Joint ICTP-IAEA International School on Nuclear Waste Vitrification

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# USE OF ION BEAMS FOR RADIATION DAMAGE AND ANALYSIS

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cost – European Cooperation in Science & Technology

hrzz – Hrvatska zaklada za znanost

CEMS

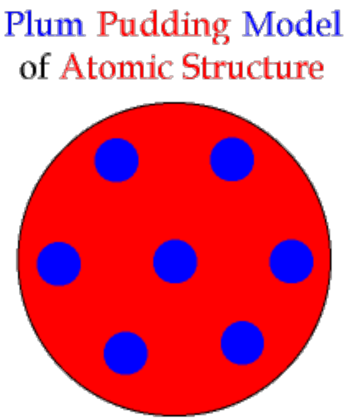
# Overview

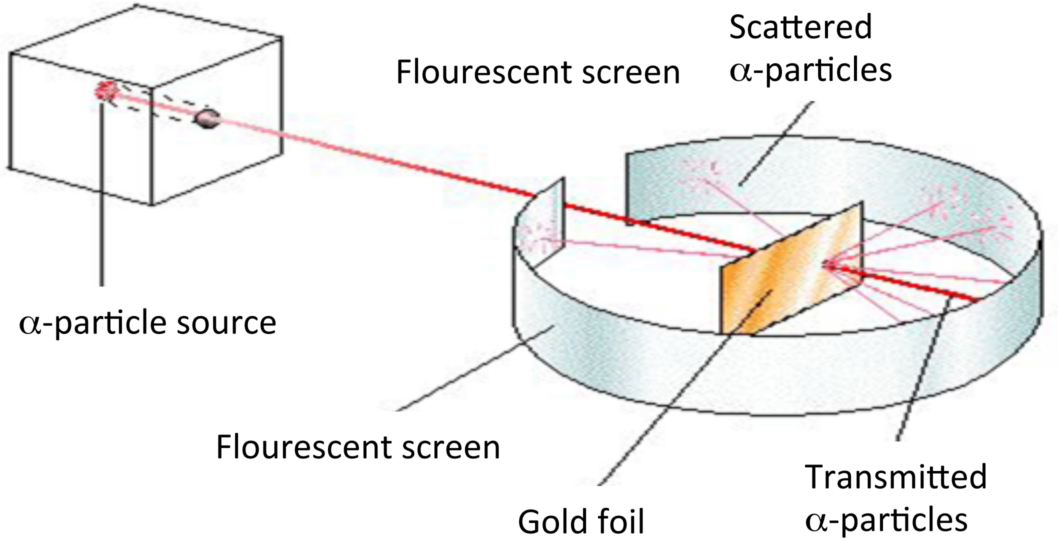
1. Introduction to IBA

2. RBS/channeling for ion tracks

3. RBS/c @ RBI

# The first ion beam analysis: Rutherford experiment




ERNEST RUTHERFORD

- 1909 – α-particle scattering experiment on gold foil
- 1911 – theory of nuclear atom

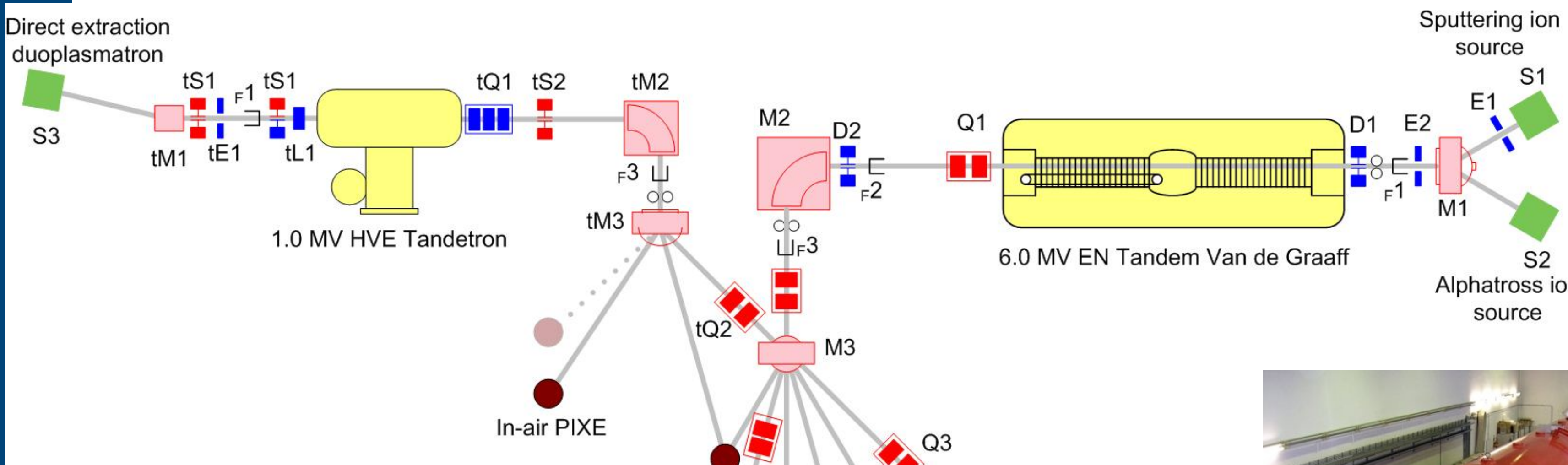
ION BEAM ANALYSIS (IBA) =
material analysis using (MeV) ion beams

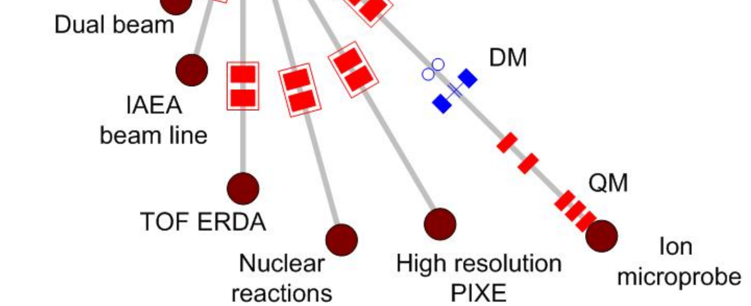
# Accelerators today

Aprox. 20.000 accelerators:

- 90% medicine & industry
  - Medicine
    - Diagnostics (isotope production)
    - Radiation treatment
  - Industry
    - Ion implanters
    - Electron accelerators for radiation processing (e.g. polimer crosslinking, sterilisation...)
- 10% research and education
  - Large scale facilities (e.g.CERN, GSI, etc.)
  - Synchrotron light sources
  - Cyclotrons
  - Electrostatic accelerators (including implanters)

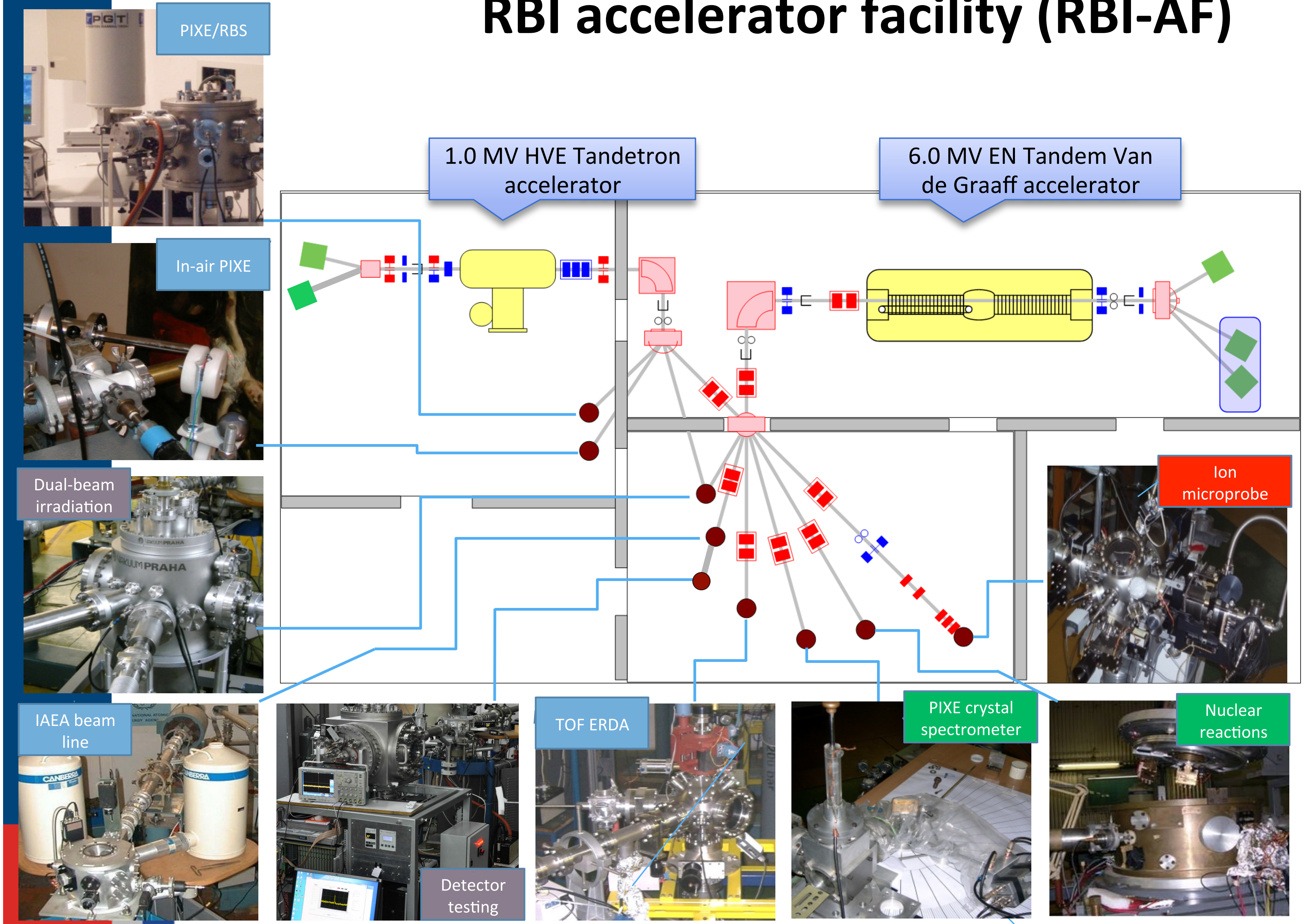
# RBI accelerator facility (RBI-AF)



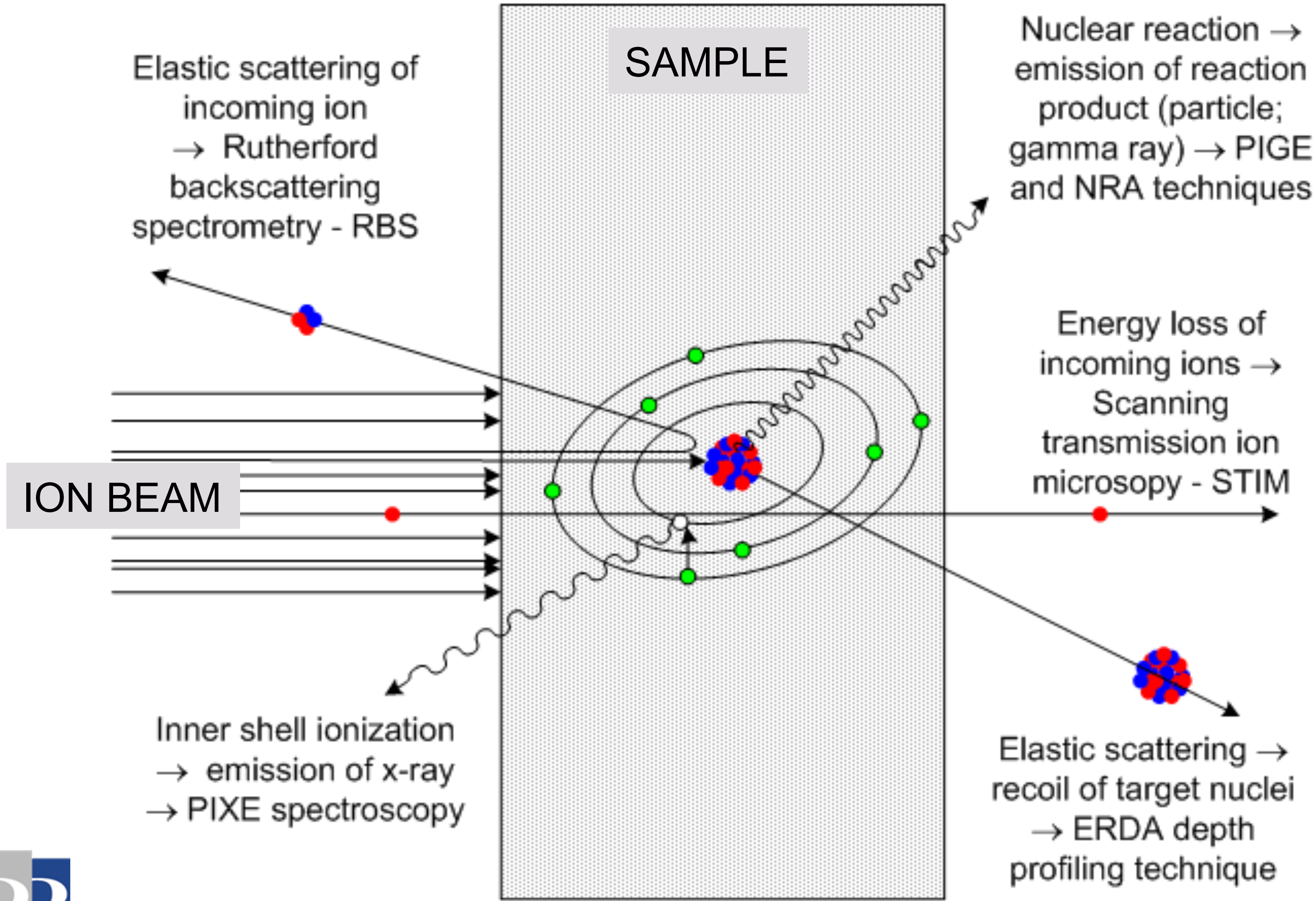



2 MeV p, 2 MeV He, 8 MeV C, 3 MeV O, 15 MeV O, 6 MeV Si, 15 MeV Si, 20+ MeV Cl, I, Au

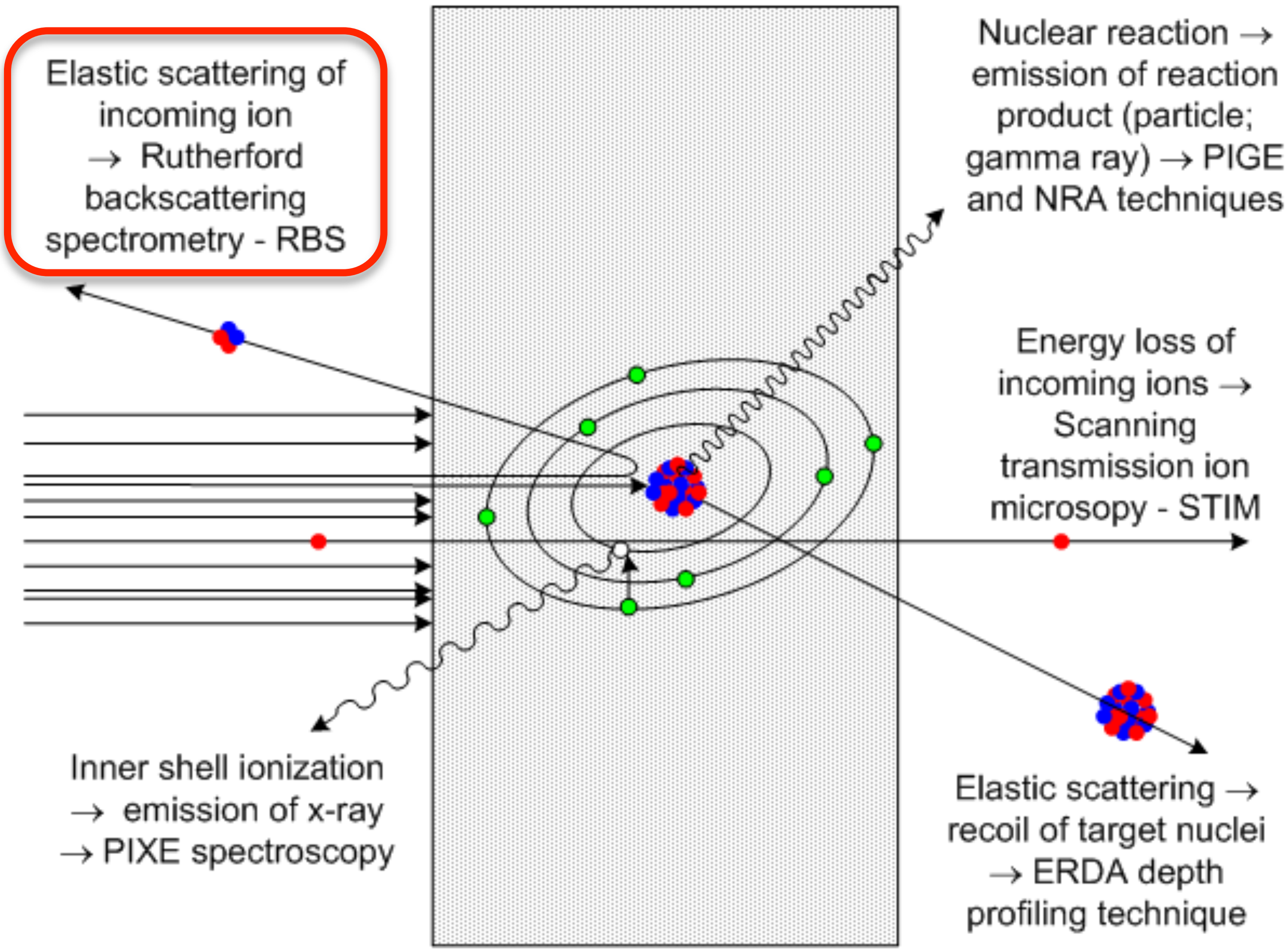
# RBI accelerator facility (RBI-AF)



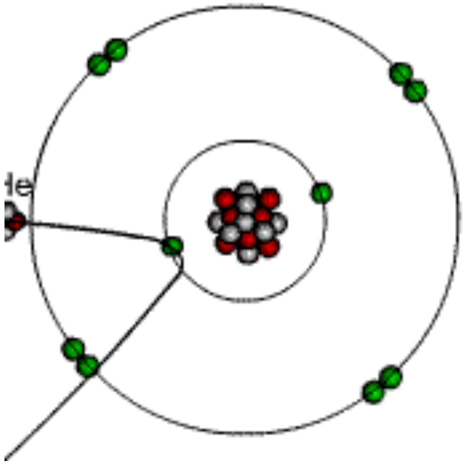
# Ion beam analysis (IBA) techniques



# Rutherford Backscattering Spectrometry (RBS)



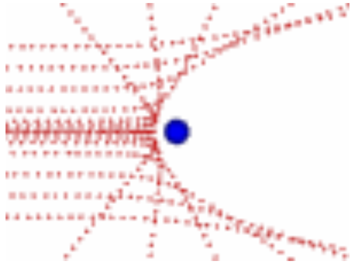
# Rutherford Backscattering Spectrometry (RBS)

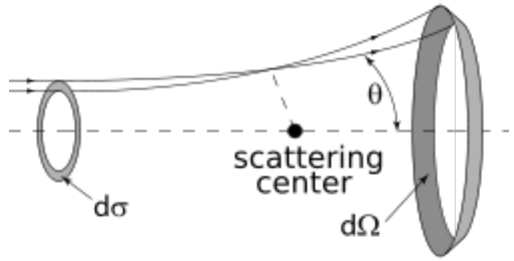


$$K = \frac{E_{scattered}}{E_{incident}} = \left[ \frac{\left(1 - \left(\frac{M_1 \sin\theta}{M_2}\right)^2\right)^{1/2} + \frac{M_1 \cos\theta}{M_2}}{1 + \frac{M_1}{M_2}} \right]^2$$

For a given scattering angle $\Theta$ , known projectile energy $E_{inc.}$ and mass $M_1$ (eg. 2 MeV $\alpha$), $E_{sc.}$ can be measured and therefore unknown mass $M_2$ can be determined

# Rutherford Backscattering Spectrometry (RBS)

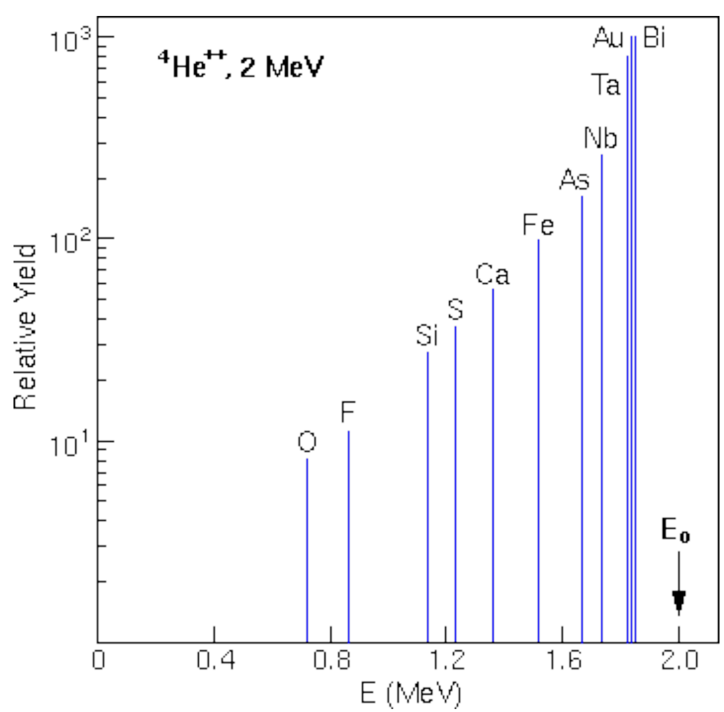




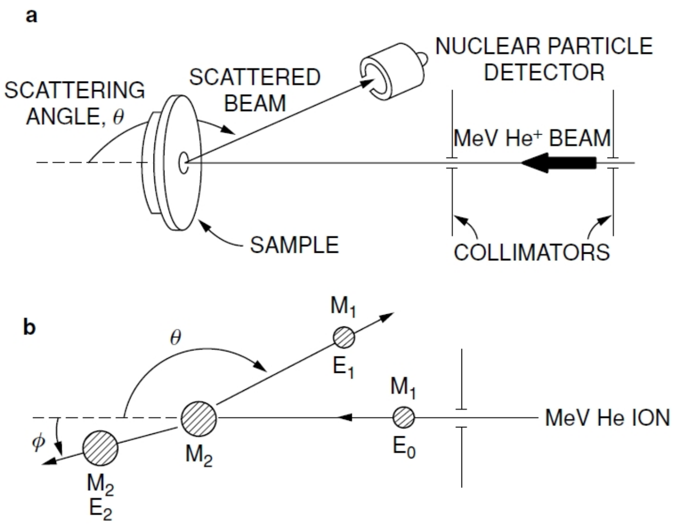

## Cross section

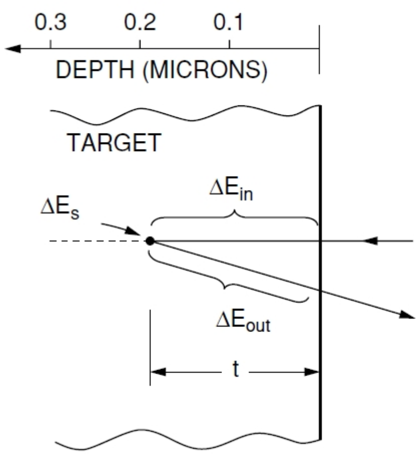
$$\frac{\partial \sigma}{\partial \Omega} = \left[\frac{Z_1 Z_2 e^2}{4E}\right]^2 \bullet \frac{4}{\sin^4\theta} \bullet \frac{\left[\sqrt{1-\left[\frac{M_1 \sin\theta}{M_2}\right]^2} + \cos\theta\right]^2}{\sqrt{1-\left[\frac{M_1 \sin\theta}{M_2}\right]^2}}$$

| | |
|---|---|
| $Z_1$ | *Atomic number of incident ion* |
| $Z_2$ | *Atomic number of target atom* |
| $E$ | *Energy of incident ion* |
| $M_1$ | *Mass of incident ion* |
| $M_2$ | *Mass of target atom* |
| $\theta$ | *Angle of incidence* |



# Rutherford Backscattering Spectrometry (RBS)




$$\Delta E_{in} = \left.\frac{dE}{dx}\right|_{E_0} \cdot t$$

$$E_t = E_0 - \Delta E_{in}$$

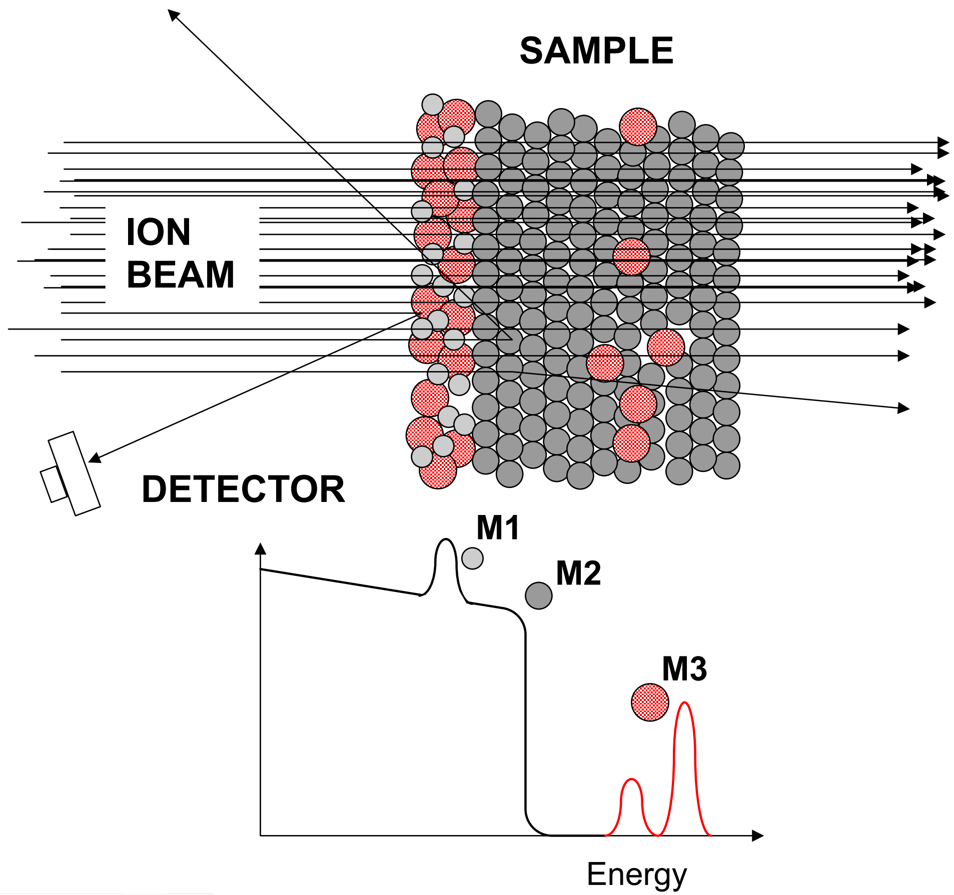
$$\Delta E_s = \left(1 - K\right) E_t$$

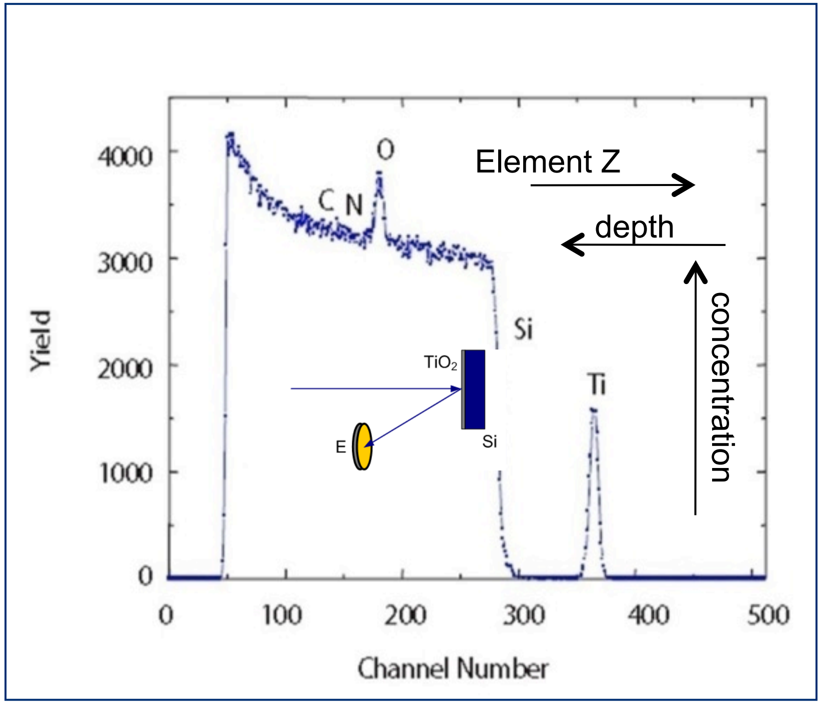
$$\Delta E_{out} = \left.\frac{dE}{dx}\right|_{E_1} \cdot \frac{t}{\cos\theta}$$

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

# Rutherford Backscattering Spectrometry (RBS)

## Depth profiling



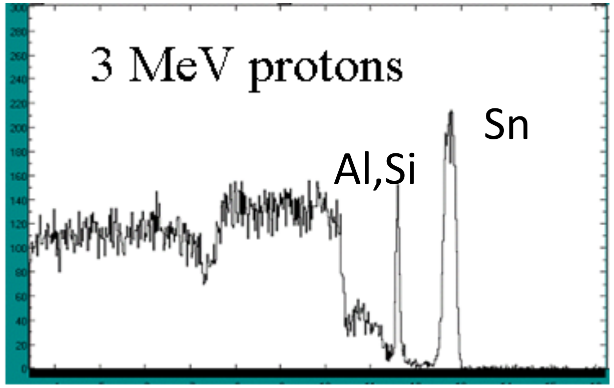

Proton beam (2 MeV)
Detector positioned at $\Theta=165^0$

Sample: thin $TiO_2$ film on Si substrate

# Rutherford Backscattering Spectrometry (RBS)

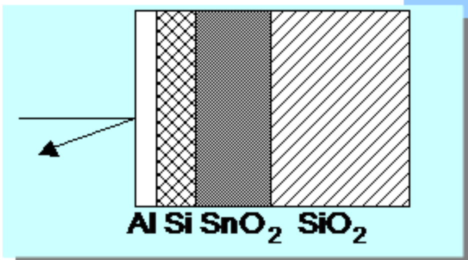
## Depth profiling

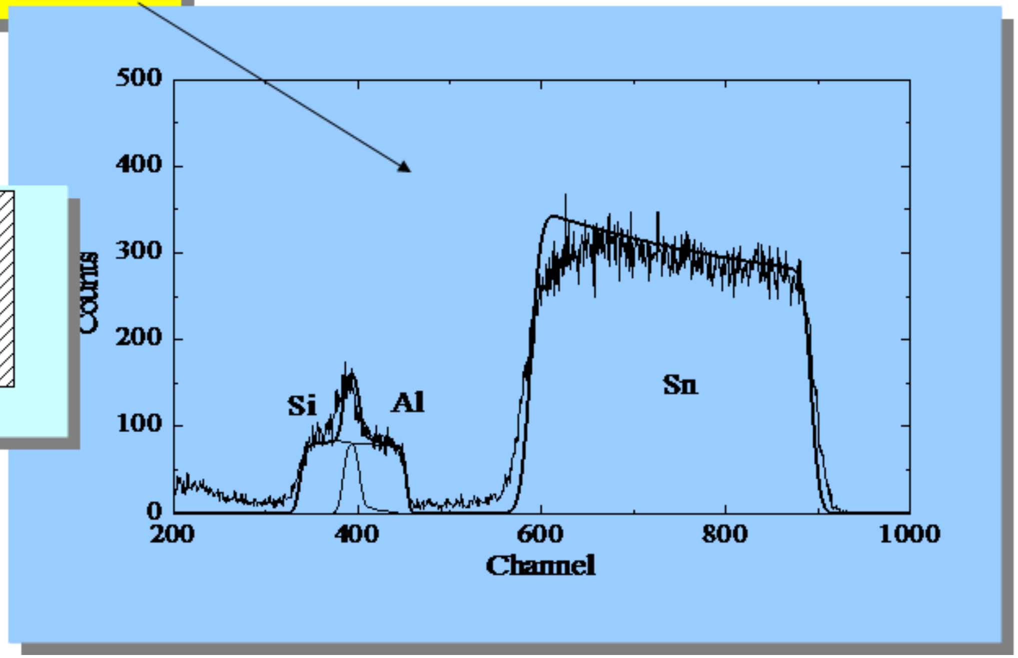
Sample:
thin film a-Si solar cell
(amorphous silicon)




5.1 MeV $Li^{2+}$ beam

$\Theta=170^{\circ}$

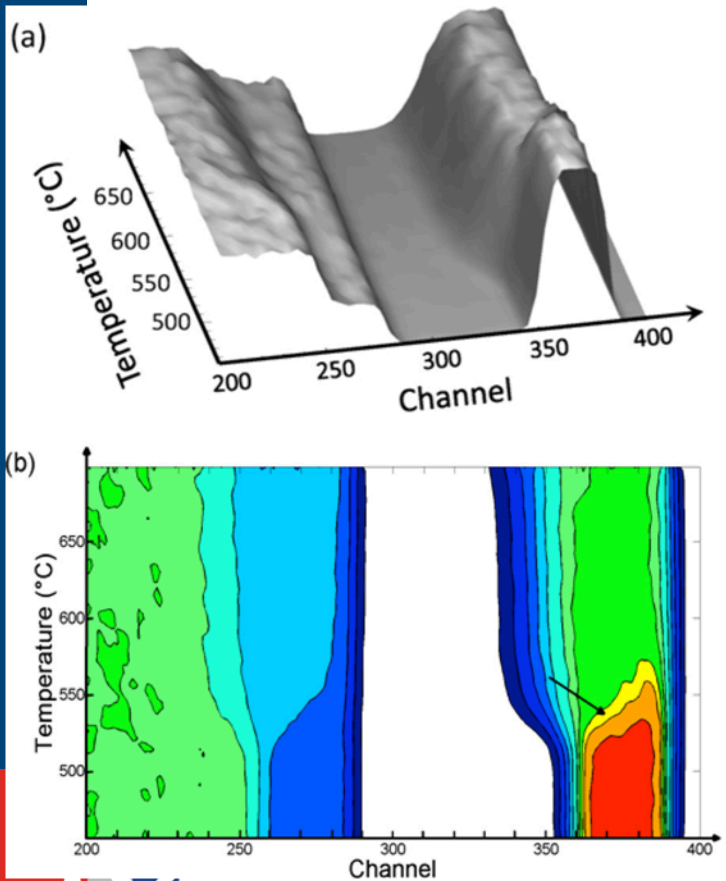


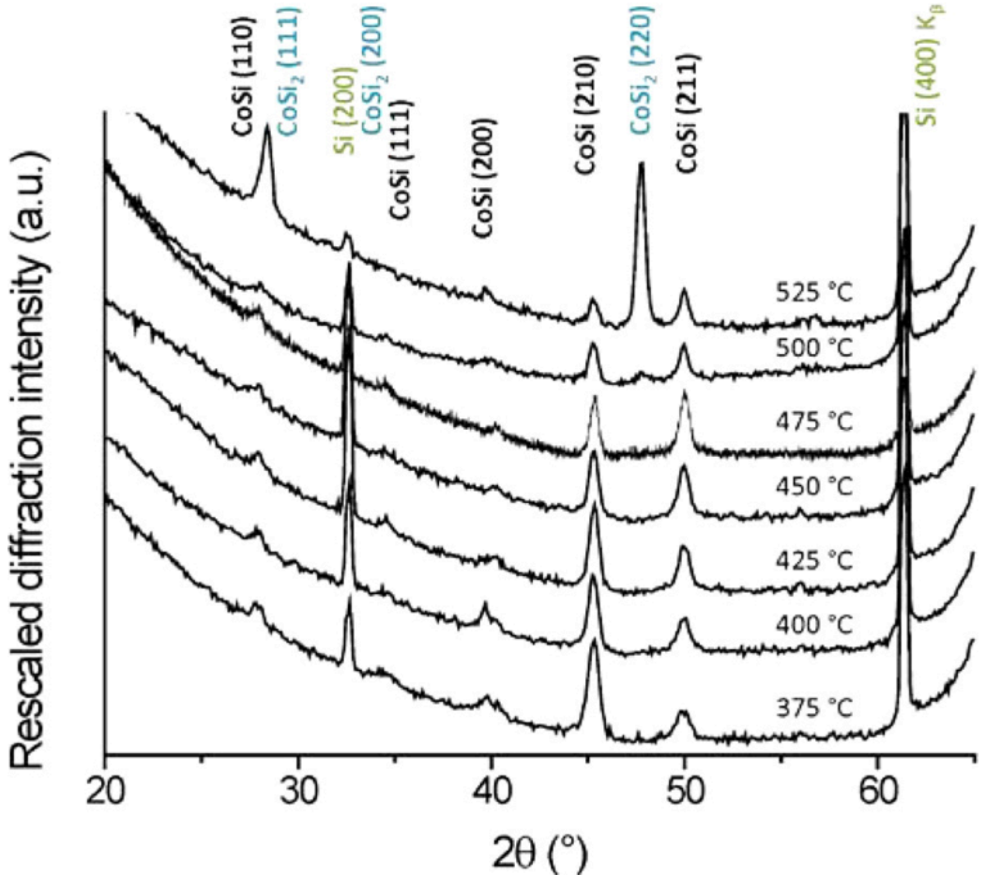



# Rutherford Backscattering Spectrometry (RBS)

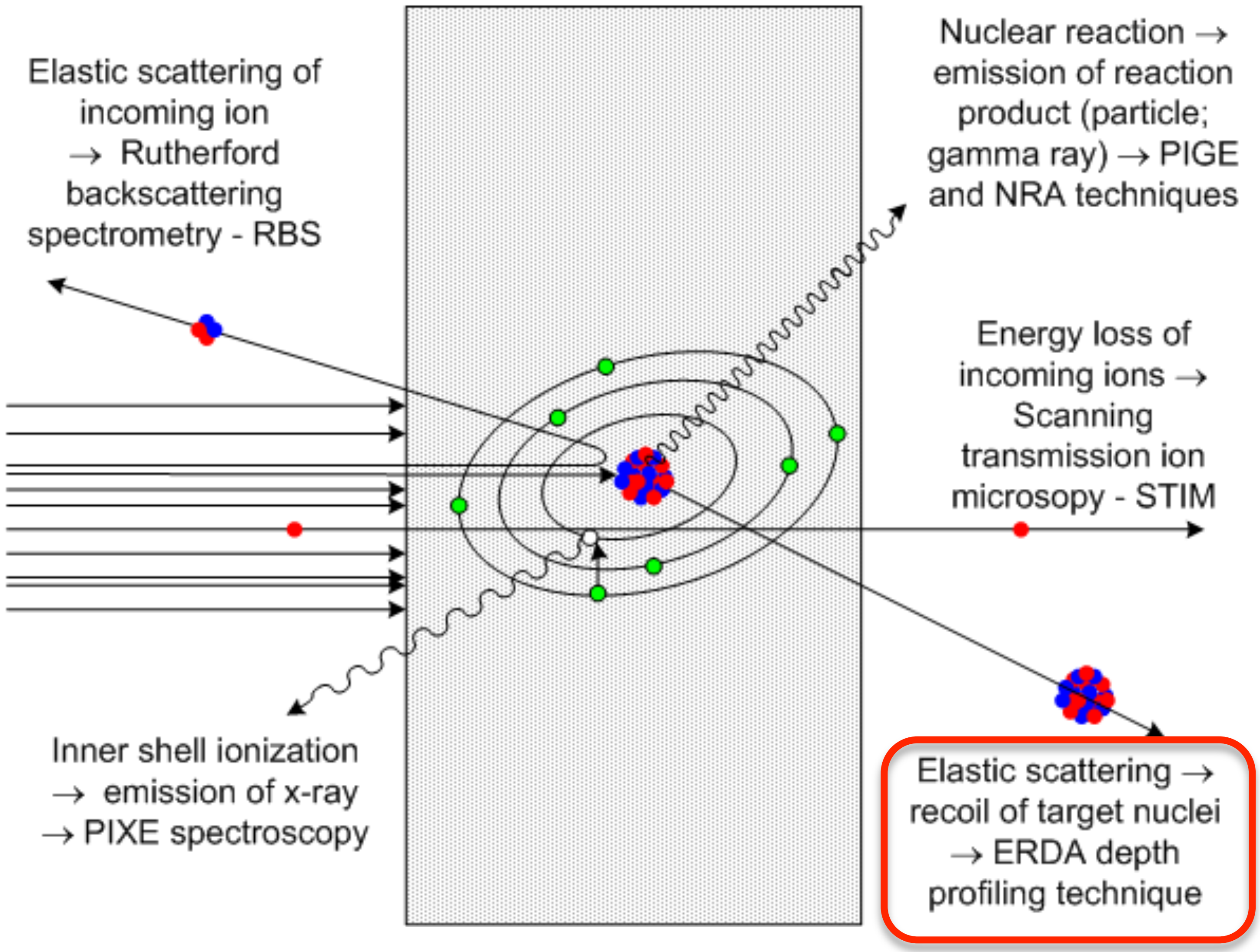
## In situ analysis

Effect of high temperature deposition on CoSi2 phase formation
C. M. Comrie, et al. J. Appl. Phys. 113 (2013)
- Identification of phase transition from CoSi to $CoSi_2$



# Elastic Recoil Detection Analysis (ERDA)



# Elastic Recoil Detection Analysis (ERDA)

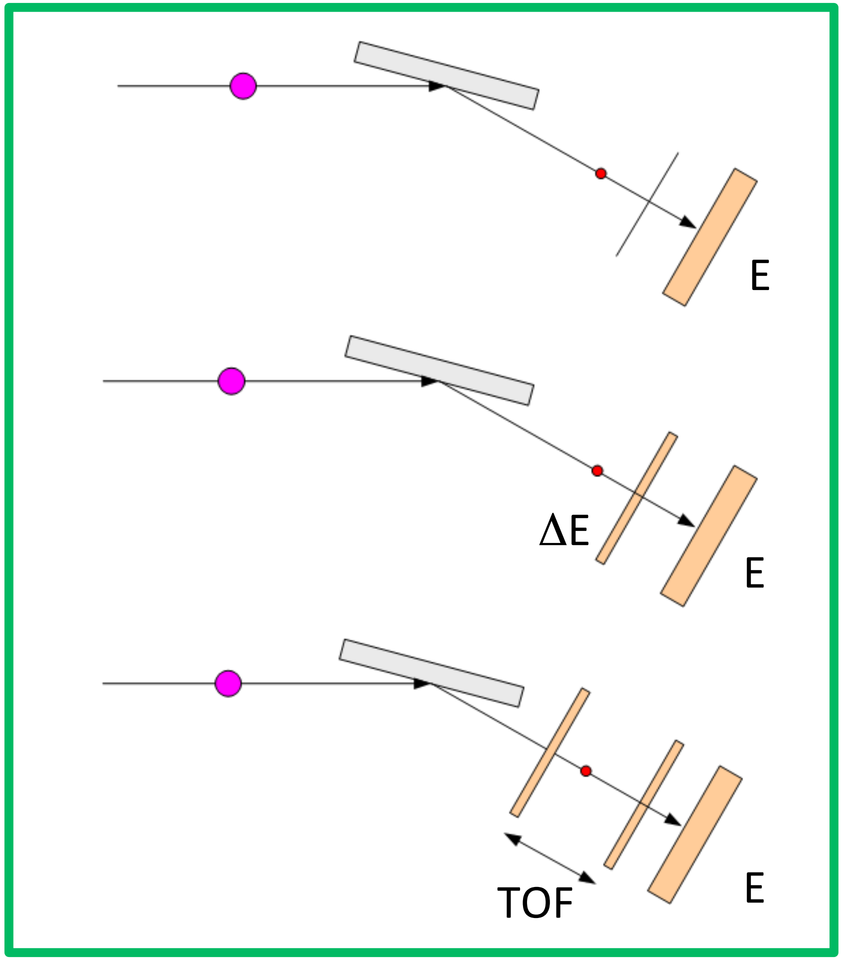
Experimental setup:

Stopping foil – by selection of appropriate thickness, system is optimized for one particular element (e.g. Hydrogen using He ion beam)

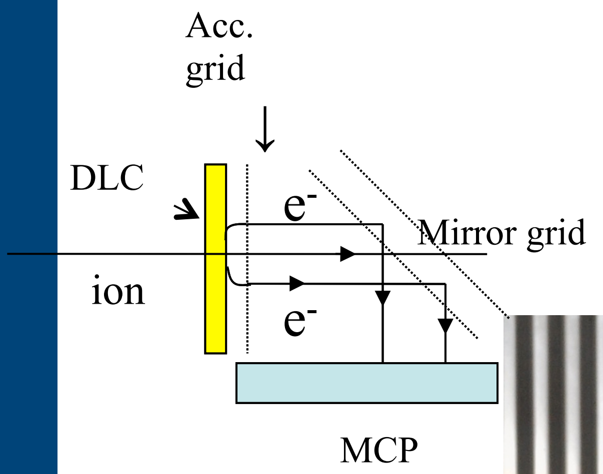
ΔE, E detector: - scattered and recoiled particles are discriminated by different dE/dx! (energy straggling ?)

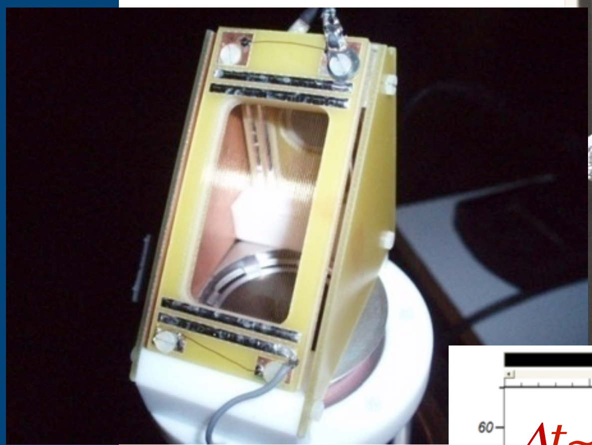
TOF, E detector:
- scattered and recoiled particles are discriminated by measurement of time of flight (with minimal straggling) – best depth resolution

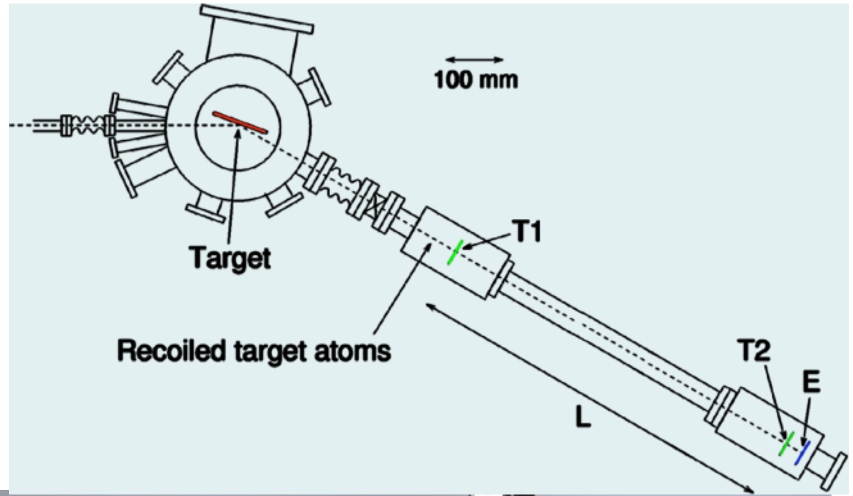
+ Magnetic spectrometer (expensive)

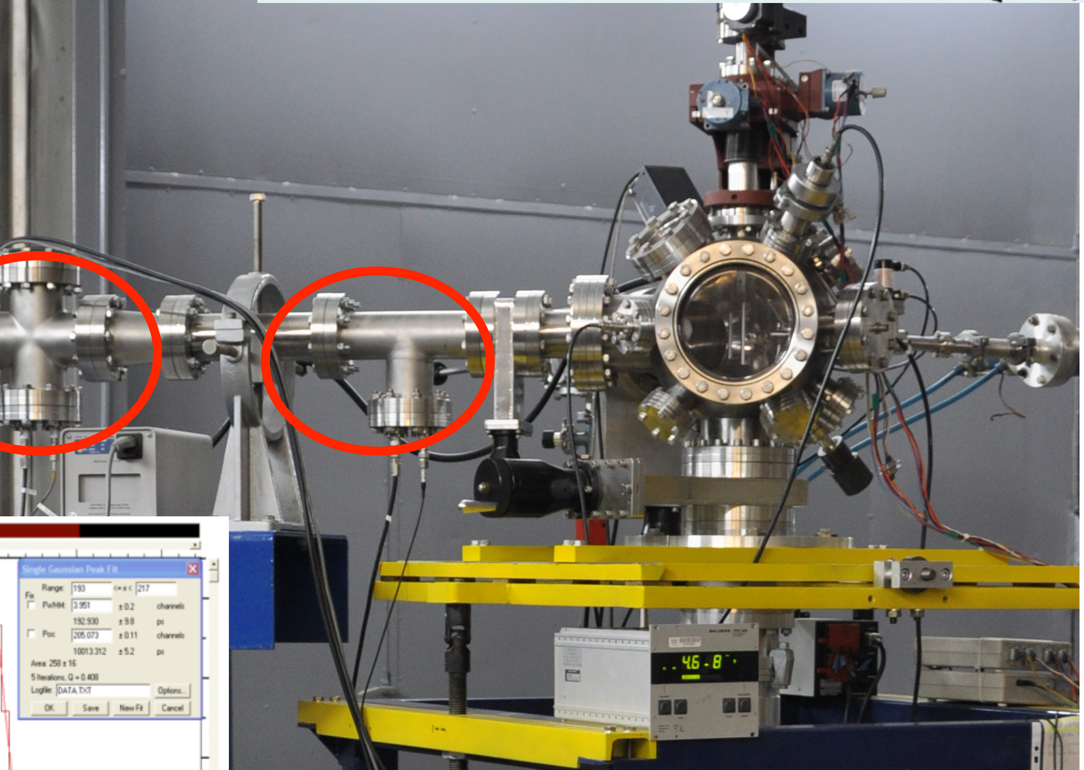


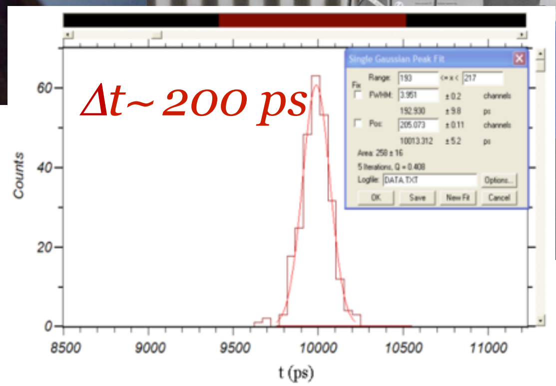
# ToF – ERDA @ RBI-AF





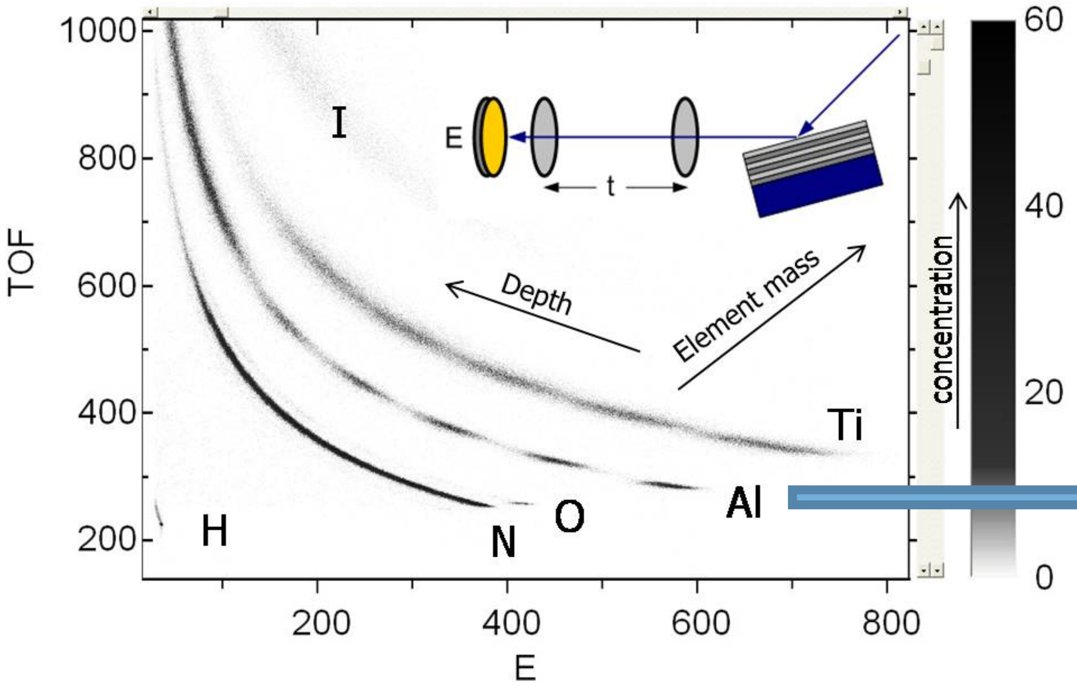



*Z. Siketić, PhD thesis (2010)*

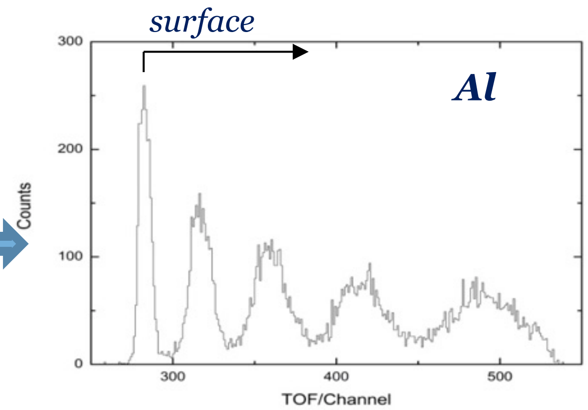
# ToF – ERDA @ RBI-AF

Heavy ion beam – e.g. 20 MeV Iodine ions

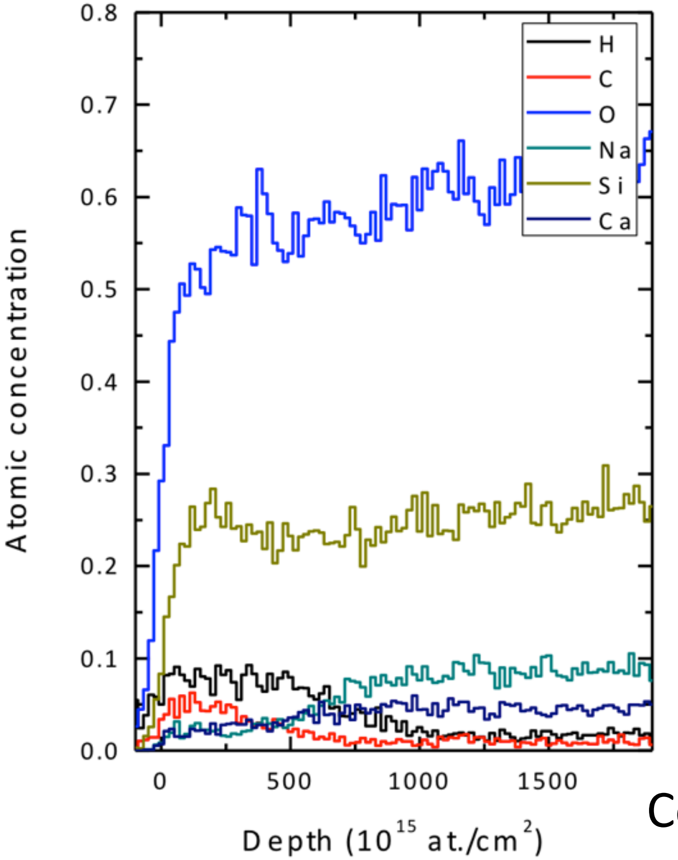
- sensitivity $10^{15}$ /cm$^2$
- 5 nm depth resolution, up to 500 nm probe depth
- all elements are resolved simultaneously

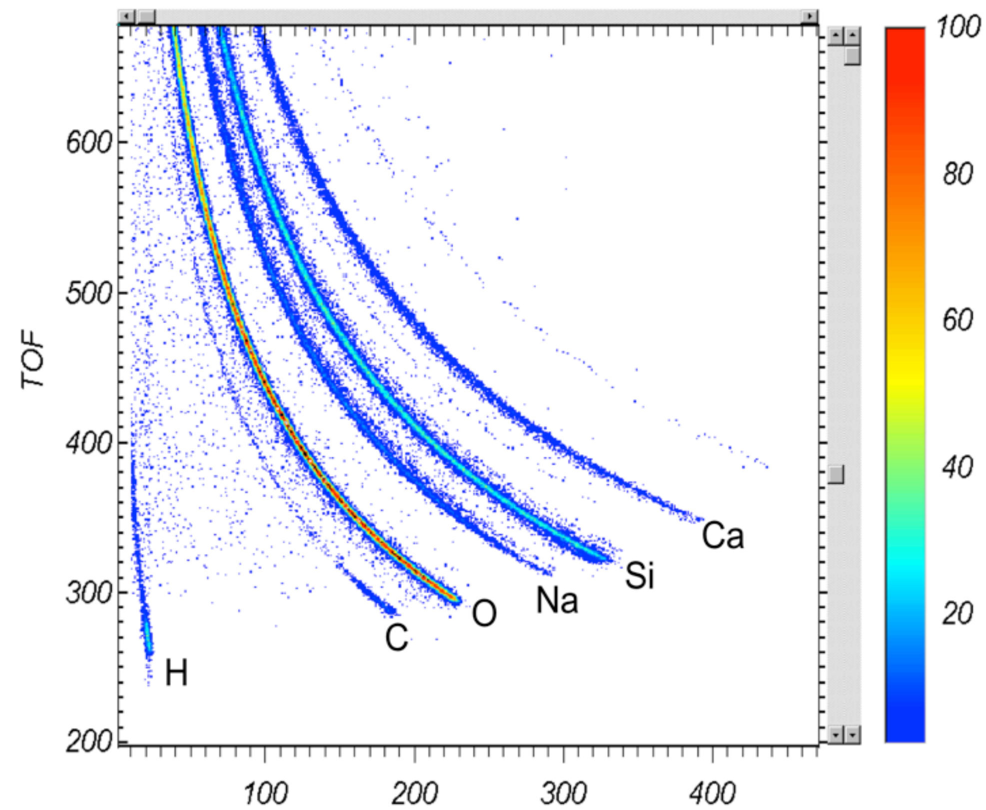



Sample:
20 nm multilayers TiN/AlN



# ToF – ERDA @ RBI-AF




Corrosion of ancient glass found at the fort Sokol (close to Dubrovnik airport)

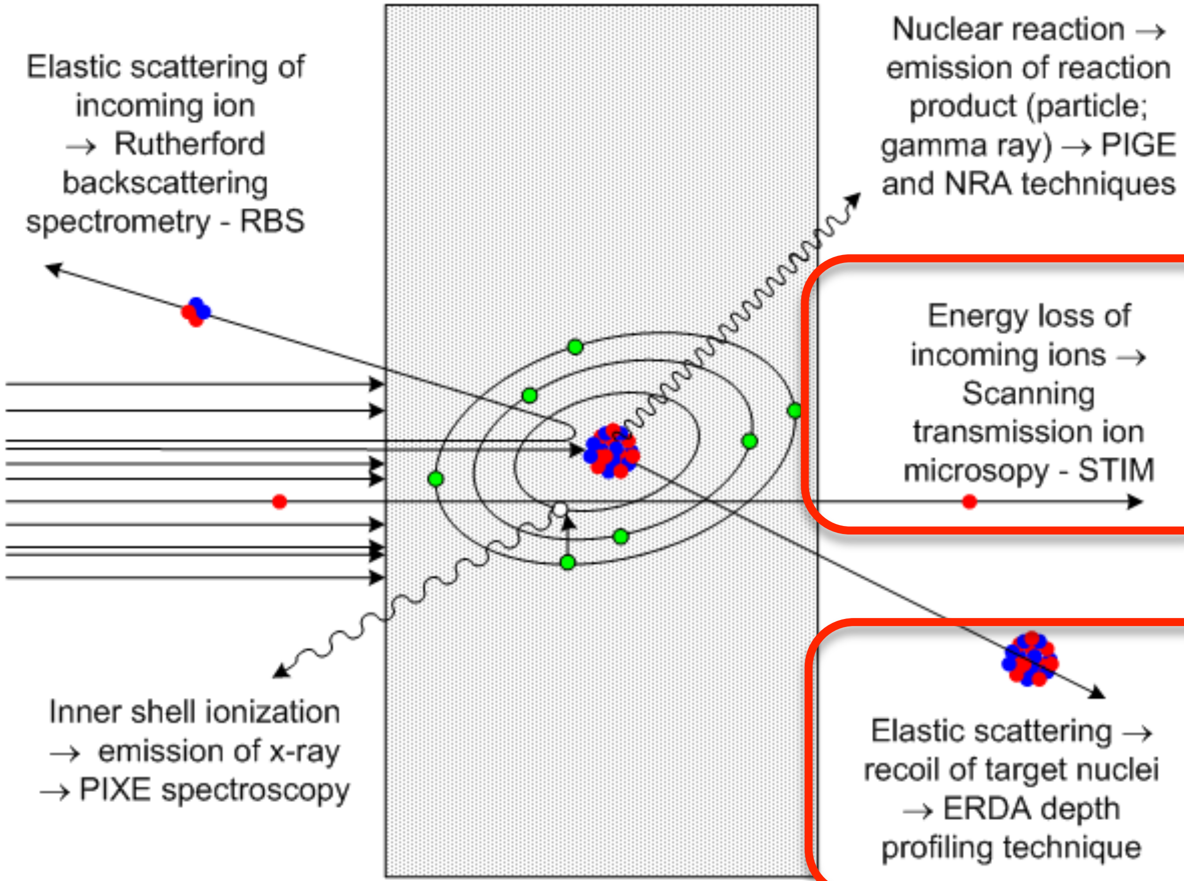
# Other IBA techniques… important for us ?

RBS in channeling (RBS/c)

Secondary electrons SE imaging

Ionolumine scence (IL)

High resolution HR-PIXE




MeV-SIMS

Ion beam induced charge (IBIC)

P-p & C-C scattering

## Resources - books

Y. Wang, M. Nastasi, *Handbook of Modern Ion Beam Materials Analysis* (MRS 2009)

W.K. Chu, W.J. Mayer, M.A. Nicolet, *Backscattering Spectrometry* (AP 1978)

LC Feldman, JW Mayer, ST Picraux:
*Materials Analysis by Ion Channeling* (Elsevier 1982)

W.R. Leo, *Techniques for Nuclear and Particle Physics Experiments: a How-to Approach* (Springer 1987)

# Overview

1. Introduction to IBA

2. RBS/channeling for ion tracks

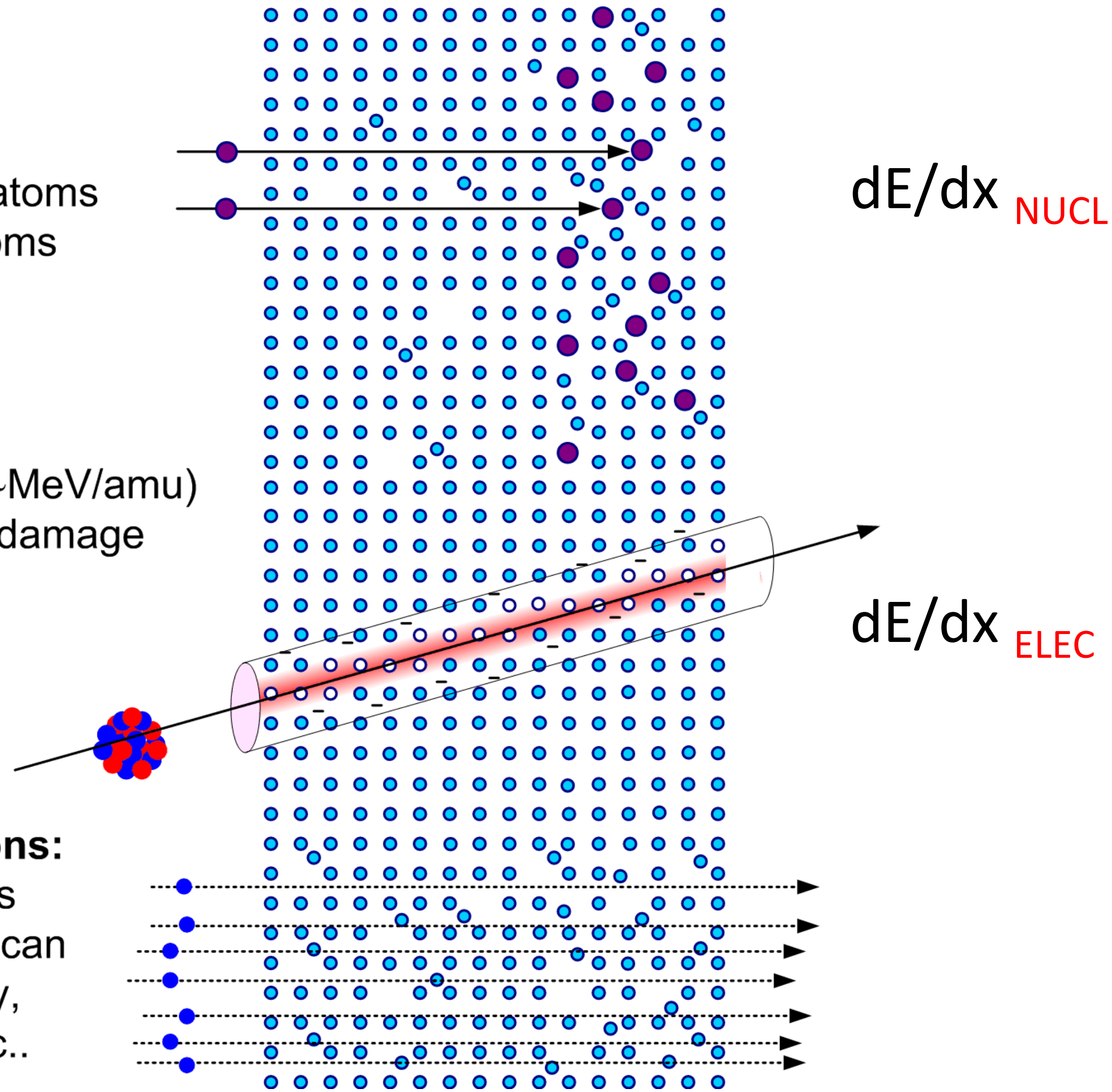
3. RBS/c @ RBI

# MATERIALS MODIFICATIONS USING ION BEAMS

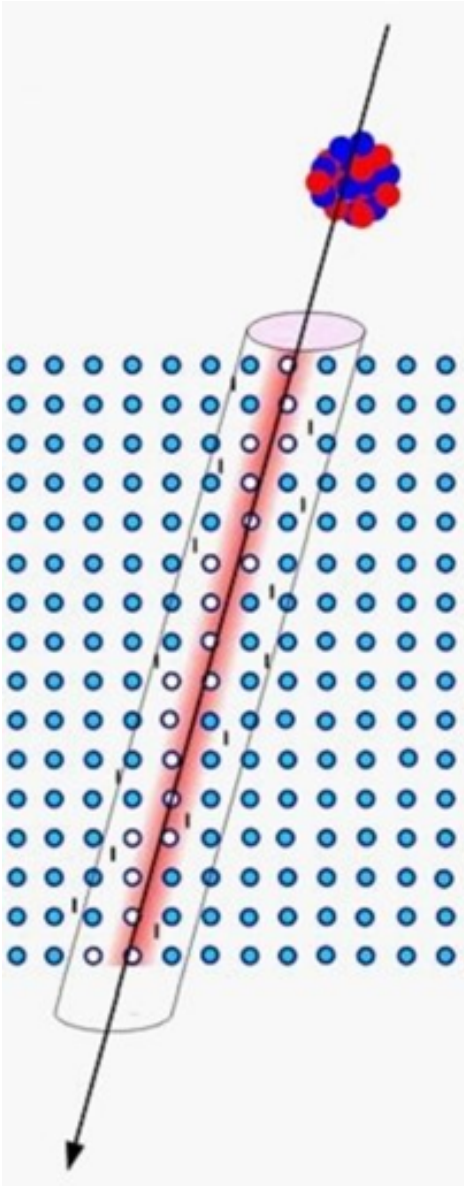
**Ion implantation:**
a) Injection of foreign atoms
b) Displacement of atoms

**Single ion tracks:**
Fast and heavy ions (~MeV/amu) create latent tracks of damage used as a template in nanostructuring

**Irradiation with protons:**
Produce homogeneous radiation damage that can be used for lithography, defect engineering, etc..

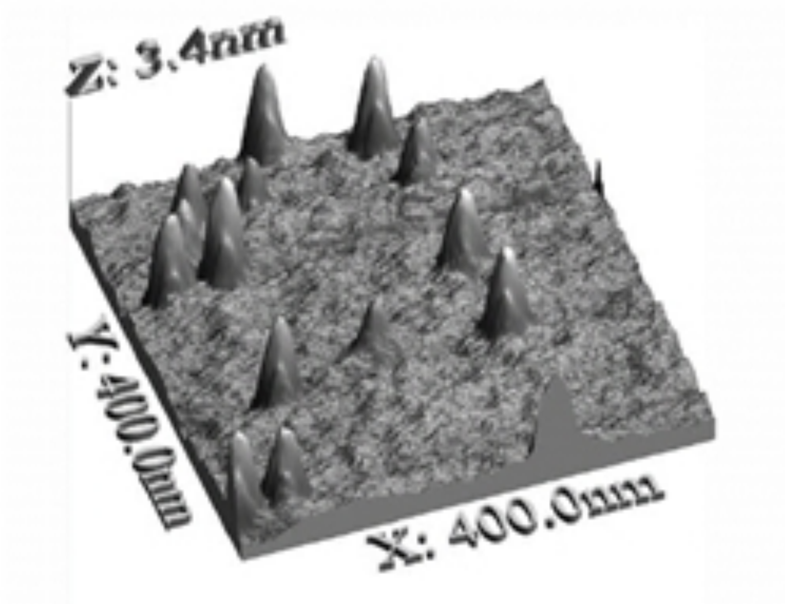


# SWIFT HEAVY ION BEAMS FOR MATERIALS MODIFICATIONS

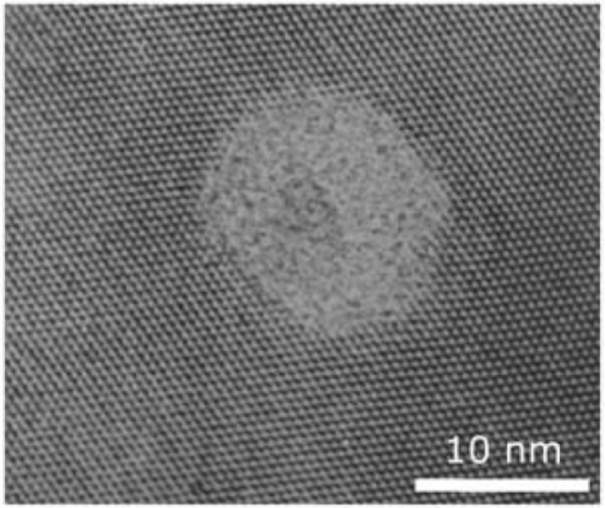


- SWIFT (>1 MeV/amu)
- HEAVY (>20 amu)
- ION TRACK: permanent damage after passage of SWIFT HEAVY ION
- THRESHOLD (melting): relevant is $dE/dx_{ELEC}$, not E !

- FISSION FRAGMENTS
- LARGE ACCELERATOR FACILITIES



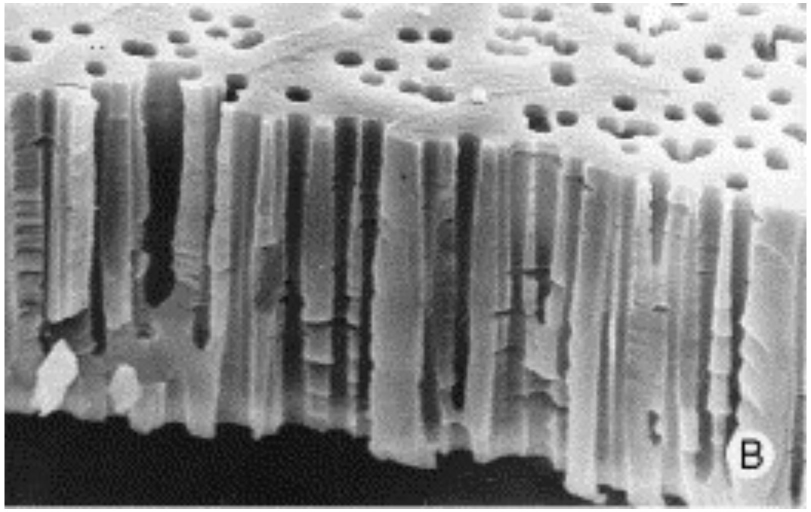

*Zollondz (2004): 1GeV U* ⇨ DLC



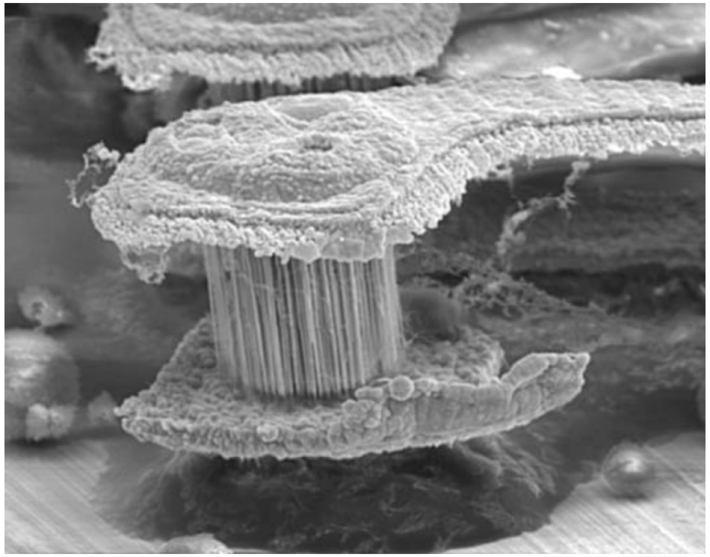

*Vetter (1998):*
*2.4 GeV Pb* ⇨ mica

- SWIFT (>1 MeV/amu)
- HEAVY (>20 amu)
- ION TRACK: permanent damage after passage of SWIFT HEAVY ION
- THRESHOLD (melting): relevant is $dE/dx_{ELEC}$, not E !

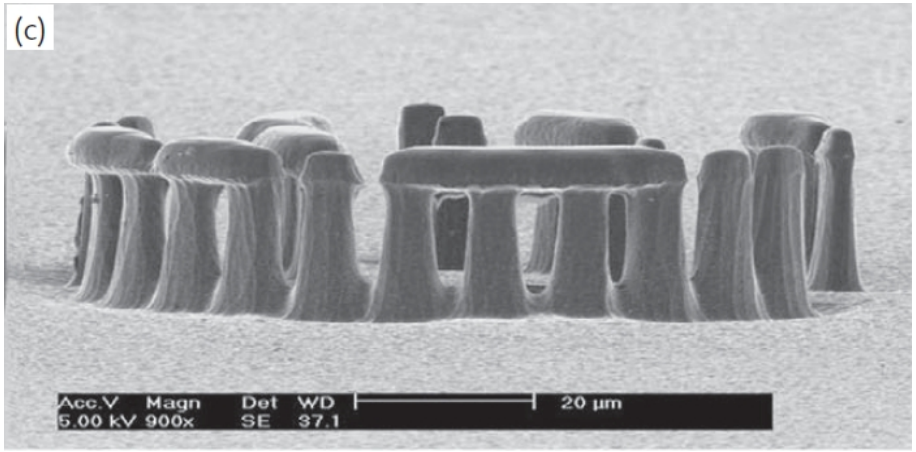
- FISSION FRAGMENTS
- LARGE ACCELERATOR FACILITIES




*P. Apel, NIMB 2003*



*Lindenberg et al., Microsys. Techn. 2004*

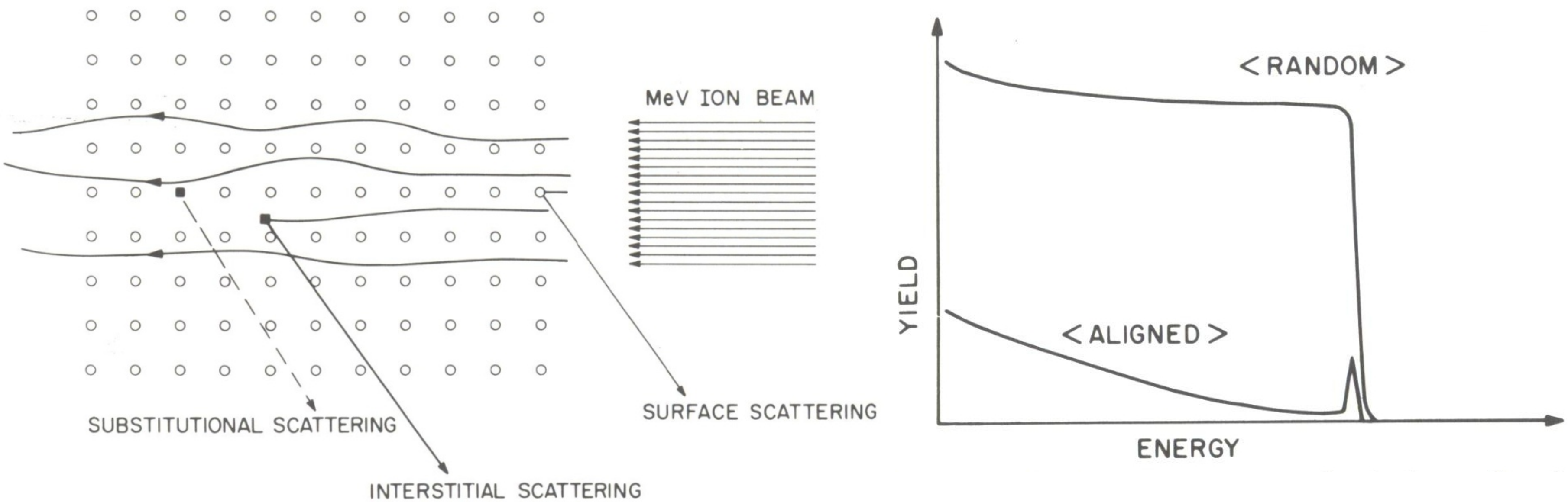



*F. Watt et al., Mat. Today (2007)*

# Ion track analysis using RBS/channeling

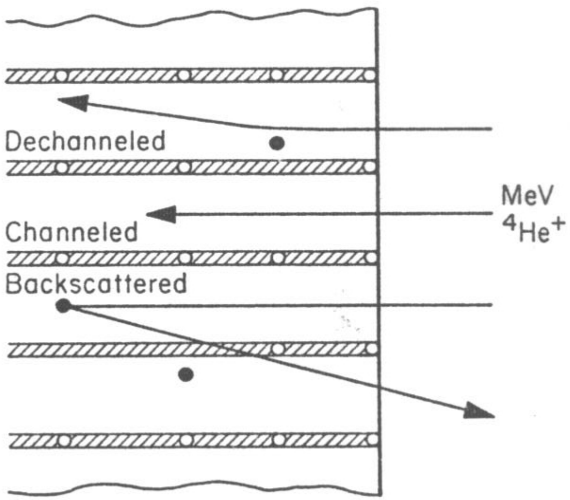
- Applicable for any type of damage (nuclear/electronic dE/dx)
- Possible to analyse greater number of samples than TEM
- Applicable for single crystal targets !

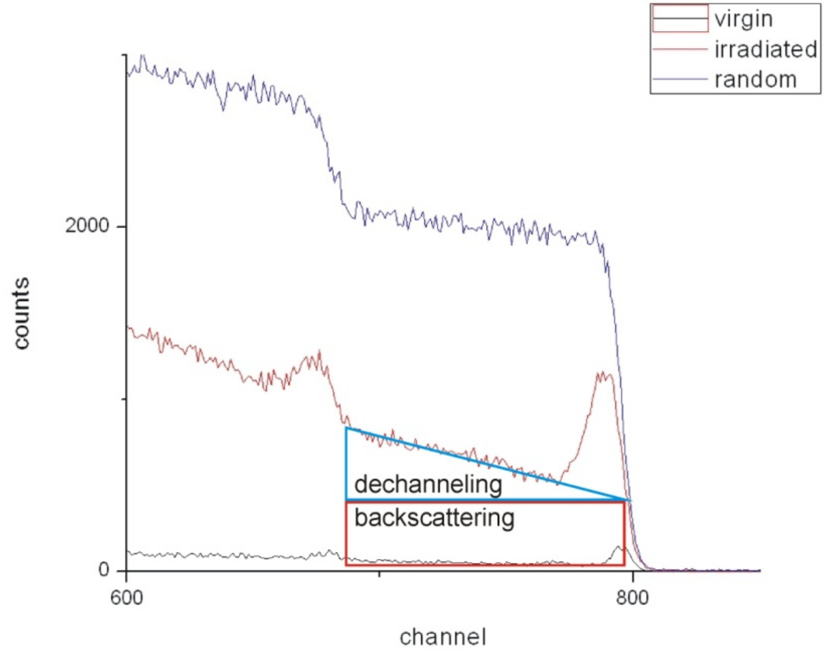
*LC Feldman, JW Mayer, ST Picraux:*
*Materials analysis by Ion Channeling (1982)*




Critical channeling angle: $\psi_c = \left( \frac{Z_1 Z_2 e^2}{Ed} \right)^{1/2}$

# Ion track analysis using RBS/channeling

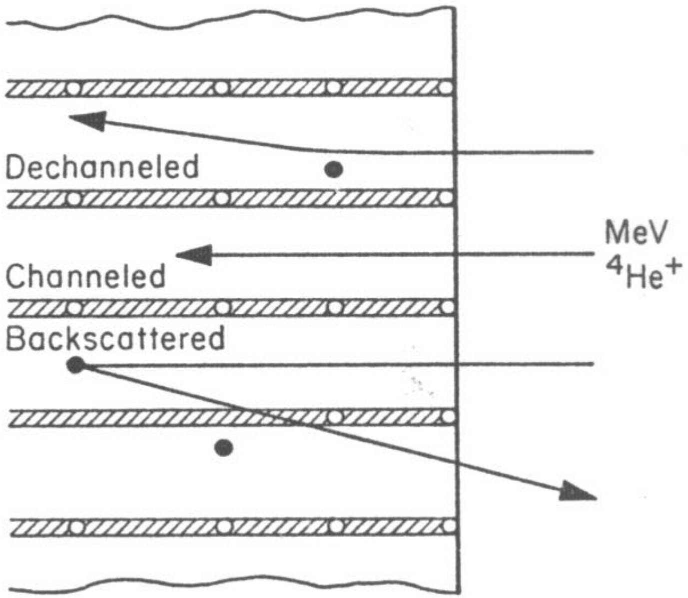


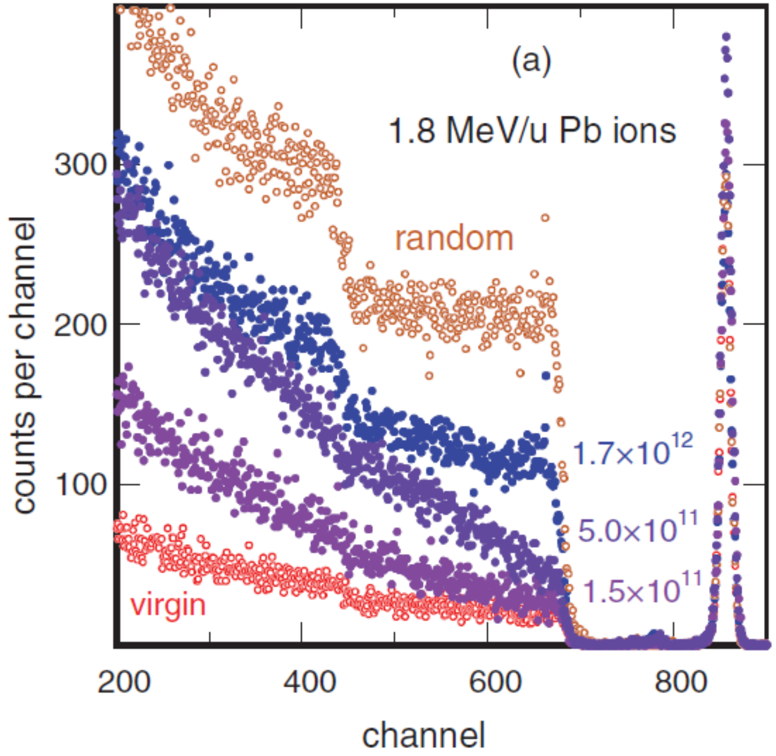




*Surface approximation*

$$F_d = \frac{\chi_{irrad} - \chi_{virgin}}{\chi_{random} - \chi_{virgin}}$$

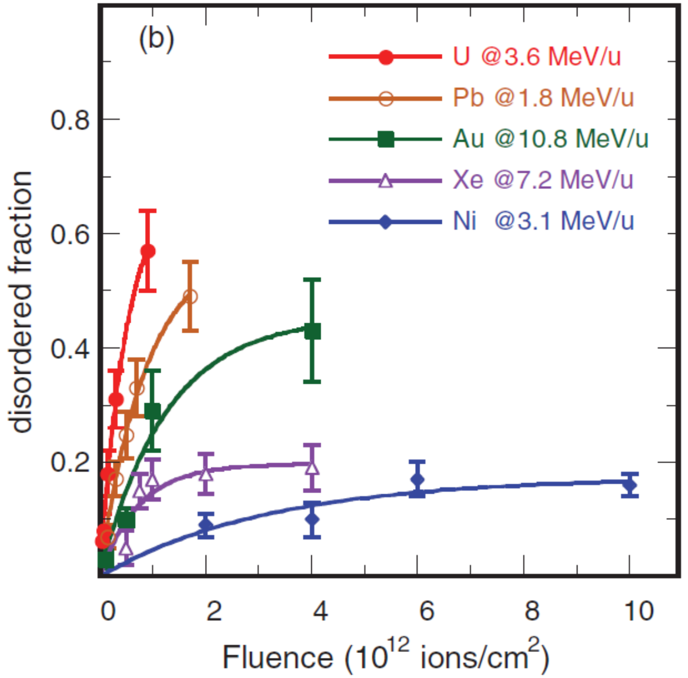
# Ion track analysis using RBS/channeling

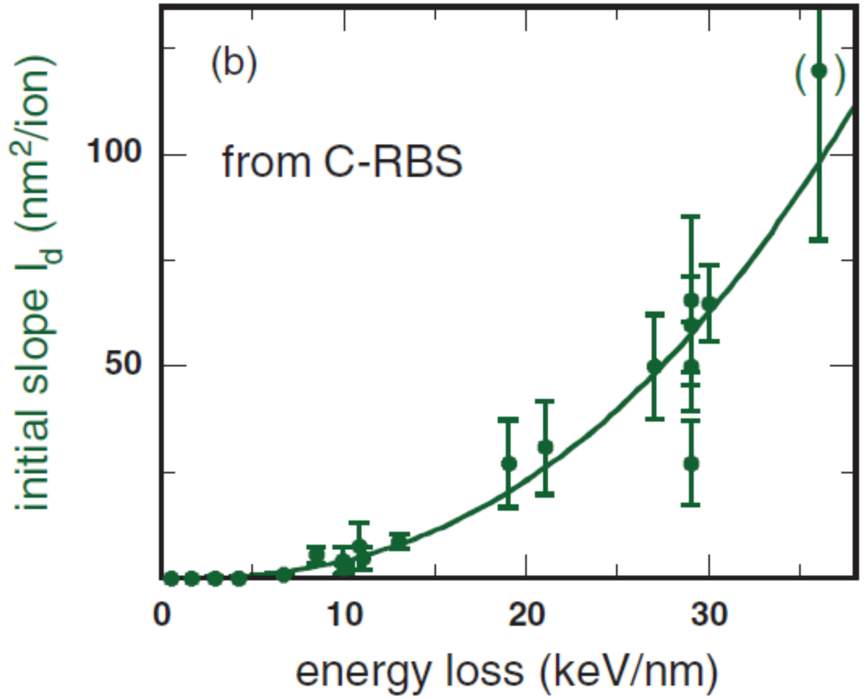



*Toulemonde et al., PRB (2012): $CaF_2$*

# Ion track analysis using RBS/channeling



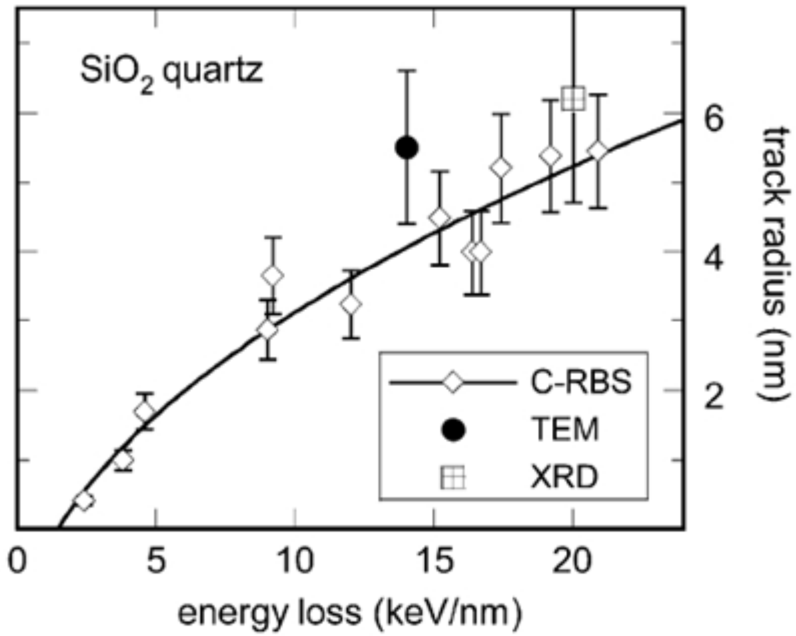

*Toulemonde et al., PRB (2012): $CaF_2$*

$$F_d = \alpha\left(1 - e^{-R^2\pi\Phi}\right)$$

*Poisson law*

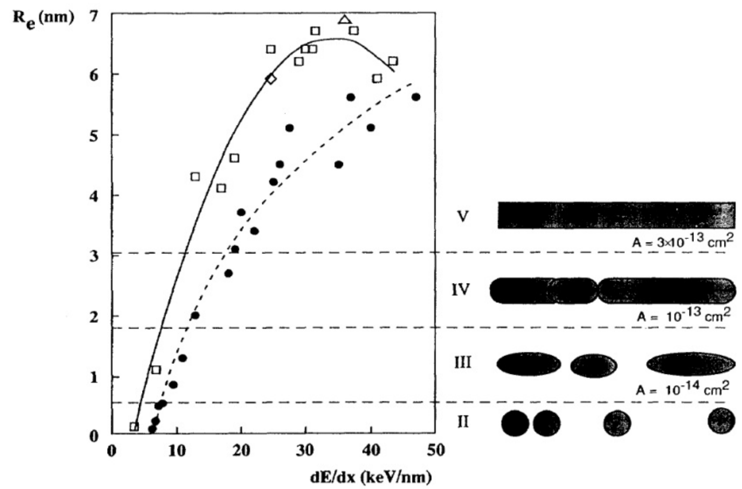
*For 1 data point, ~ 5 samples measured with RBS/c*

# Ion track analysis using RBS/channeling




Toulemonde MfM (2006)

*Overall good agreement RBS/c with other techniques (amorphizable materials)*




*Meftah PRB (1993)*

*But close to threshold ion tracks are discontinuous*

*RBS/c measures effective ion track cross section*

*Different but perhaps more appropriate than TEM!*

# Ion track analysis using RBS/channeling

## Discontinuous tracks

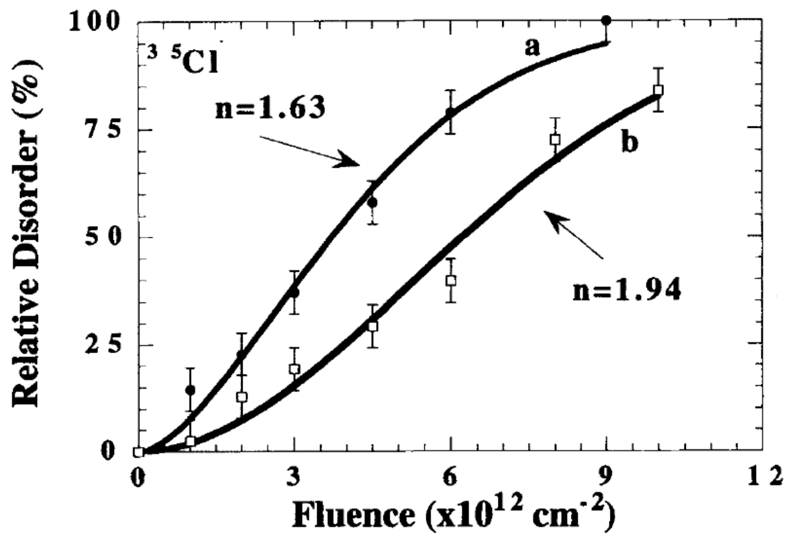



FIGURE 4 Relative disorder in $LiNbO_3$ versus the chlorine fluence. Irradiations performed at two different energies: 10 MeV (circles) and 7 MeV (squares). The continuous lines correspond to the best fits of experimental data by using the AVRAMI model (Eq. (4): $\alpha = 1 - \exp(-(\phi/\phi_c)^n)$). The $\phi_c$ values obtained for these two energies were $4.6 \times 10^{12}$ and $7.5 \times 10^{12}\ cm^{-2}$, respectively.

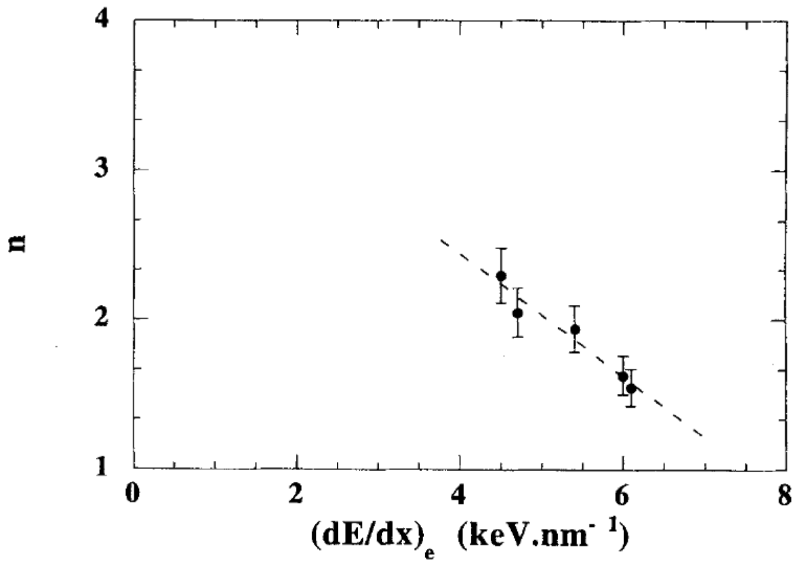



FIGURE 5 Evolution of the exponent $n$, fitted from Eq. (4), versus the electronic stopping power.

*SMM Ramos et al., REDS (1998)*

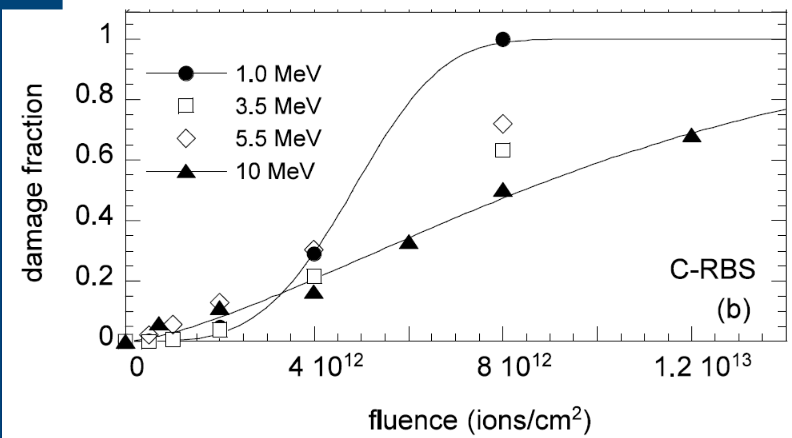
$$\alpha = 1 - \exp(-(\phi/\phi_c)^n)$$

*For 1 data point,*
*5+ samples measured*
*with RBS/C*

*Avrami equation: sigmoidal shape, incubation fluence*

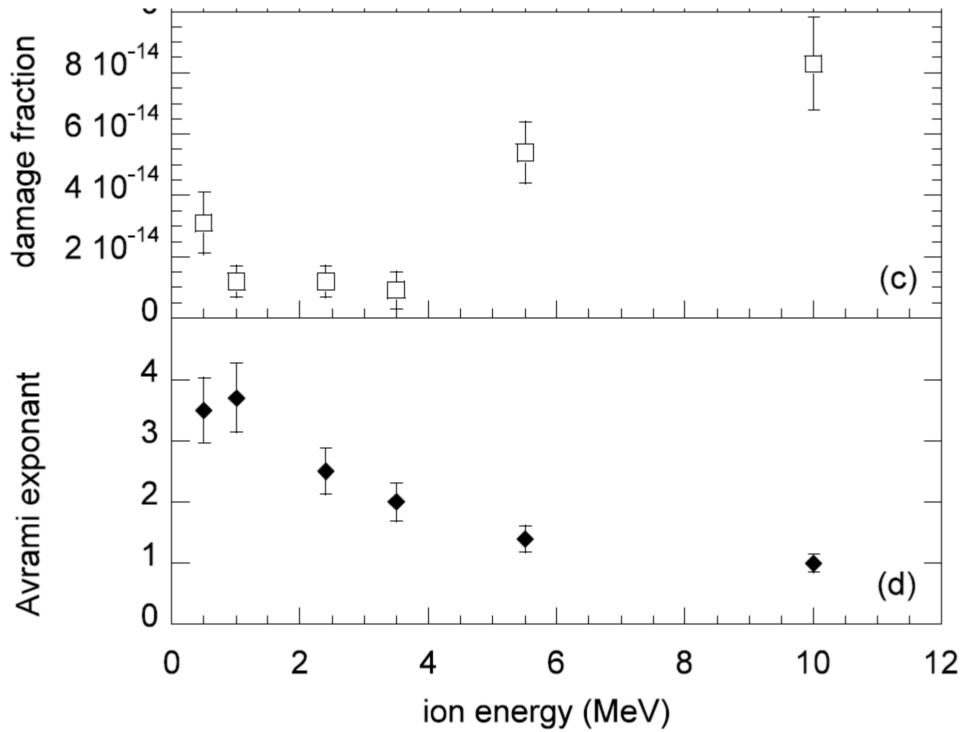
# Ion track analysis using RBS/channeling

## Nuclear stopping contribution




*Au irradiation of $SiO_2$ quartz*

*Bernas et al., NIMB (2001)*




*Avrami formalism is useful extension of the Poisson law,*
*but many measurements are necessary for 1 data point*
*In situ RBS/c is an excellent solution for saving beamtime!*

# Ion track analysis using RBS/channeling

## Nuclear stopping contribution

Table 1
Main irradiation parameters and some of the swelling and C-RBS results

| Beam | Au | Au | Au | Au | Au | Au | Pb | Pb |
|---|---|---|---|---|---|---|---|---|
| Energy (MeV) | 0.5 | 1 | 2.4 | 3.5 | 5.5 | 10 | 250 | 850 |
| Range (μm)[a] | 0.15 | 0.25 | 0.56 | 0.81 | 1.3 | 2.2 | 16 | 40 |
| Total $dE/dx$ (keV/nm)[a] | 4.23 | 4.3 | 4.3 | 4.3 | 4.5 | 4.8 | 22.2 | 28.1 |
| Nuclear $dE/dx$ (keV/nm)[a] | 3.3 | 3.1 | 2.4 | 2.1 | 1.7 | 1.2 | 0.15 | 0.06 |
| Avrami exponent[b] | 3.5 | 3.7 | 2.5 | 2.0 | 1.35 | 1 | 1 | 1 |
| Nuclear cross-section $\sigma_n$ ($10^{-14}$ cm$^2$) | 23.5 | 19 | (16)[c] | (14)[c] | (12)[c] | (8)[c] | – | – |
| Electronic $dE/dx$ (keV/nm)[a] | 0.93 | 1.2 | 1.9 | 2.2 | 2.8 | 3.6 | 22 | 28 |
| Electronic cross-section $\sigma_e$ ($10^{-14}$ cm$^2$) | – | – | 0.95 | 1.2 | 5.9 | 6.6 | 109 | 105 |
| Mean $dE/dx$ (keV/nm)[d] | | | | 4.3 | 4.2 | 4.5 | 15.6 | 21.3 |

*Ramos, NIMB (2000)*

# Ion track analysis using RBS/channeling

## Core-halo ion track structure

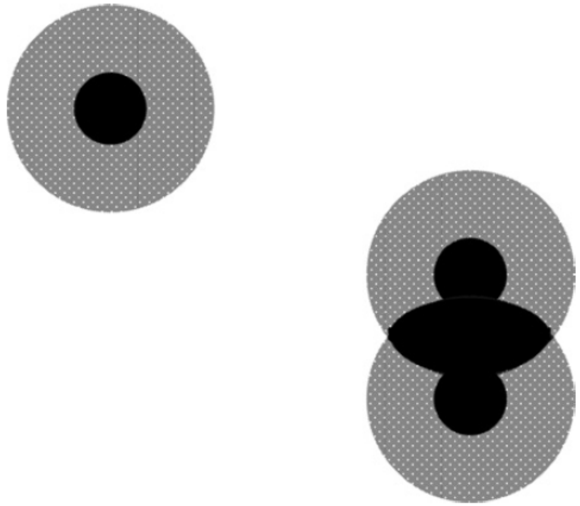


**Fig. 3.** Schematics of the physical process underlying the multi-impact model, with $N = 2$. Amorphized areas (one core or two halo impacts) are shown in black, whereas pre-amorphized areas (one halo impact) are shown in grey.

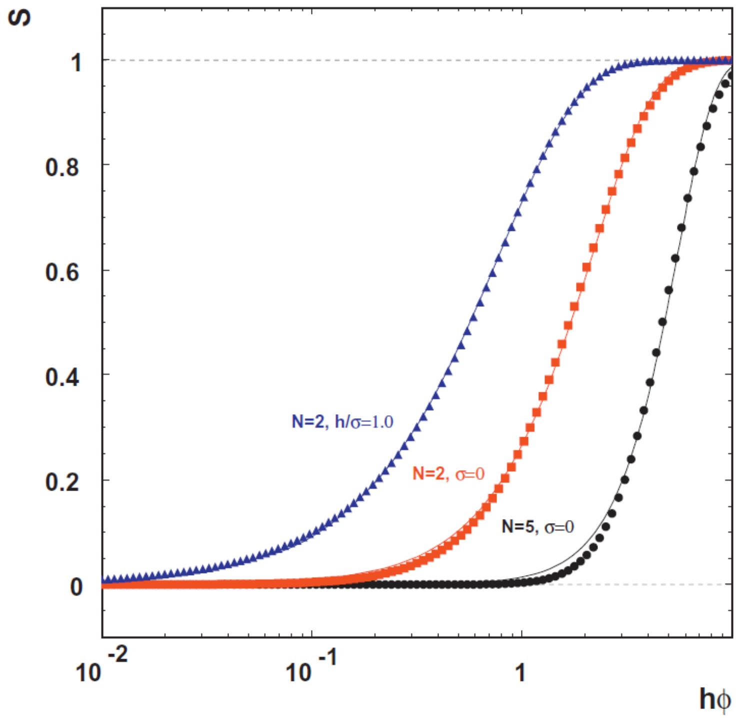
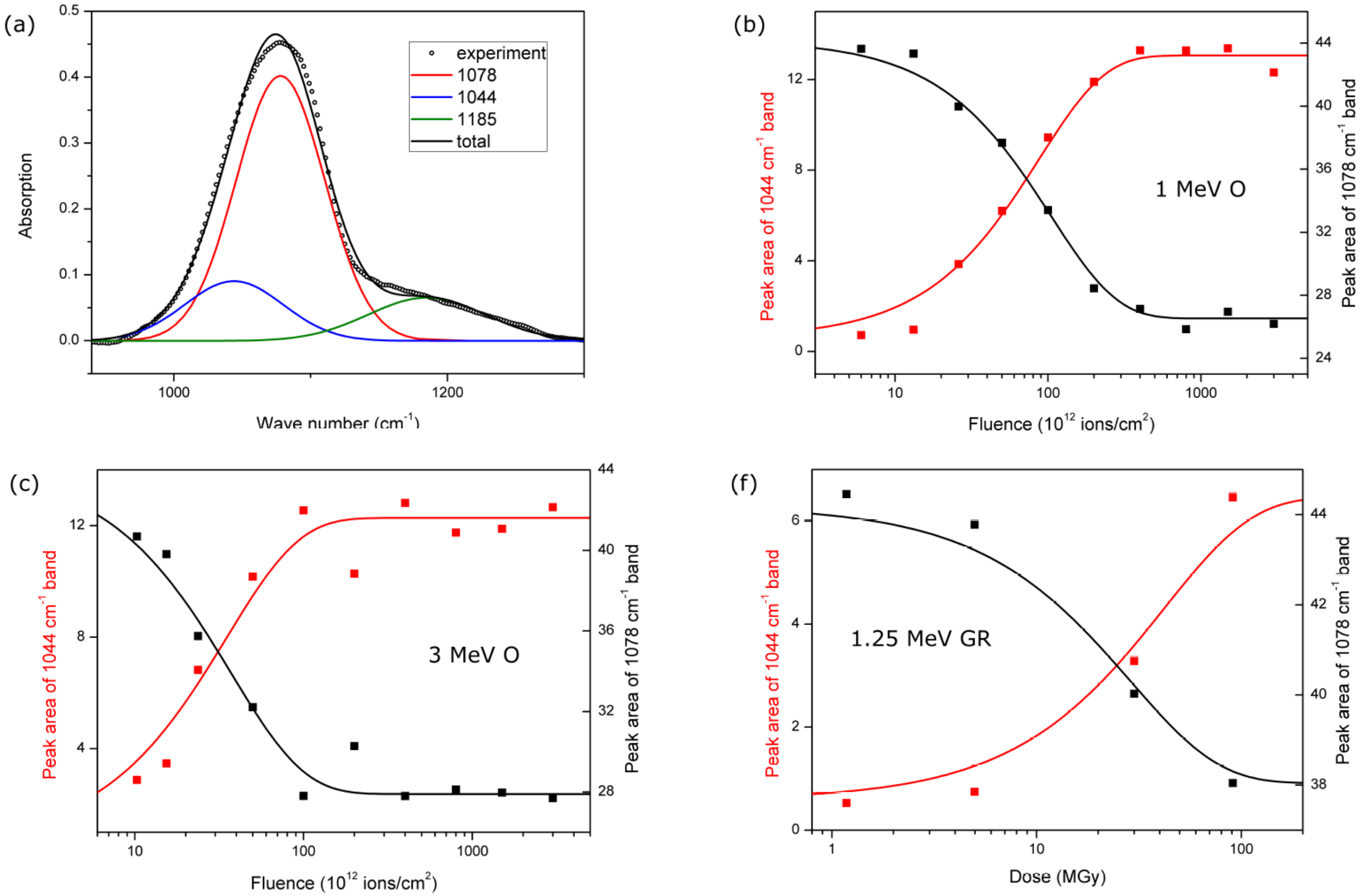



**Fig. 6.** Fractional amorphized area $S$, calculated according to the impact-overlapping model with the values indicated in the graph for the parameters $N$, $\sigma$, as a function of the fluence normalized to the inverse area of a halo $h$ (black circles $N = 5$, $\sigma = 0$; red squares $N = 2$, $\sigma = 0$; blue triangles $N = 2$, $\sigma = h$). The solid lines show the result of an Avrami fit to each of these three cases. (For interpretation of the

*Garcia et al., NIMB (2011)*

# Ion track analysis using other techniques

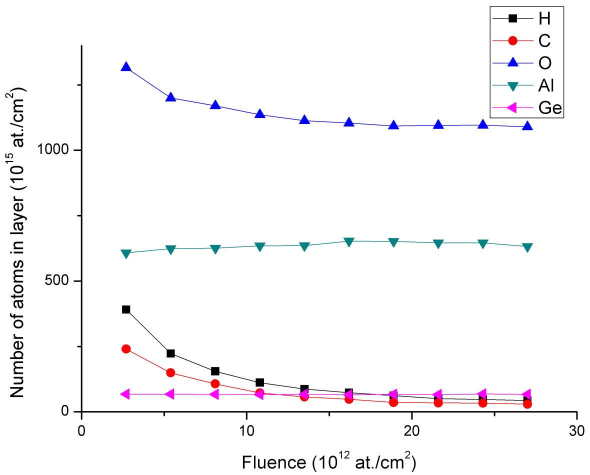
## IR spectroscopy of ion tracks in a-$SiO_2$



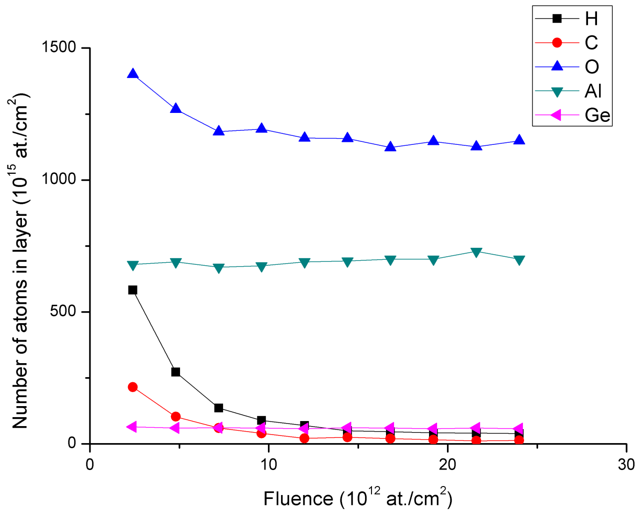

*M. Karlusic et al., J. Nucl. Mater. (2019)*

# Ion track analysis using other techniques

## ToF ERDA of hydrogen loss from $Al_2O_3$ film




16 MeV I, Θ = 20°



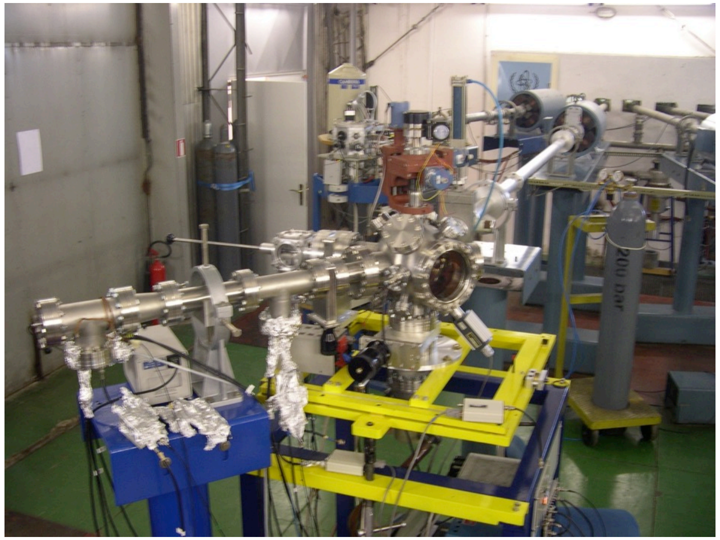

23 MeV I, Θ = 20°

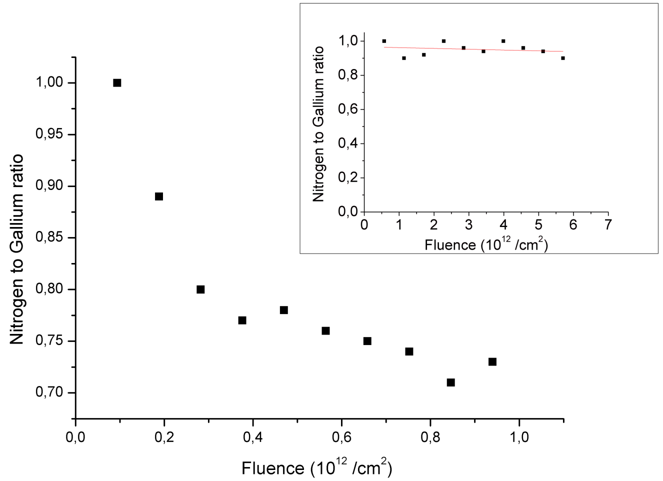
Ion track radius 1-2 nm, 20% bigger for higher energy

*M. Karlusic et al., unpublished*

# Ion tracks on the surfaces: GaN, $TiO_2$

*In situ* grazing incidence ToF-ERDA





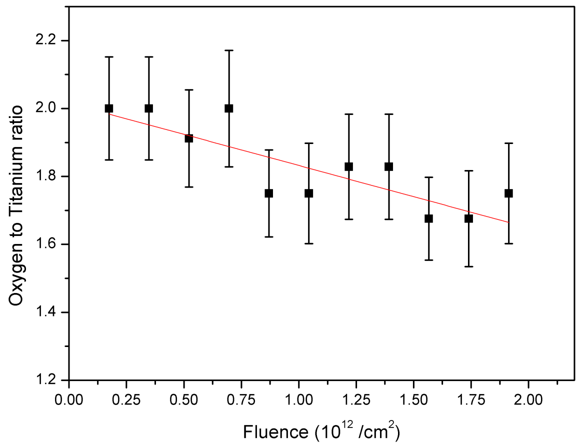

GaN: J. Phys. D: Appl. Phys. (2015)

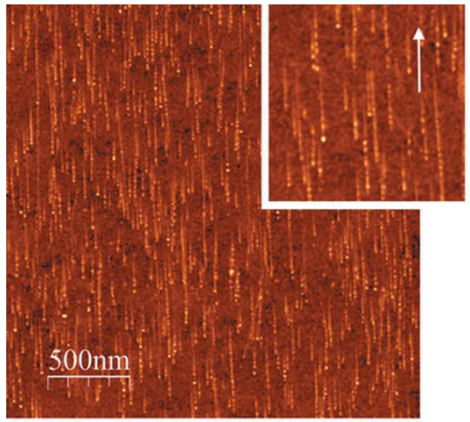
SrTiO$_3$, SiO$_2$, muscovite mica: Materials (2017)

CaF$_2$: New J. Phys. (2017)

MgO, Al$_2$O$_3$, MgAl$_2$O$_4$: unpublished

$TiO_2$: J. Appl. Cryst. (2016)



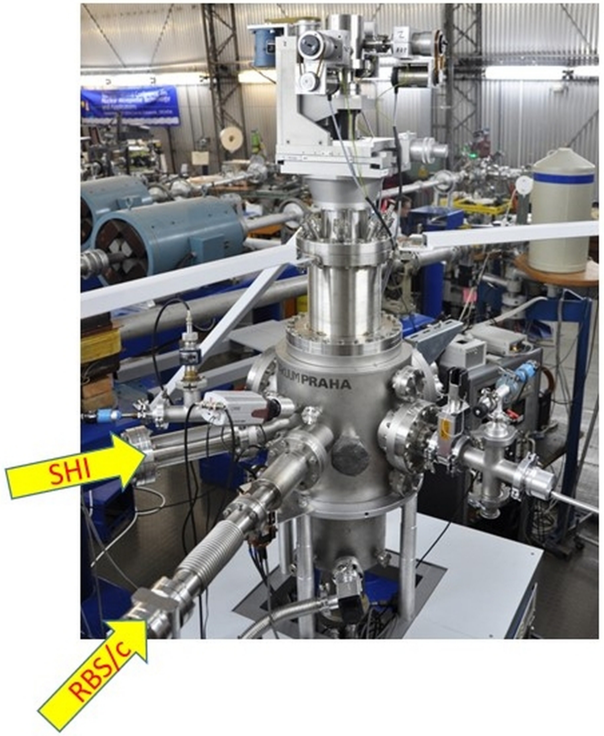
# Overview

1. Introduction to IBA

2. RBS/channeling for ion tracks

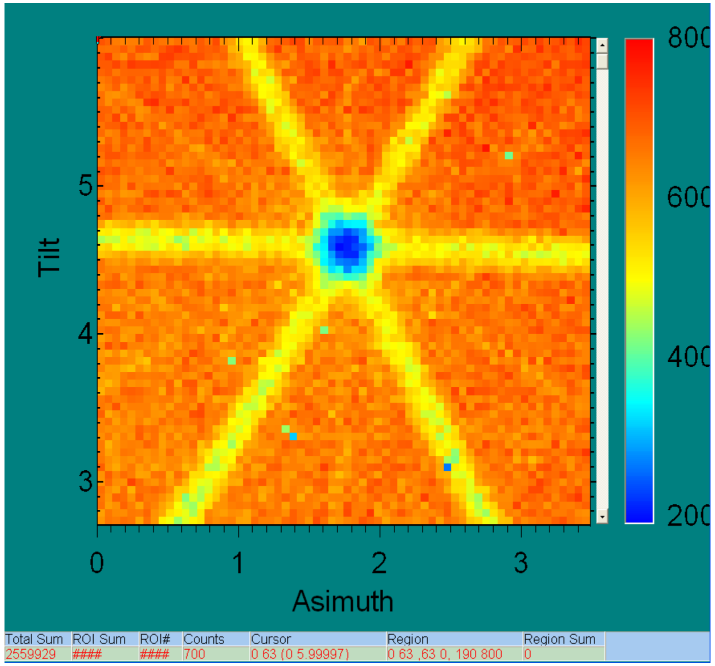
3. RBS/c @ RBI

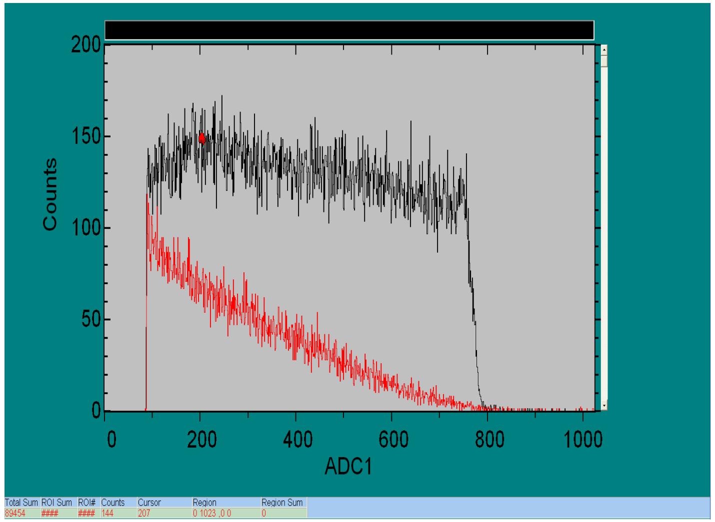
# RBS/C @ RBI-AF
## (DUAL BEAM END STATION)



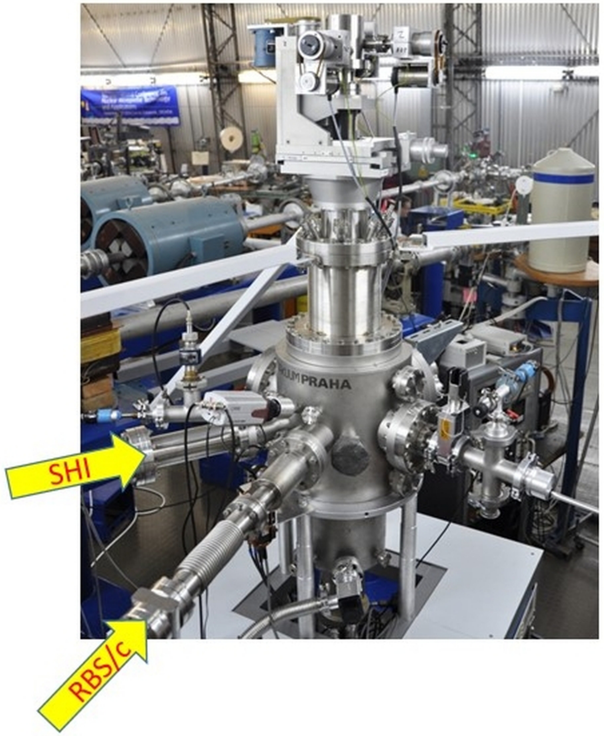

6 MV Tandem Van de Graaff

1 MV Tandetron



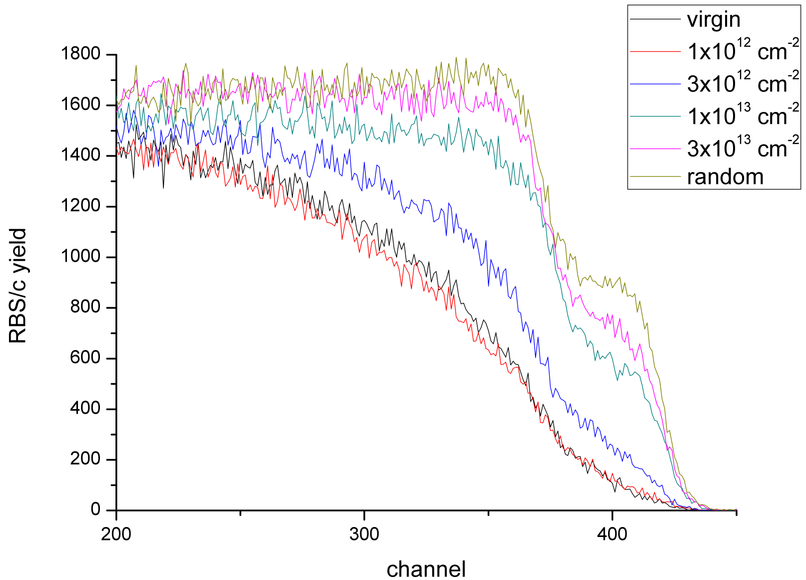



# RBS/C @ RBI-AF
## (DUAL BEAM END STATION)




6 MV Tandem Van de Graaff
1 MV Tandetron

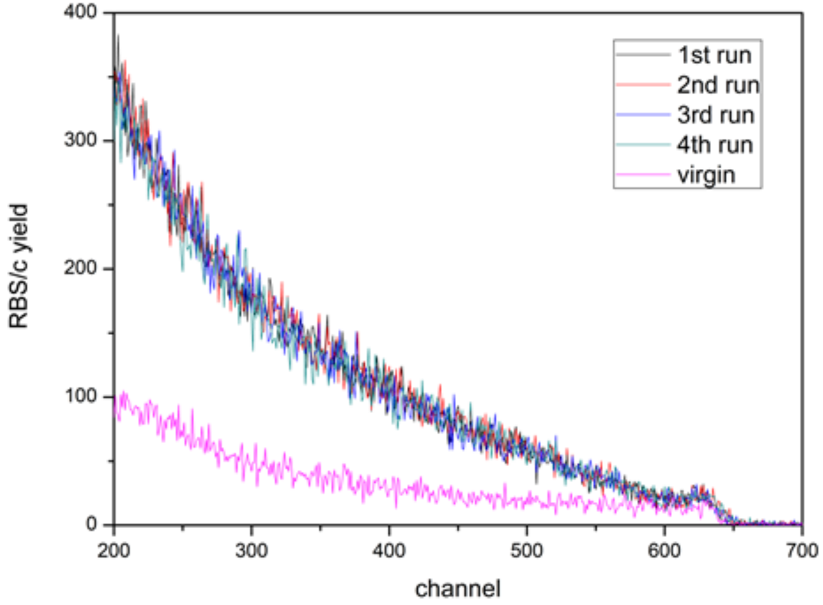
*In situ* RBS/c

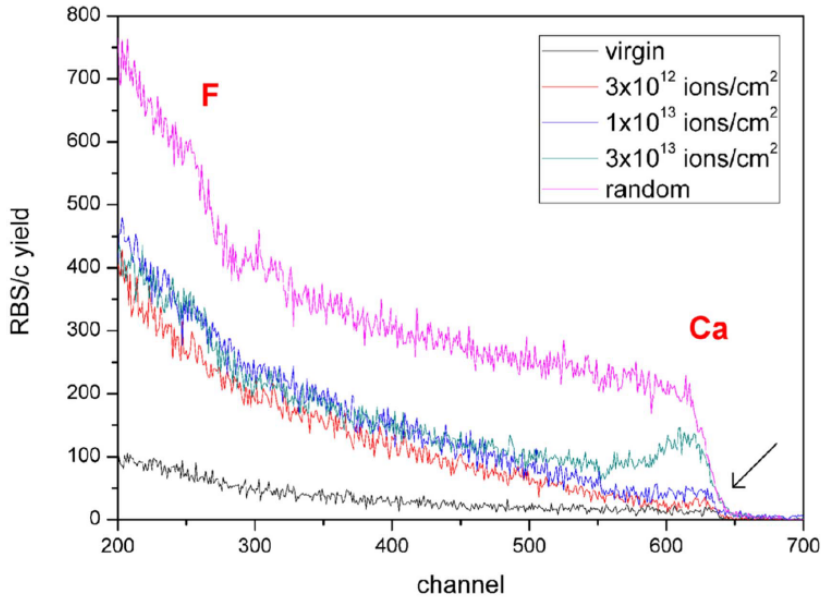



5 MeV Si ⇨ $SiO_2$ quartz
RBS/c: 1 MeV protons

*M. Karlusic et al., Materials (2018)*

# RBS/C @ RBI-AF
## (DUAL BEAM END STATION)



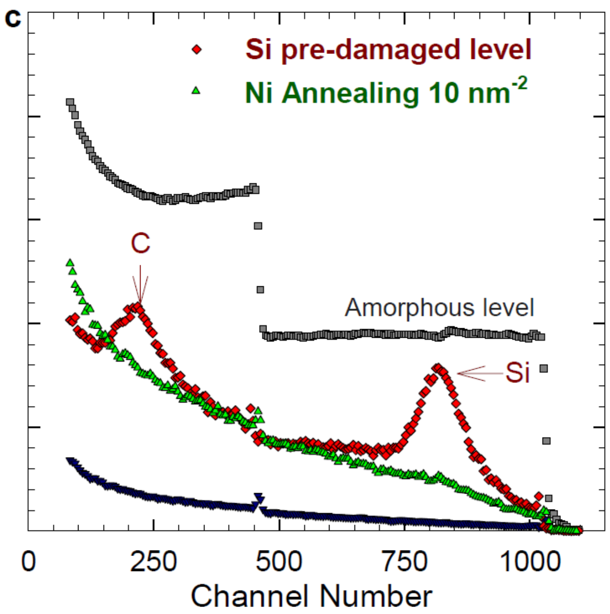




23 MeV I, $3\times10^{12}$ ions/cm$^2$
RBS/c using 2 MeV Li

23 MeV I @ $CaF_2$
RBS/c: 2 MeV Li

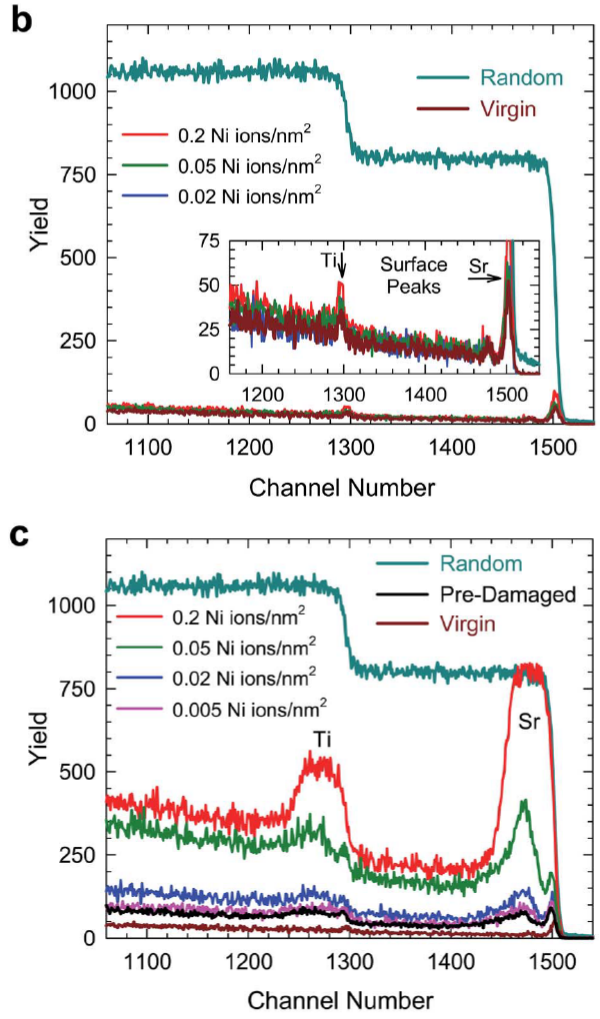
*M. Karlušić et al., New J. Phys. (2017)*

# SHIBIEC: SiC
# ANTI-SHIBIEC: $SrTiO_3$



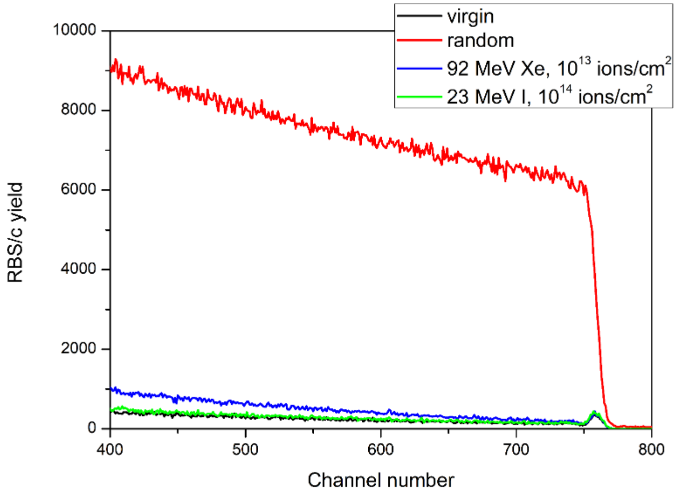

*Y. Zhang et al., Nat. Comm. (2015)*

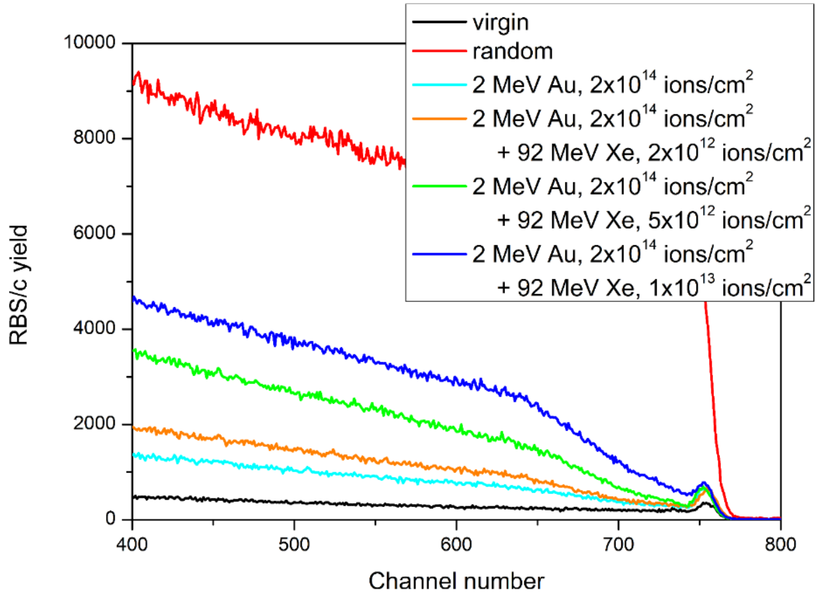
*A. Benyagoub et al., Appl. Phys. Lett. (2006)*




*Weber et al., Sci. Rep. (2015)*

# Ion tracks in PRE-damaged GaN



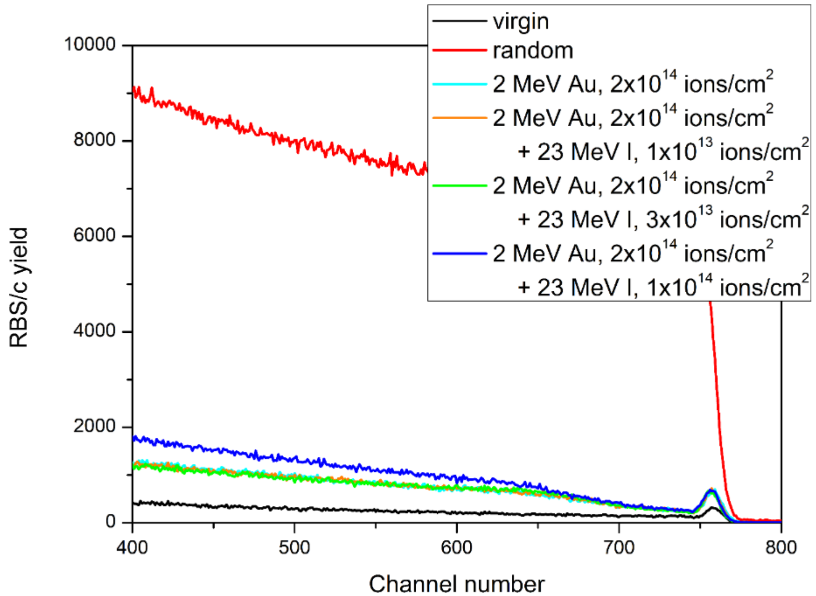

HZDR: 2 MeV Au

GANIL: 90 MeV Xe

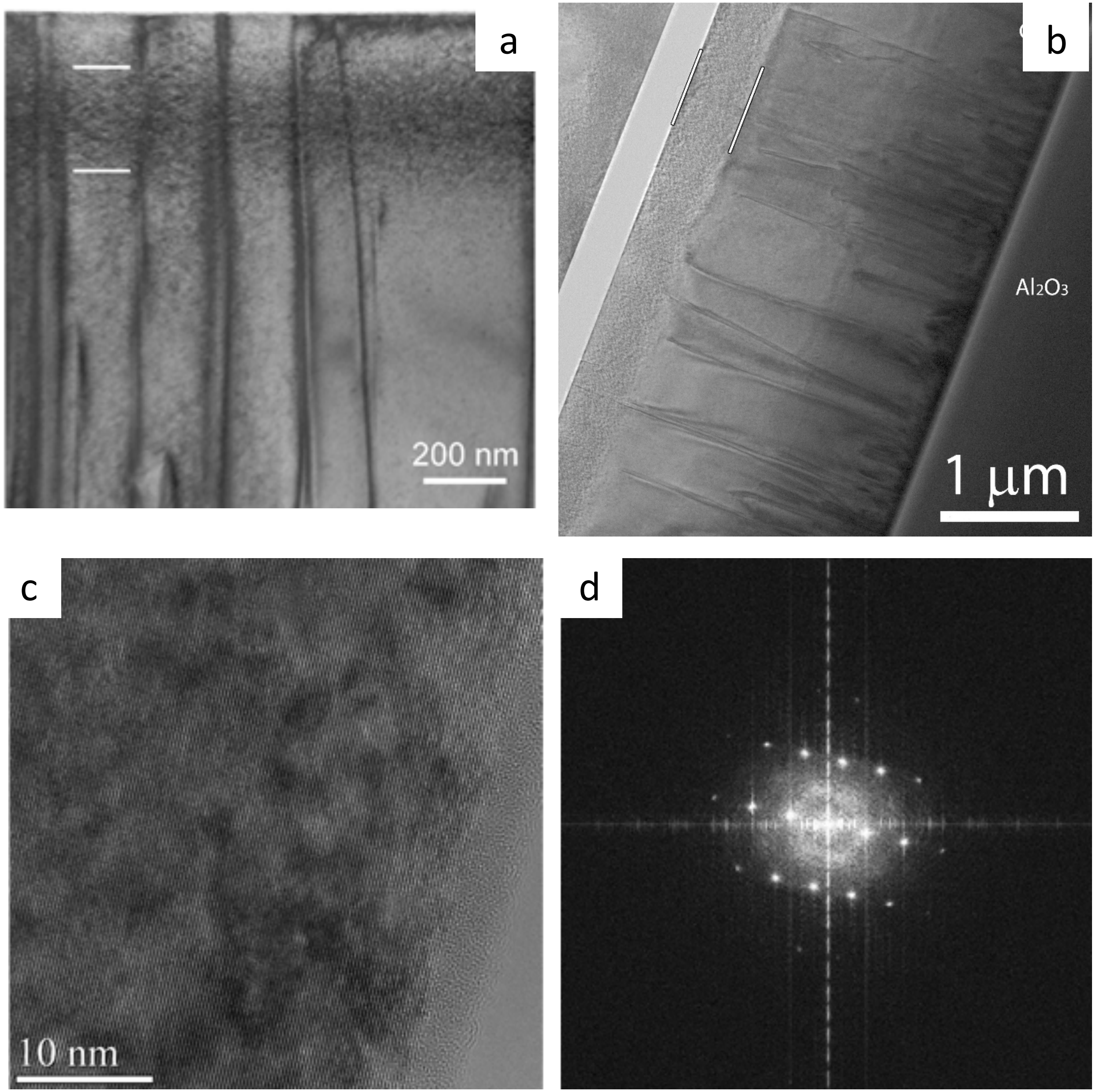
RBI: 23 MeV I

HZDR: 1.7 MeV He RBS/c

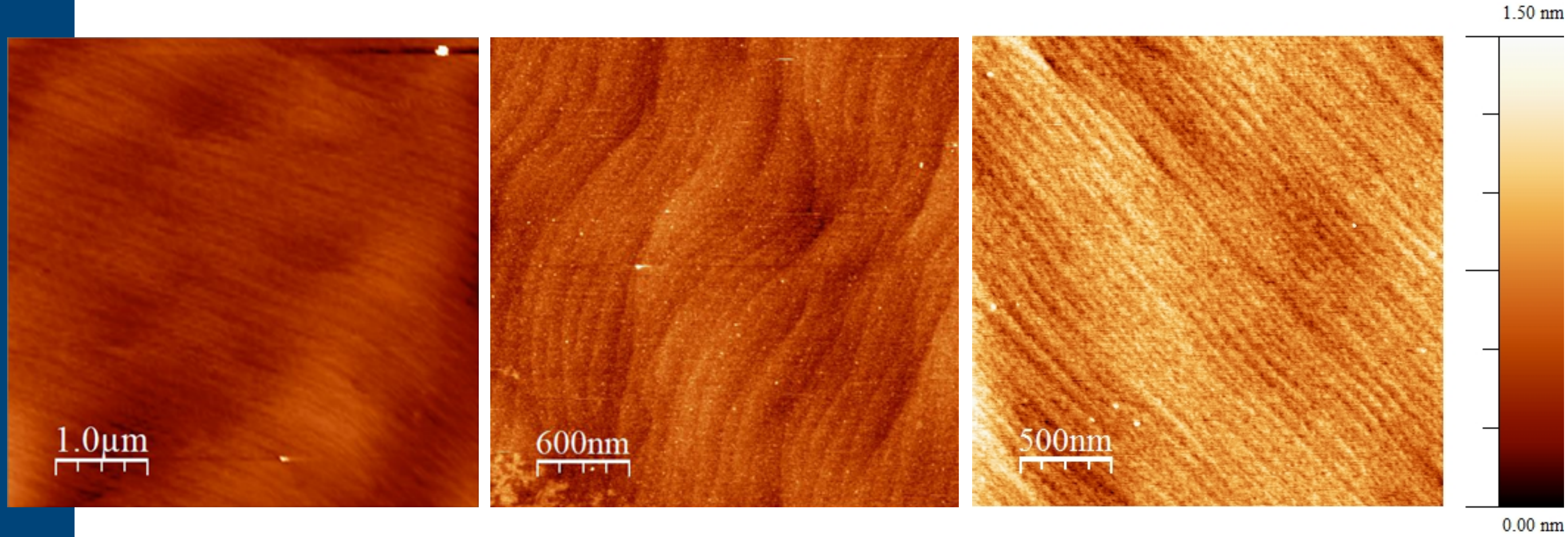
*Karlusic et al., unpublished*



# Ion tracks in PRE-damaged GaN



# Ion tracks in PRE-damaged GaN

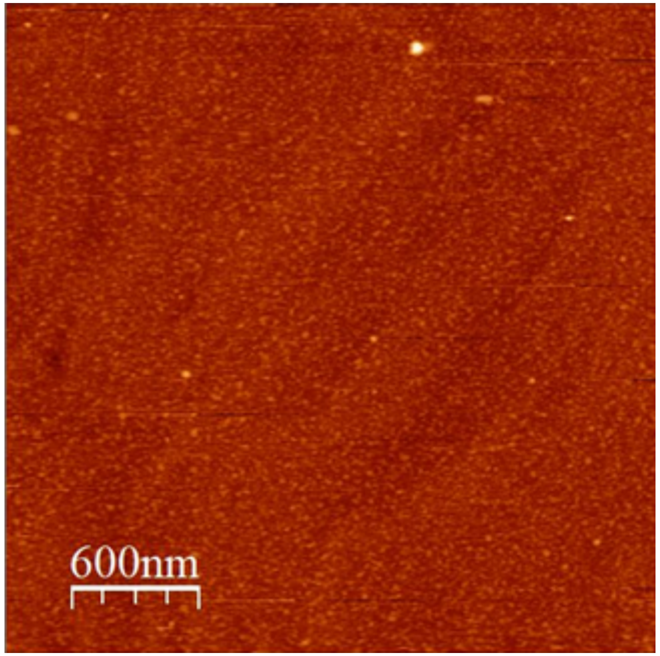



Virgin:
RMS roughness
= 0.27 nm

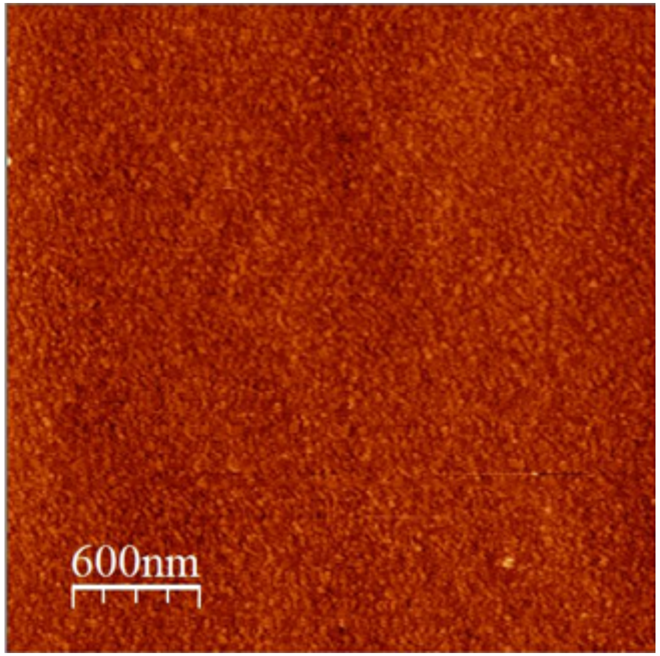
2 MeV Au
(2x$10^{14}$ ions/$cm^2$):
RMS roughness
= 0.39 nm

90 MeV Xe
($10^{13}$ ions/$cm^2$):
RMS roughness
= 0.3 nm

# Ion tracks in PRE-damaged GaN




2 MeV Au +
90 MeV Xe
($10^{12}$ ions/cm$^2$):
RMS roughness
= 0.83 nm




2 MeV Au +
90 MeV Xe
($10^{13}$ ions/cm$^2$):
RMS roughness
= 1.31 nm

# SUMMARY

Ion track threshold: depends on $dE_e/dx$, not E!
Complementary to higher energy accelerator facility
IBA (RBS/C, ERDA) available for track measurements
Higher fluences can be achieved (simulate n, $\gamma$)

RBS/c - used for structural analysis of single crystals
Avrami model useful for distinguishing nuclear and electronic stopping damage
Avrami model also useful for other techniques