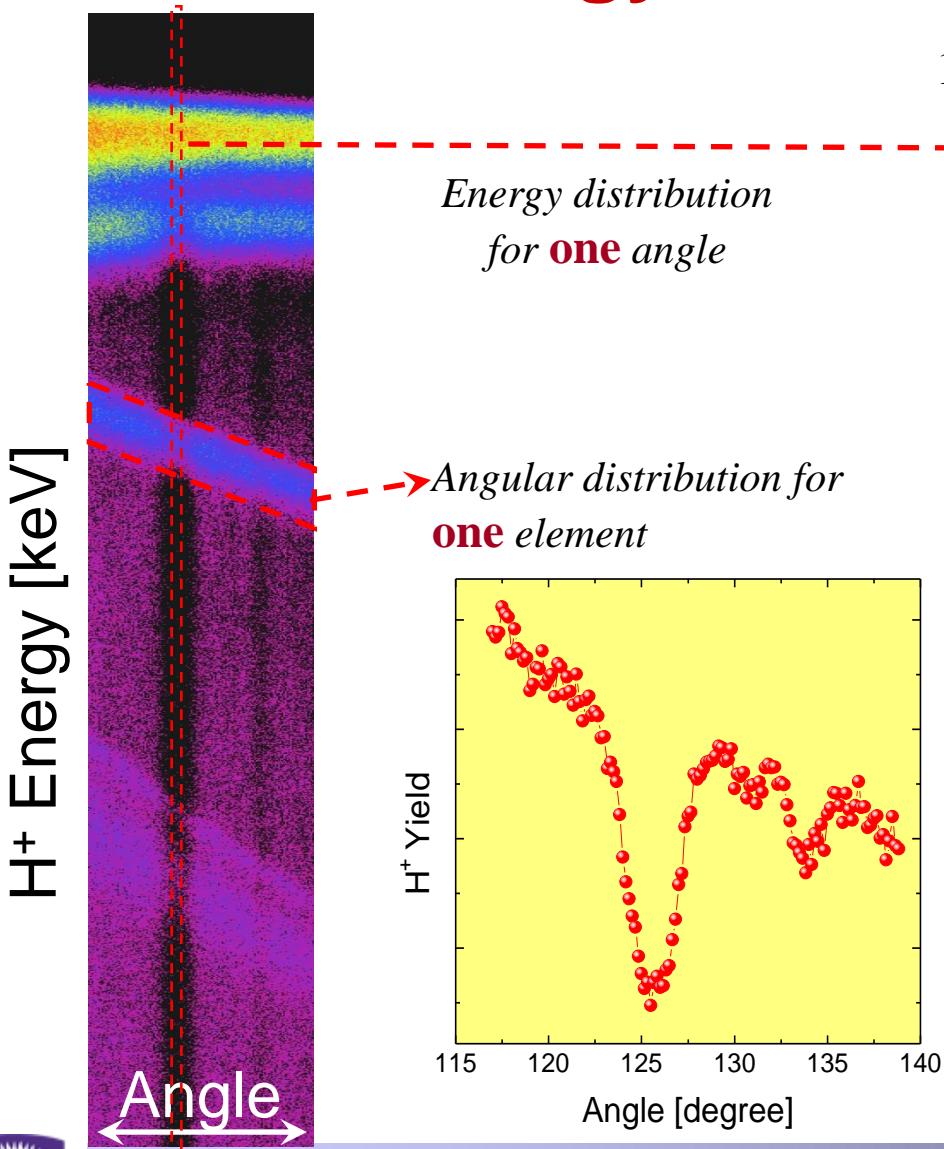
Close to maximum of $\sim 14 \text{ eV}/\text{\AA}$ at $\sim 100 \text{ keV}$!
This helps, but the greater advantage is the
use of better ion detection equipment!



	RBS	MEIS
Ion energy	$\sim 2 \text{ MeV}$	$\sim 100 \text{ keV}$
Detector resolution	$\sim 15 \text{ keV}$	$\sim 0.15 \text{ keV}$
Depth resolution	$\sim 100 \text{ \AA}$	$\sim 3 \text{ \AA}$

2 basic advantages vs. RBS: Often better dE/dx , superior detection equipment

Medium Energy Ion Scattering (MEIS)



Energy distributions:

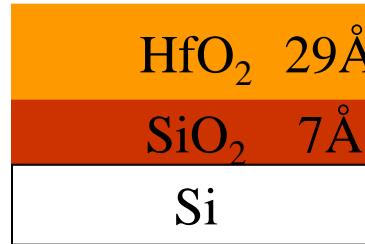
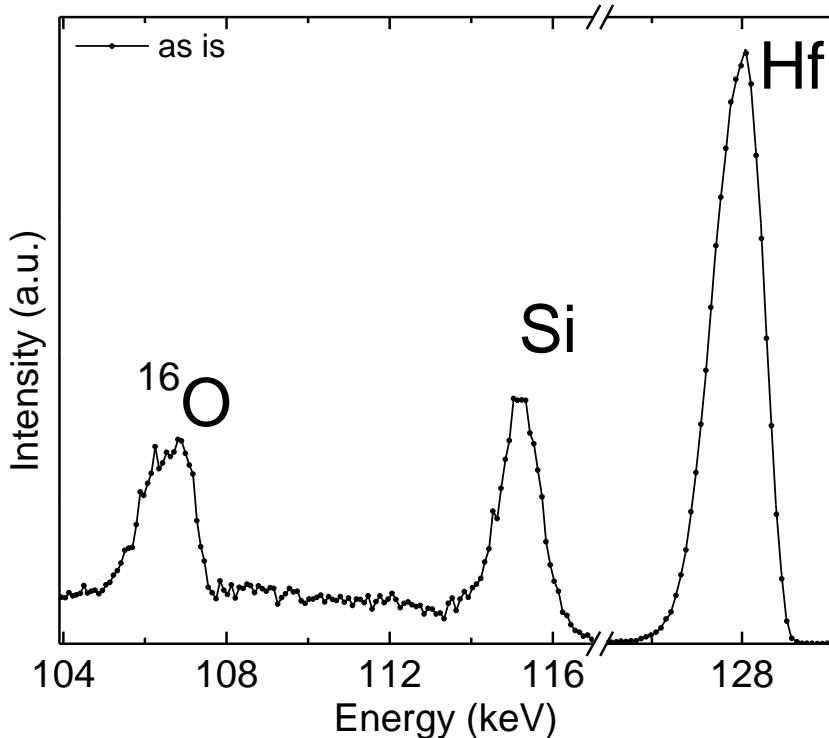
- mass (isotope) specific
- quantitative (2% accuracy for high-Z)
- depth sensitive (at the sub-nm scale)

MEIS analysis of as-deposited films

98keV H⁺

Sample Alignment:

Si(001) incident; Si(110) outgoing



TEM:
2.8nm HfO₂/1nm SiO₂/Si(001)

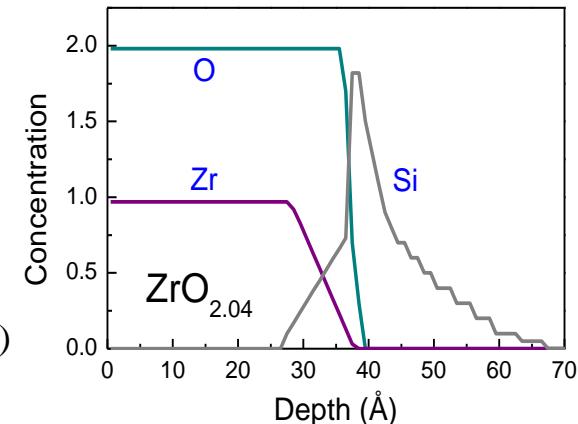
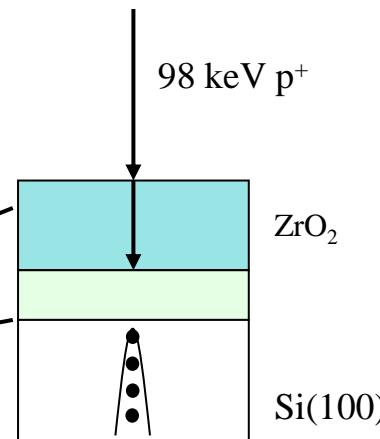
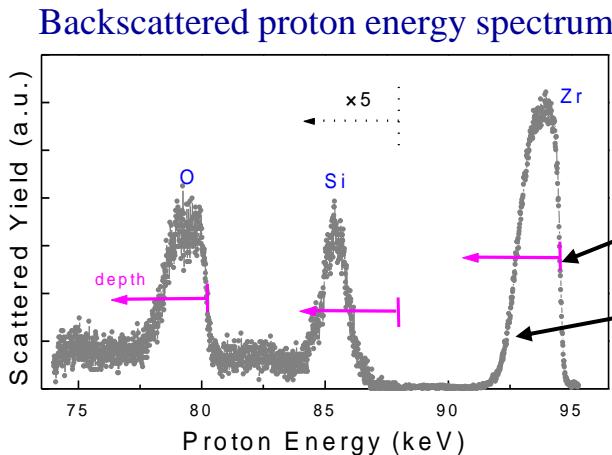
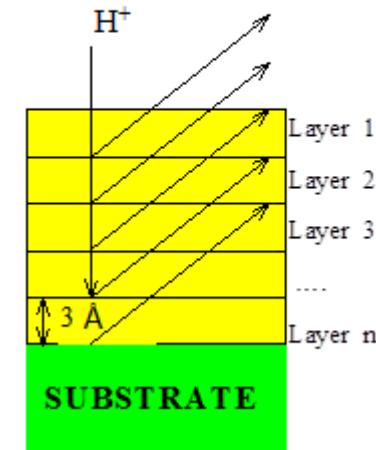
Depth resolution and concentration profiling

Basic concept: Depth profile is based on the energy loss of the ions traveling through the film (stopping power $\varepsilon \propto dE/dx$).

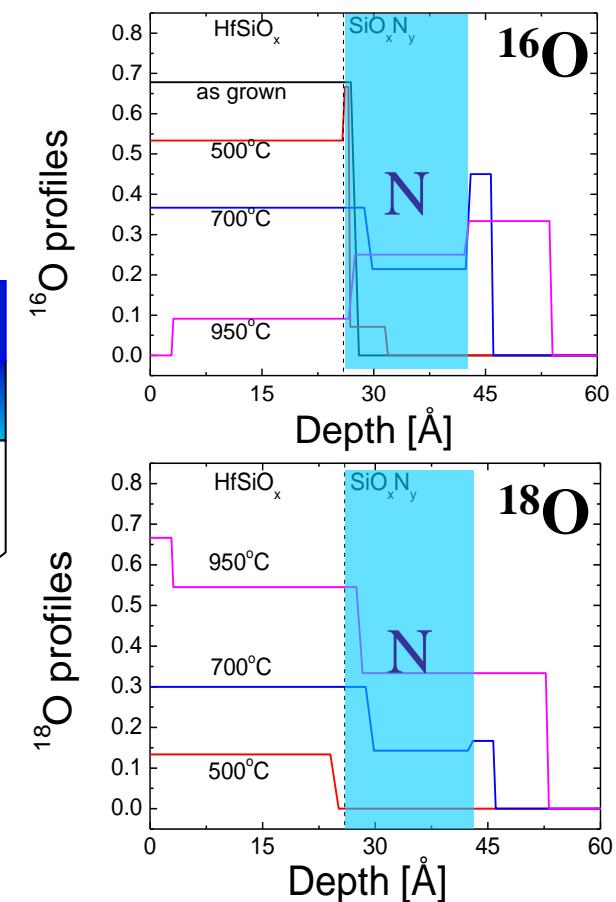
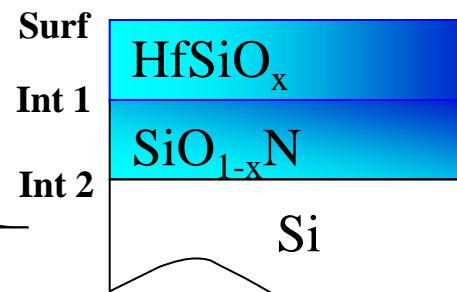
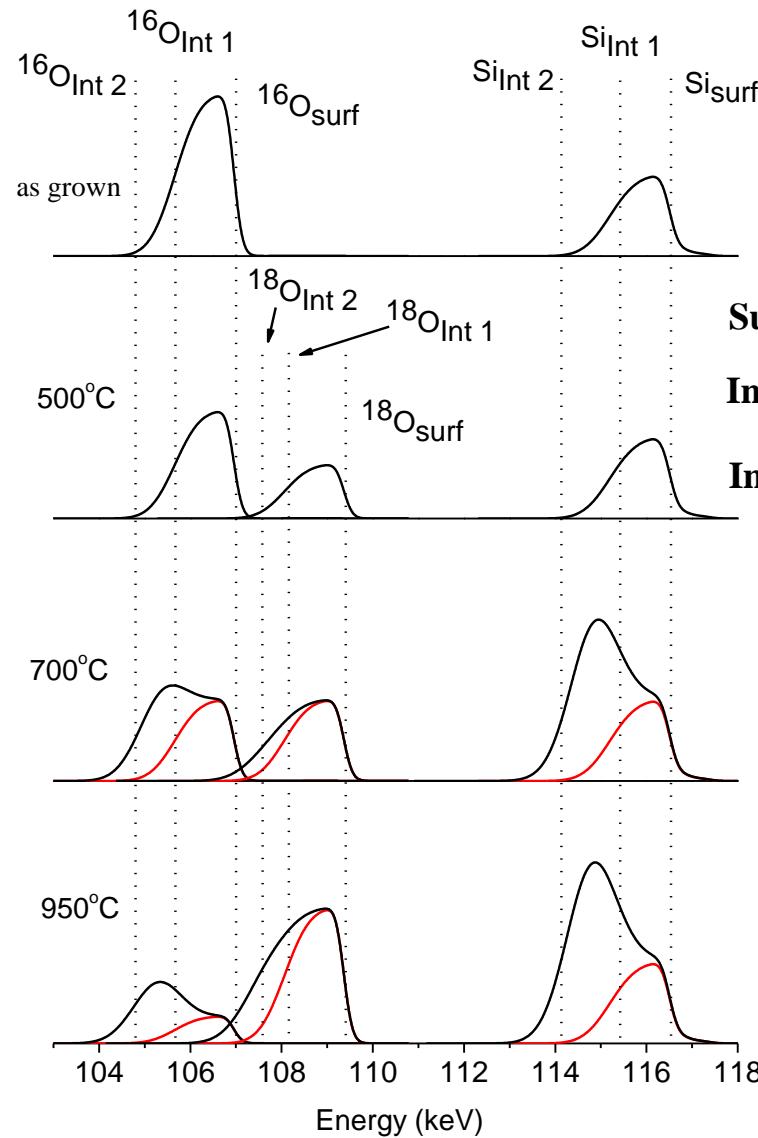
Example: Depth resolution for ≈ 95 keV protons
With MEIS spectrometer ≈ 180 eV vs RBS detector ≈ 15 keV

- Stopping power $\text{SiO}_2 \approx 12 \text{ eV}/\text{\AA}$; $\text{Si}_3\text{N}_4 \approx 20 \text{ eV}/\text{\AA}$;

Layer model:



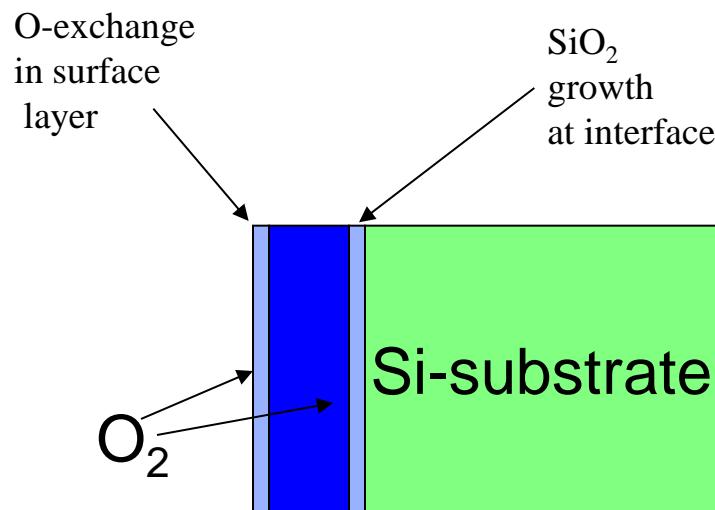
Oxidation temperature dependence: ^{16}O and ^{18}O



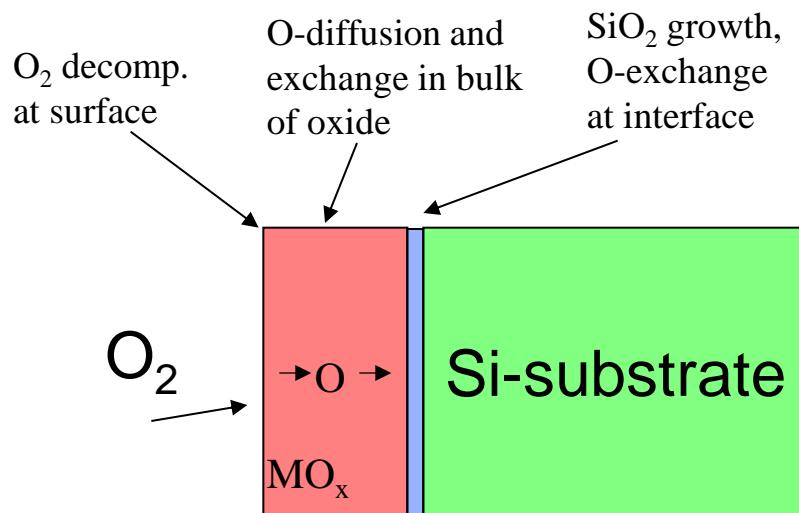
O reaction with Si \rightarrow deeper than N distribution

Oxygen diffusion in oxides

Oxygen (O_2) transport in SiO_2

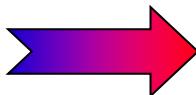


Atomic oxygen (O) transport in metal oxide films



SiO_2 films:

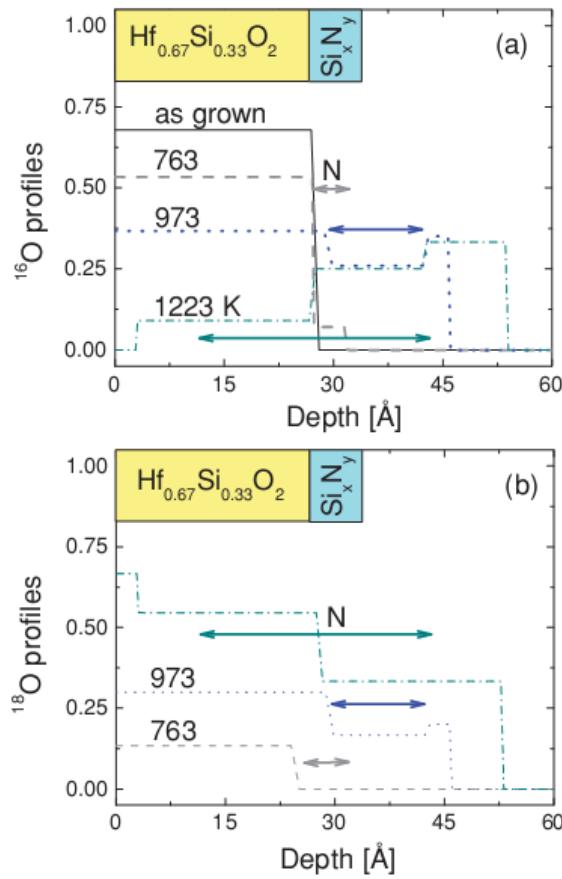
- **amorphous** after annealing
- molecular O_2 transport in SiO_2
- decomposition by SiO desorption



(Many) metal oxide films:

- tend to crystallize at **low T**
- atomic O transport in the film
- high oxygen mobility

Diffusion and interface growth in HfO_2 and HfSiO_x ultrathin films on Si(001)

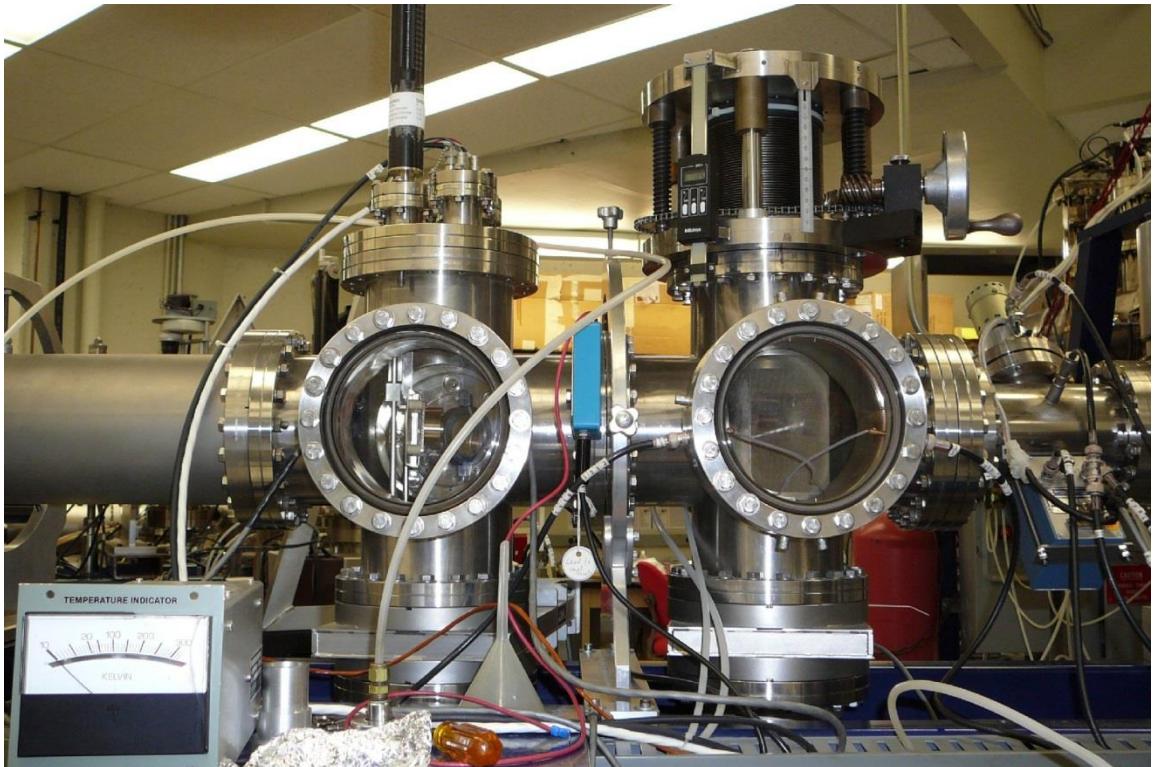
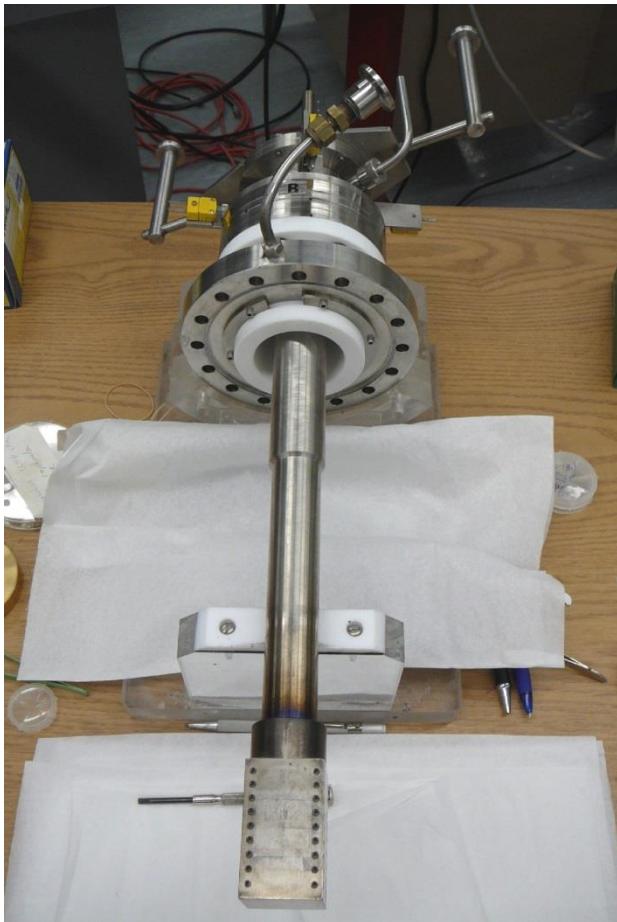


	T (°C)	Time (min)	Oxide growth (Å)
High-k	700	30	11
	800	30	18
	950	30	25
SiO_2^*	750	165	5
		2640	10
	900	60	10
		1860	27

- Faster interfacial SiO_2 growth in case of high- κ oxides in comparison to the SiO_2 thickness growth for bare Si

L.V. Goncharova, M. Dalponte, T. Feng, et al, *PRB* **83** (2011) 115329

Part II: Ion Implantation



- Implantation chamber and implantation stage

Periodic Table



WebElements: the periodic table on the world-wide web

www.webelements.com

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																										
hydrogen 1 H 1.0079	boronium 2 Be 9.0122	lithium 3 Li 6.941	beryllium 4 Be 9.0122	sodium 11 Na 22.990	magnesium 12 Mg 24.305	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vandium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.38	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180																						
potassium 19 K 39.088	calcium 20 Ca 40.078	rutherfordium 103 Rf [262]	zirconium 40 Zr [267]	niobium 41 Nb [268]	molybdenum 42 Mo [271]	technetium 43 Tc [272]	ruthenium 44 Ru [270]	rhodium 45 Rh [276]	palladium 46 Pd [281]	silver 47 Ag [280]	gold 48 Au [285]	mercury 79 Hg [284]	thallium 81 Tl [284]	lead 82 Pb [207.2]	bismuth 83 Bi [208.98]	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]																									
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	lanthanum 57 Lu 132.91	cerium 58 Ce 147.97	praseodymium 59 Pr 178.49	neodymium 60 Nd 180.95	promethium 61 Pm 183.84	samarium 62 Sm 186.21	euroopium 63 Eu 190.23	gadolinium 64 Gd 192.22	terbium 65 Tb 195.08	dysprosium 66 Dy 196.97	holmium 67 Ho 200.59	erbium 68 Er 204.38	thulium 69 Tm 207.2	yterbium 70 Yb 208.98	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	euroopium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	yterbium 70 Yb 173.06	lanthanum 57 La [223]	cerium 58 Ce [226]	praseodymium 59 Pr [227]	neodymium 60 Nd [231.04]	promethium 61 Pm [238.03]	samarium 62 Sm [237]	euroopium 63 Eu [244]	gadolinium 64 Gd [243]	terbium 65 Tb [247]	dysprosium 66 Dy [251]	holmium 67 Ho [252]	erbium 68 Er [257]	thulium 69 Tm [258]	yterbium 70 Yb [259]
francium 87 Fr [223]	radium 88 Ra [226]	**	lawrencium 103 Lr [262]	rutherfordium 104 Rf [267]	dubnium 105 Db [268]	seaborgium 106 Sg [271]	bhertium 107 Bh [272]	hassium 108 Hs [270]	meitnerium 109 Mt [276]	damstadium 110 Ds [281]	roentgenium 111 Rg [280]	uramium 112 Uub [285]	uraniuntrium 113 Uut [284]	unquadrium 114 Uuo [289]	unpentium 115 Uup [288]	unhexium 116 Uuh [293]	unseptium 117 Uuh —	ununoctium 118 Uuo [294]																									
*lanthanoids																																											
**actinoids																																											

Symbols and names: the symbols and names of the elements, and their spellings are those recommended by the International Union of Pure and Applied Chemistry (IUPAC - <http://www.iupac.org>). Names have yet to be proposed for the most recently discovered elements beyond 112 and so those used here are IUPAC's temporary systematic names. In the USA and some other countries, the spellings aluminium and cesium are normal while in the UK and elsewhere the common spelling is sulphur.

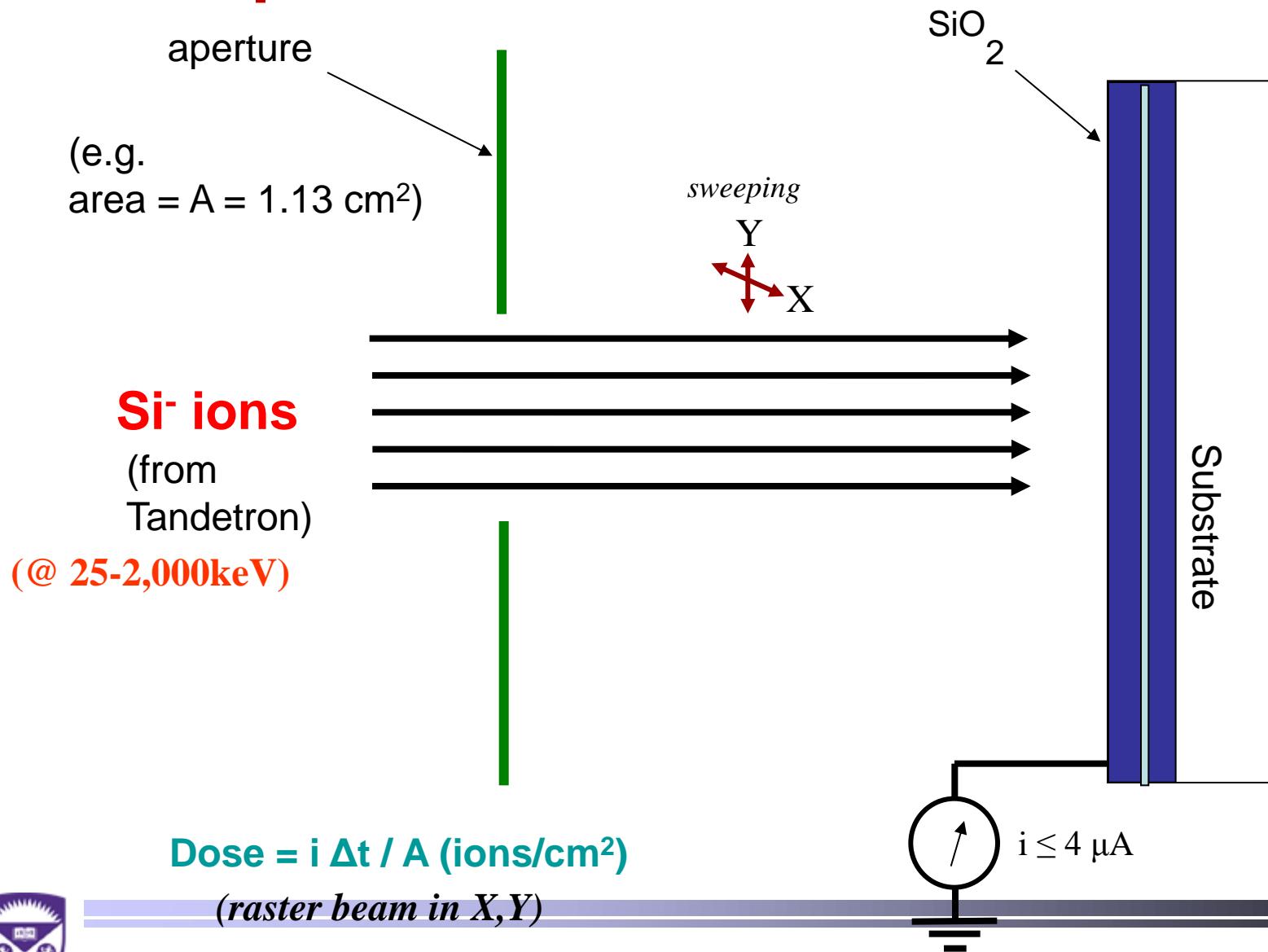
Group labels: the numeric system (1-18) used here is the current IUPAC convention.

Atomic weights (mean relative masses): Apart from the heaviest elements, these are the IUPAC 2007 values and given to 5 significant figures. Elements for which the atomic weight is given within square brackets have no stable nuclides and are represented by the element's longest lived isotope reported at the time of writing.

©2007 Dr Mark J Winter iWebElements Ltd and University of Sheffield. webelements@sheffield.ac.uk. All rights reserved. For updates to this table see http://www.webelements.com/nexus/Printable_Periodic_Table.html Version date: 21 September 2007.

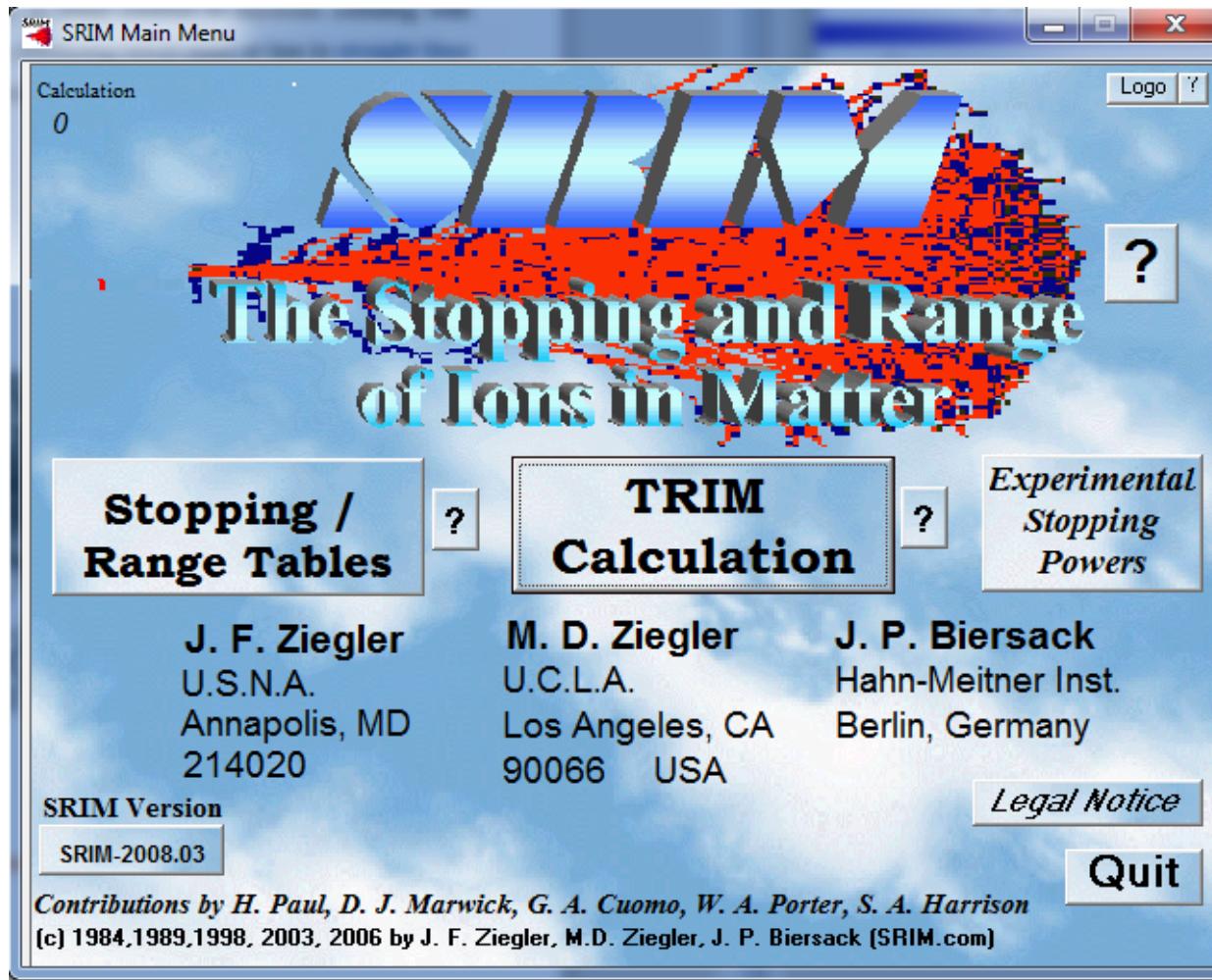
- *We can produce beams of all those elements shown in yellow !*

Ion Implantation

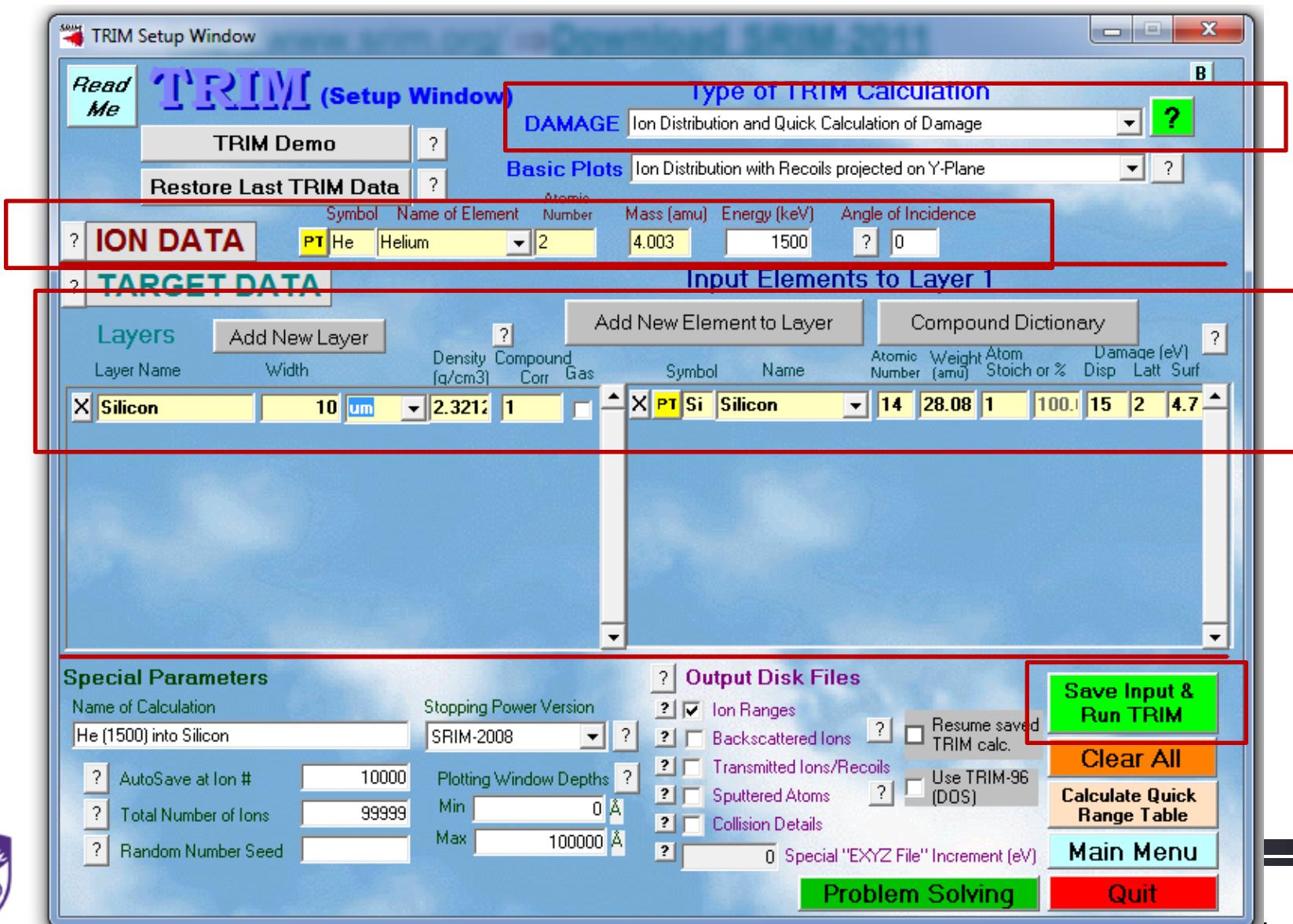


Stopping and Range of Ions in Matter (SRIM)

<http://www.srim.org/> → Download SRIM-2008

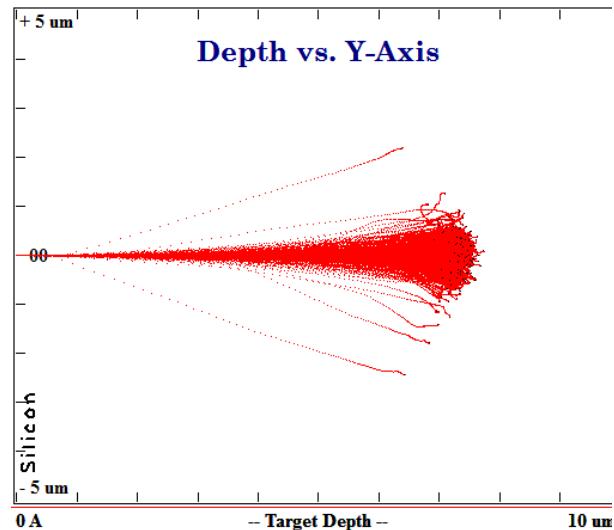


SRIM Setup Window

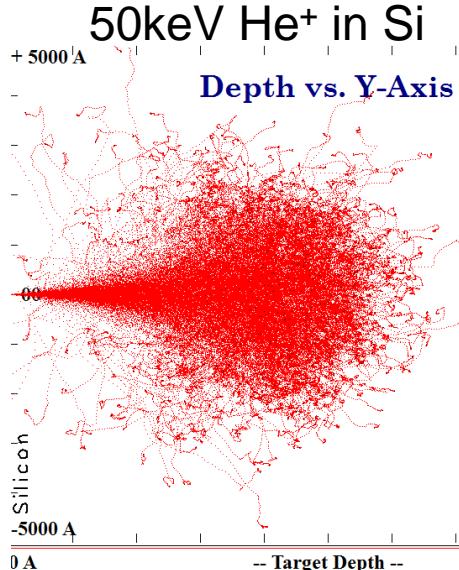


Calculated Ion Trajectories

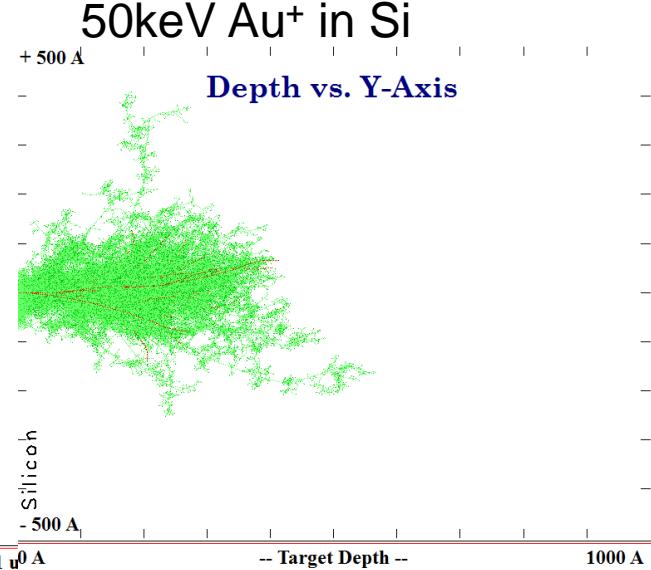
2MeV He⁺ in Si



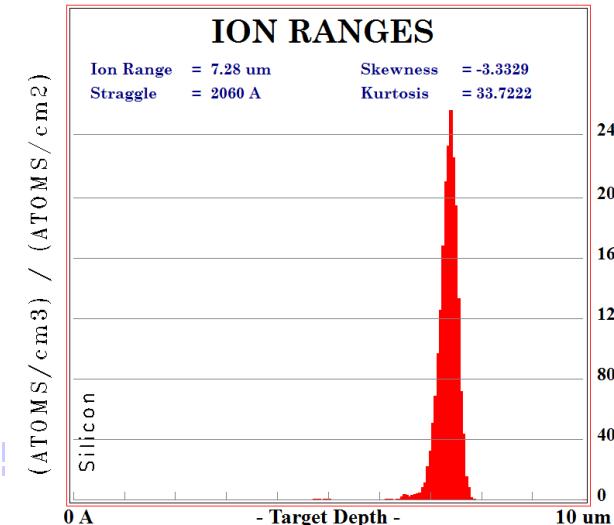
50keV He⁺ in Si



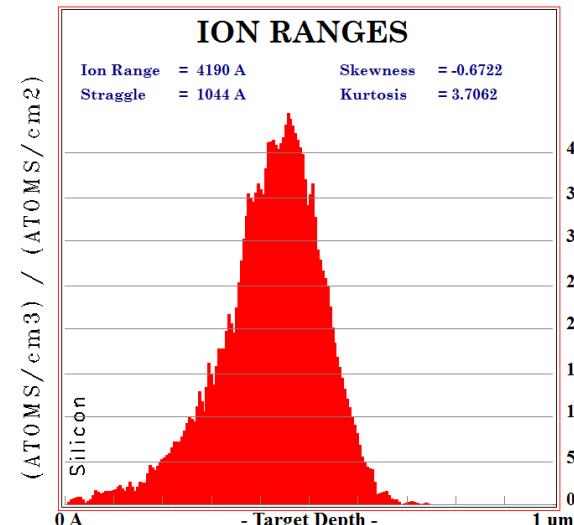
50keV Au⁺ in Si



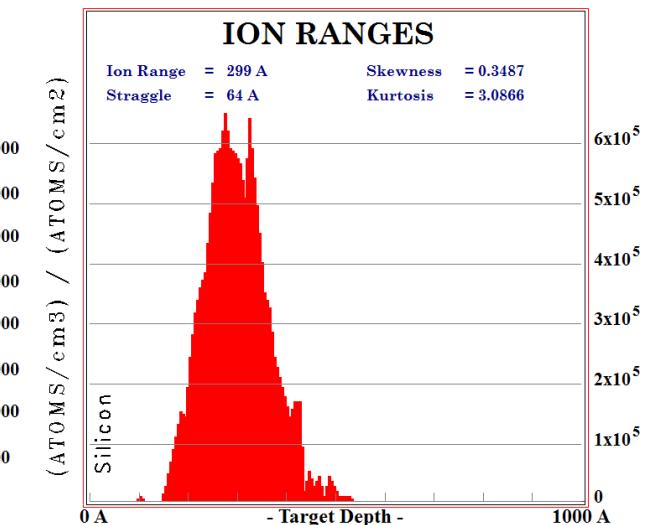
ION RANGES



ION RANGES

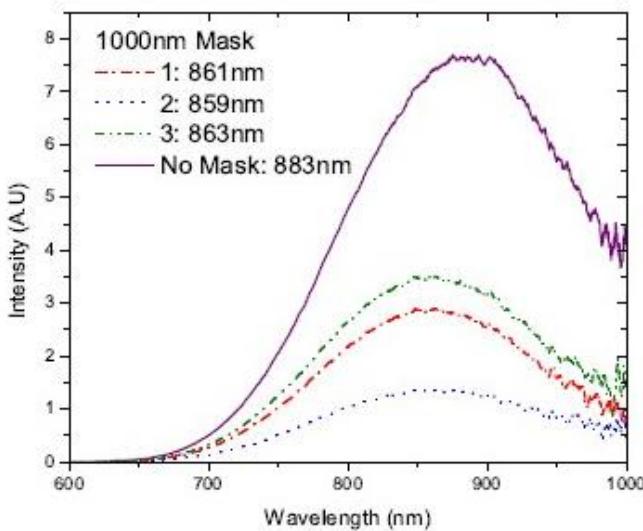


ION RANGES

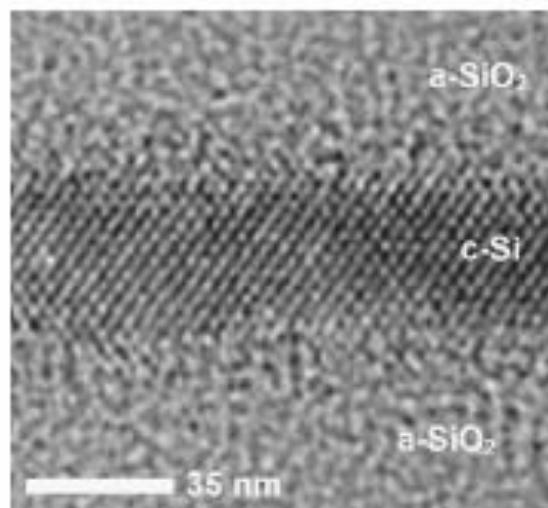


Ion-implanted Si and Ge quantum dots in dielectrics

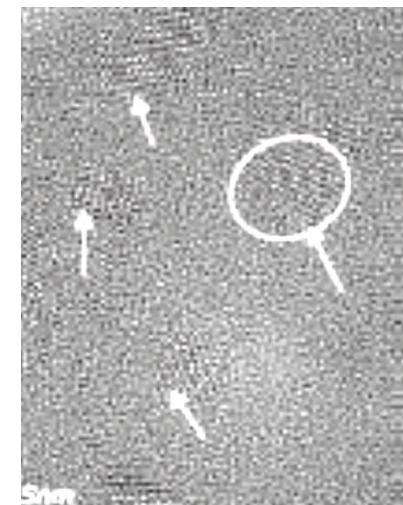
- Second generation Si and Ge photonics
- Strong light emission from nanocrystals or quantum dots (QD) by reducing the size of Si to $< a_{\text{Bohr}}$ (Si ~3-5nm; Ge ~ 24nm)
- Porous Si and crystalline QW
- Bonafos et al. used TEM to relate Si QD to excess Si (10, 20, 30%)



Barbagiovanni et al, MRS (2009)



Cho et al, JAP 2007



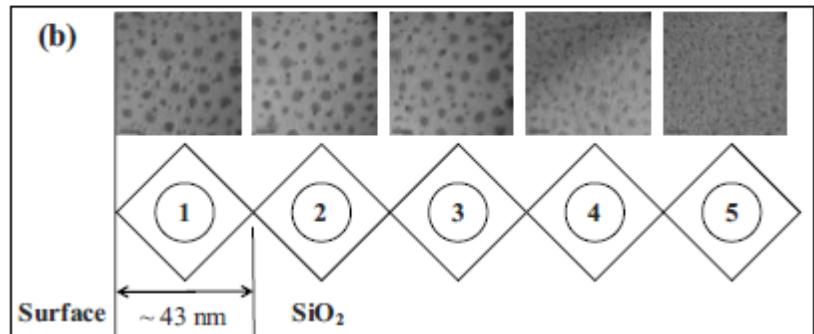
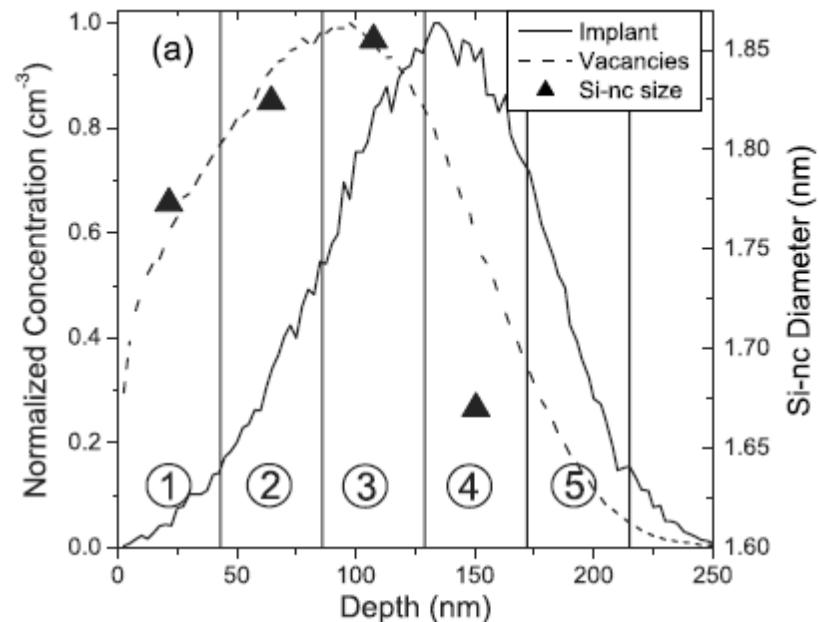
Bonafos et al, NIMB (2001)

Growth of Si-QD

- RT Implantation Si⁻ (Ge⁺) 90keV 5×10^{16} - 1×10^{17} ions/cm²
- 120min @ 1100°C (Si) or 900°C (Ge) in furnace,
- 60 min @ 500°C in N₂/H₂ gas
- Early stage of formation governed by diffusion

$$\frac{\partial C_{\text{Si}}}{\partial t} = -4\pi rND (C_{\text{Si}} - C_{\text{sol}})$$

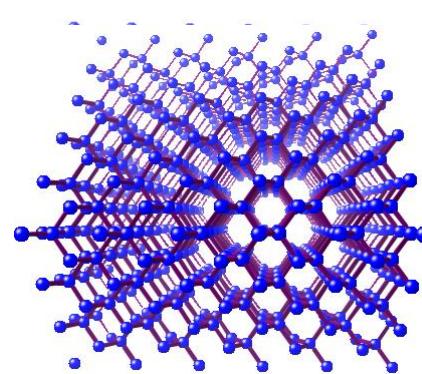
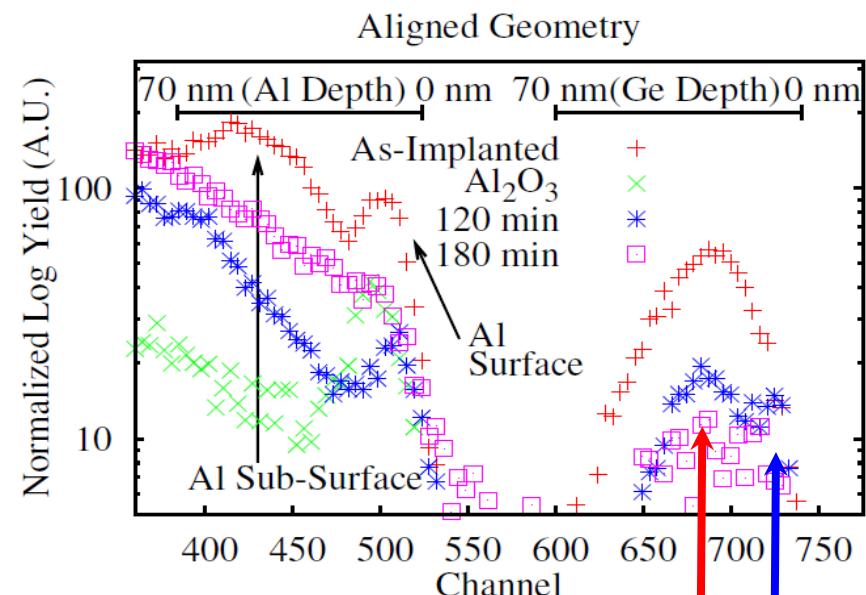
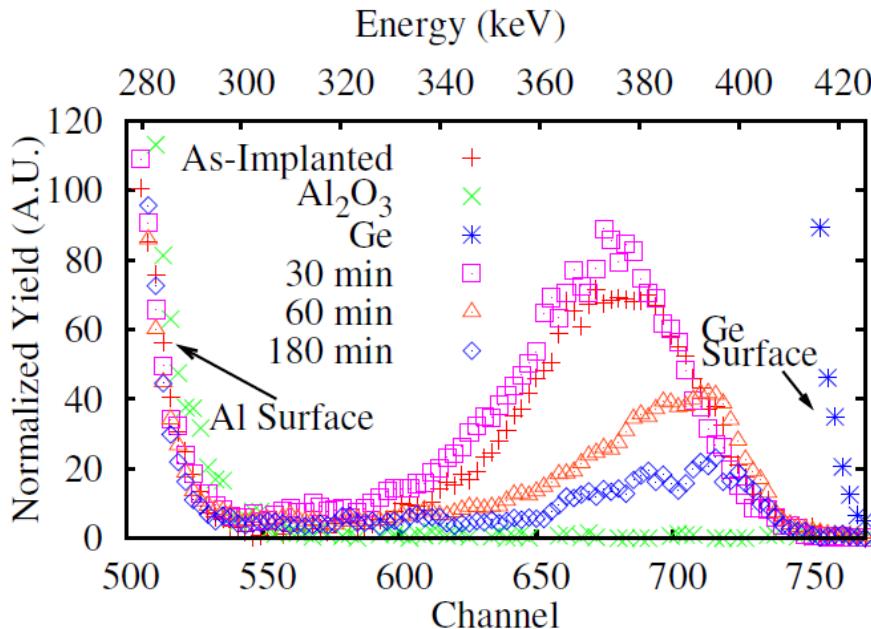
- Eventually Ostwald ripening



Link between defects in the
SiO₂ and formation of Si-QDs

Ge in $\text{Al}_2\text{O}_3(0001)$: crystallization and ordering

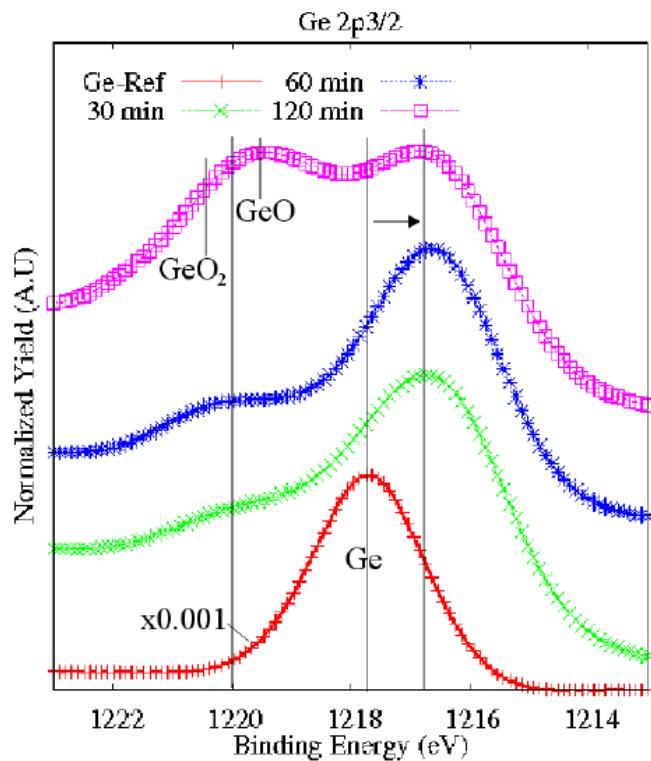
Ge Peak in Random Geometry



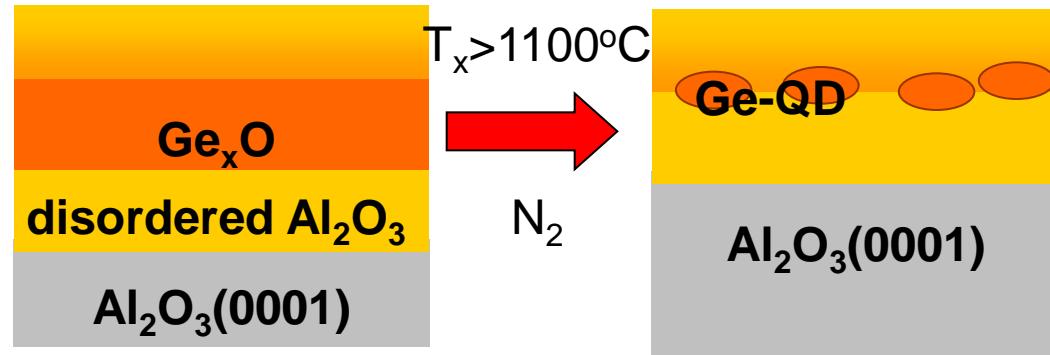
Sample (min)	Concentration ($\times 10^{15} \text{ cm}^{-2}$)	Crystalline Factor
As-Implanted	9.87	0
30	6.68	-
60	3.35	0.55
120	4.17	0.55
180	1.63	0.5

E.G. Barbagiovanni, S.N. Dedyulin, P.J. Simpson, L.V. Goncharova, *NIMB* **272** (2012) 74–77

XPS



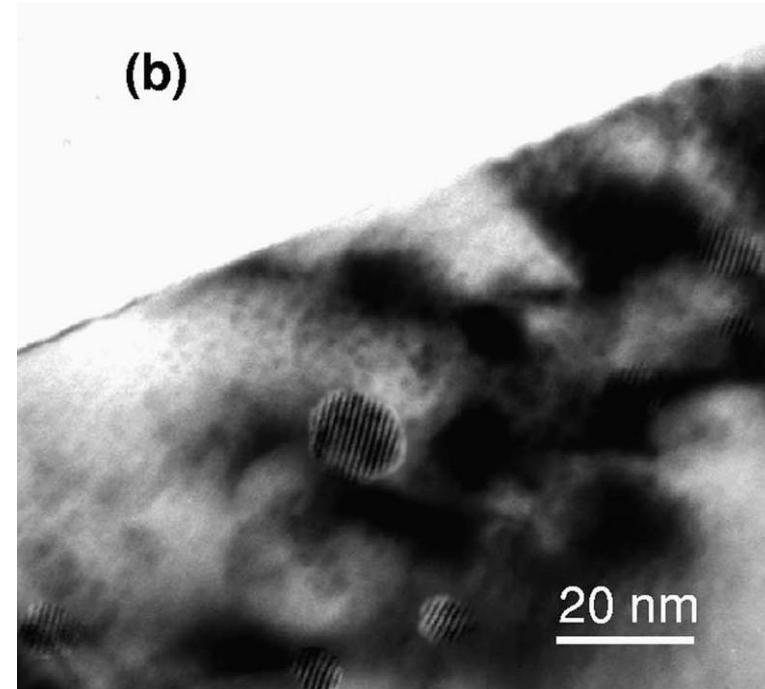
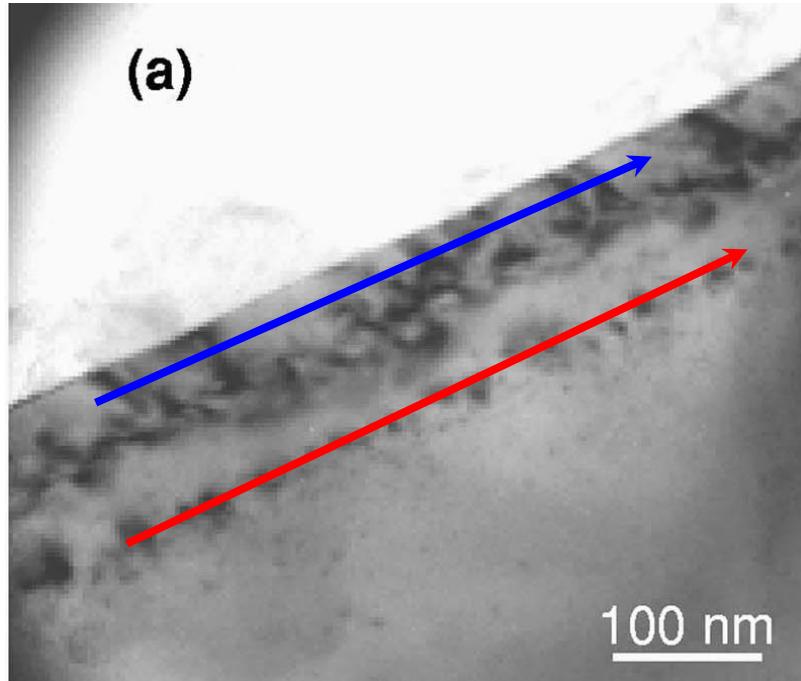
Sample (min)	Concentration ($\times 10^{15}$ cm $^{-2}$)	Crystalline Factor
As-Implanted	9.87	0
30	6.68	-
60	3.35	0.55
120	4.17	0.55
180	1.63	0.5



Ar sputtering prior to XPS analysis:
Ge layer is 3-5nm deep

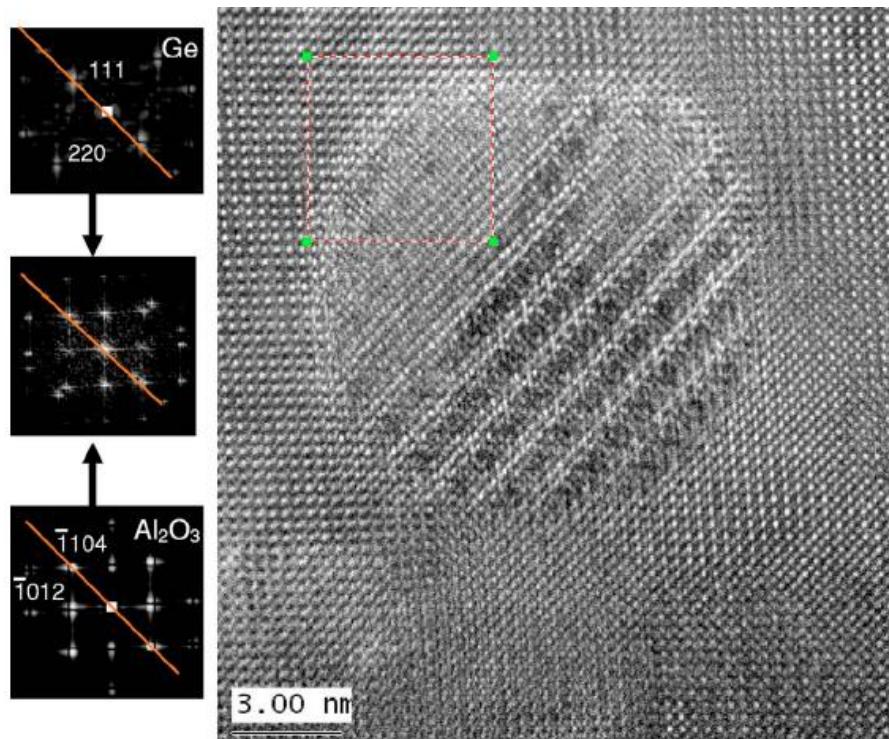
- Shift of Ge peak towards the surface (RBS)
- GeO_x peaks in XPS \Rightarrow Ge loss via GeO desorption

Cross-sectional TEM micrographs



- Contrast arising from stress fields and end of range implantation damage
- Moiré fringes become visible from the overlap of the crystal planes of Ge QD and the sapphire matrix

Ge in Al₂O₃(0001): crystallization and ordering



- Slow diffusion rate of the alumina matrix atoms at $< T_{\text{melt}}$
- Ge blocking minimum can be related to the stereographic projection of the sapphire crystal and corresponds to the [111] scattering plane:



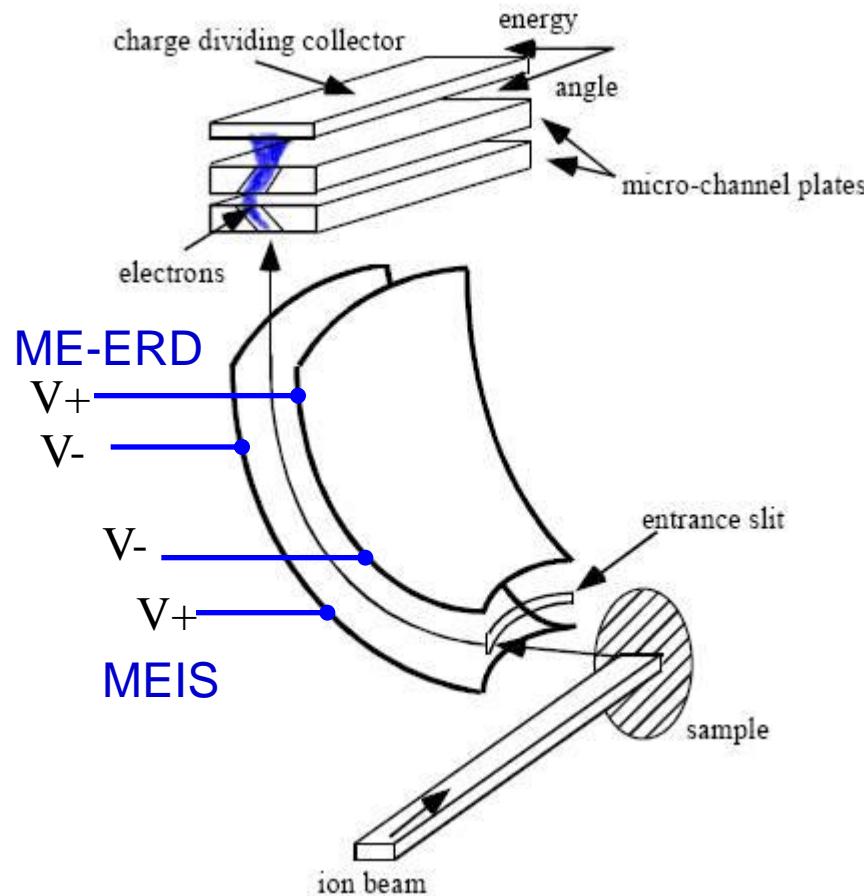
Conclusions and future directions:

- Ion Beam Analysis is an enabling technology for thin film scientists and engineers
- Our goals are to initiate collaborative research projects and stimulate multidisciplinary interactions, To enable the use of ion beams, including the introduction of ion beam methods to new discipline areas
- Development of novel ion beam analyses techniques

References:

- 1) L.C. Feldman, J.W. Mayer (1986) Fundamentals of Surface and Thin Film Analysis.
- 2) Y. Wang, M. Nastasi (2010, or previous edition) Handbook of Modern Ion Beam Materials Analysis.
- 3) The Stopping and Range of Ions in Matter (SRIM),
<http://www.srim.org/>

Elastic recoil detection for negative ions



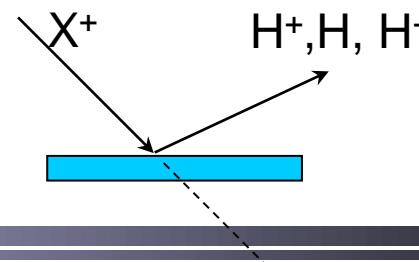
Toroidal Ion Energy Analyzer (HVEng, Amersfoort, The Netherlands)

Crucial points for detecting H ion recoils directly are:

- To increase the recoil cross-section
- To reduce (to suppress) the background originating mainly from elastically scattered incident ions

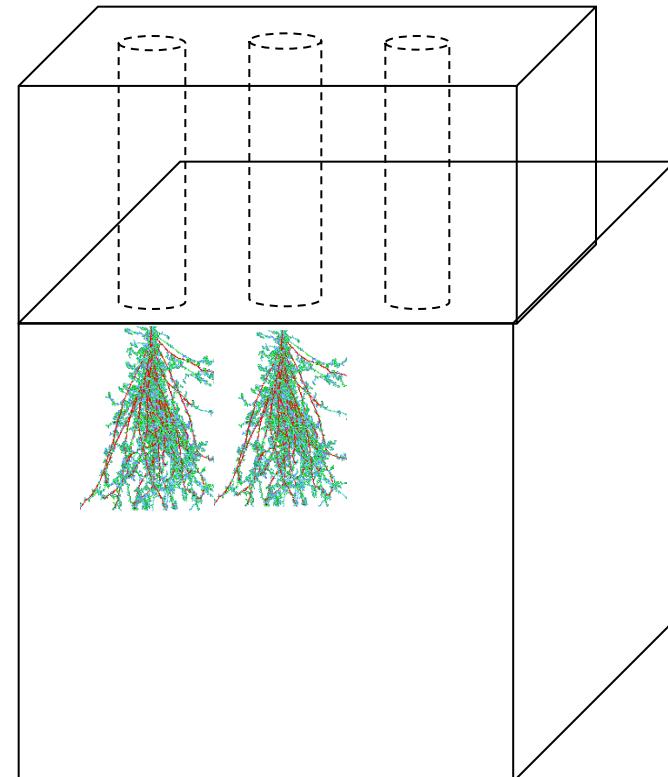
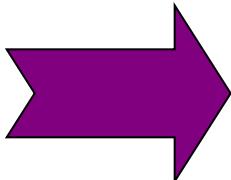
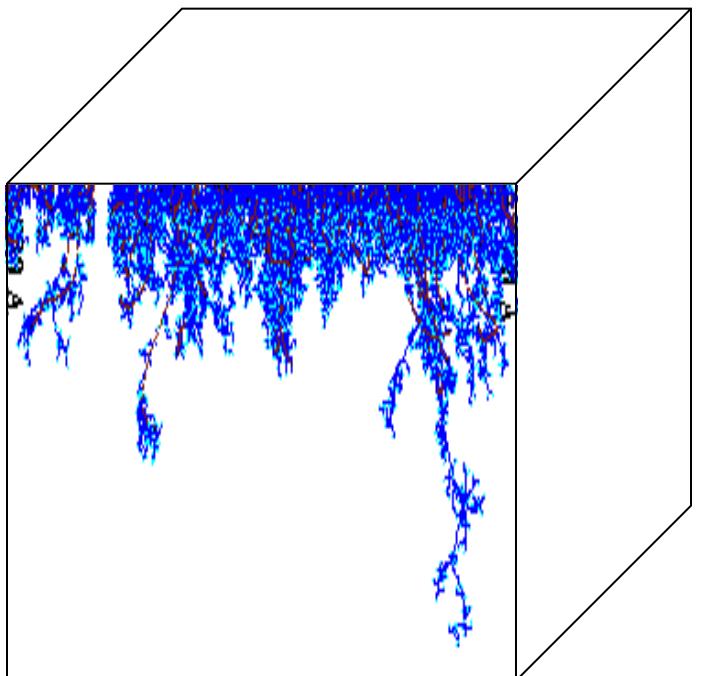
Only charged particles are detected by TEA

⇒ use incident beam ions without negative ion fractions and detect negative H^- recoils



Control QD Distribution with Mask

Si QD nucleation and growth by Si ion implantation and anneal \Rightarrow
Lateral separation between implanted regions



Thank you!

Lyudmila V. Goncharova

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

lgonchar@uwo.ca