The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

International Atomic Energy Agency

SMR/1758-6

"Workshop on Ion Beam Studies of Nanomaterials: Synthesis, Modification and Characterization"

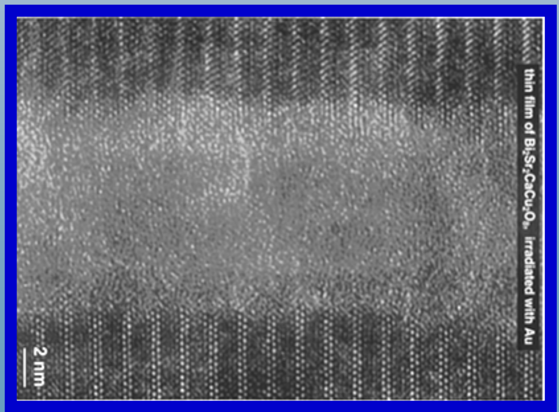
26 June - 1 July 2006

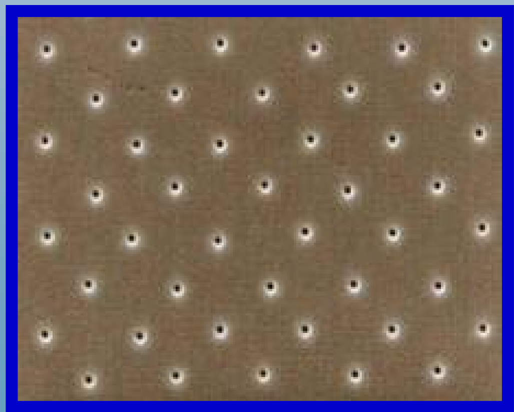
Material Modifications & Nanoscience with MeV-GeV ions

Christina Trautmann
Gesellschaft fuer Schwerionenforschung GmbH
Darmstadt, Germany

Material modifications and nanoscience with MeV-GeV ions

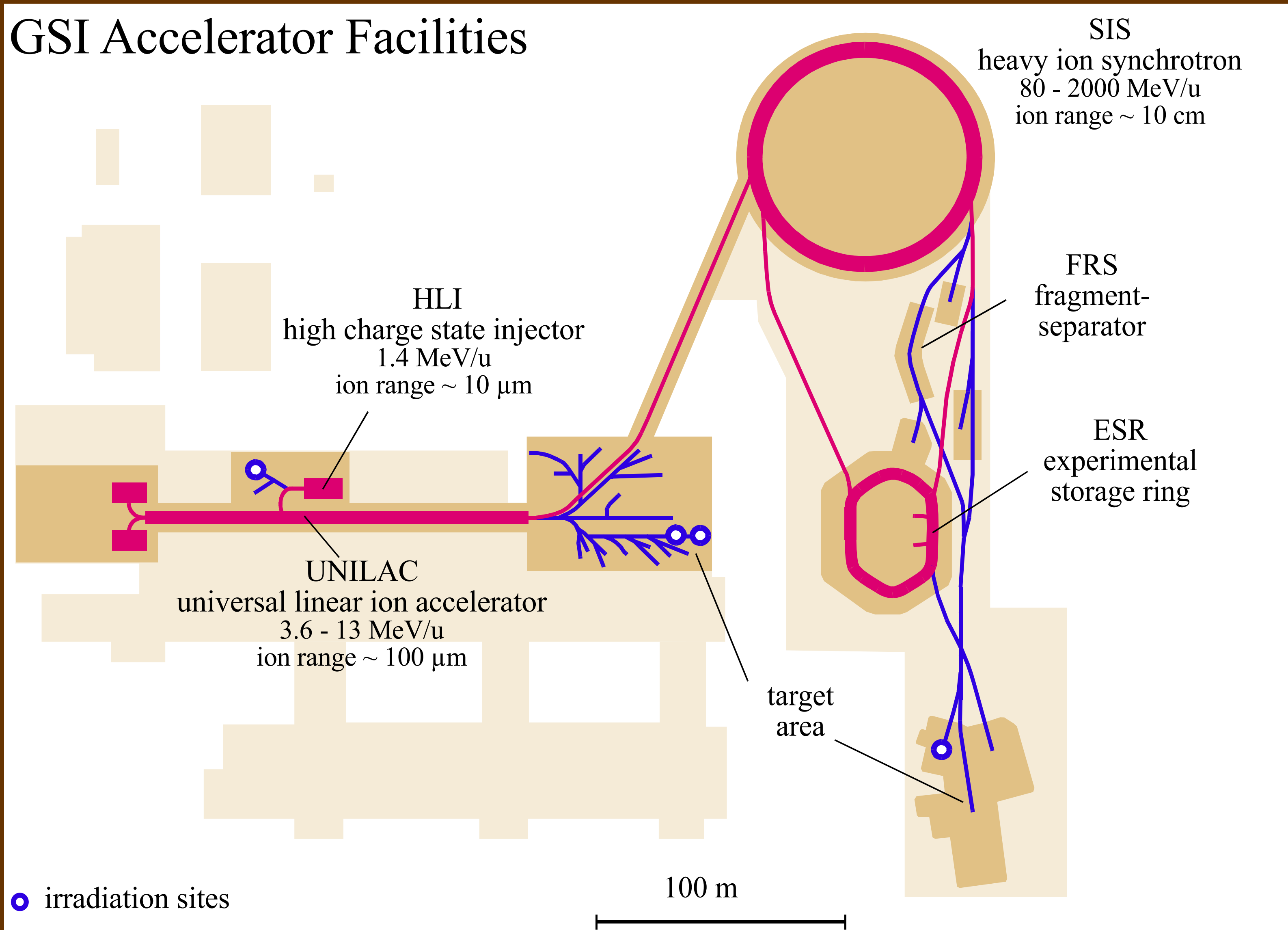
- Track formation with MeV-GeV ions
- Applications: ion track membranes
  nanowires
  single nanopores

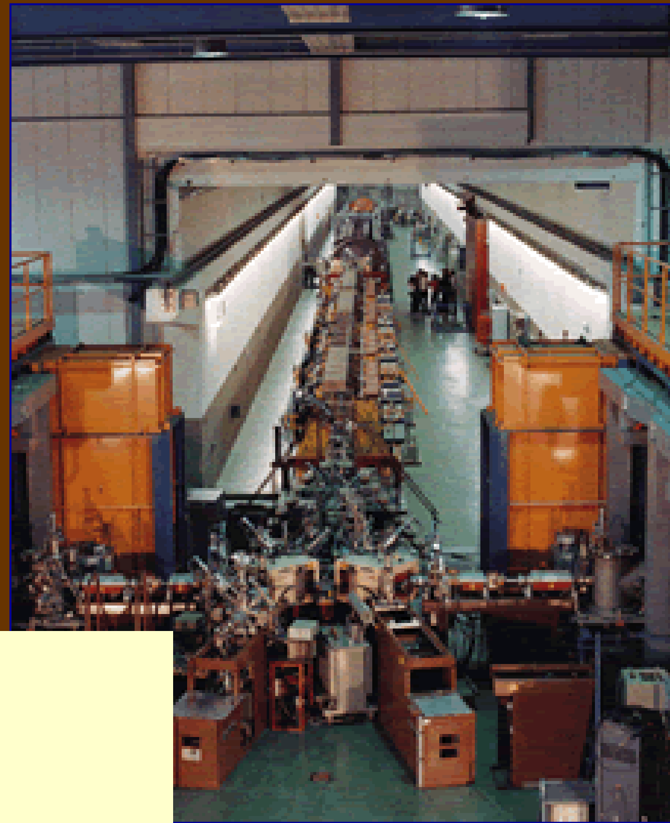


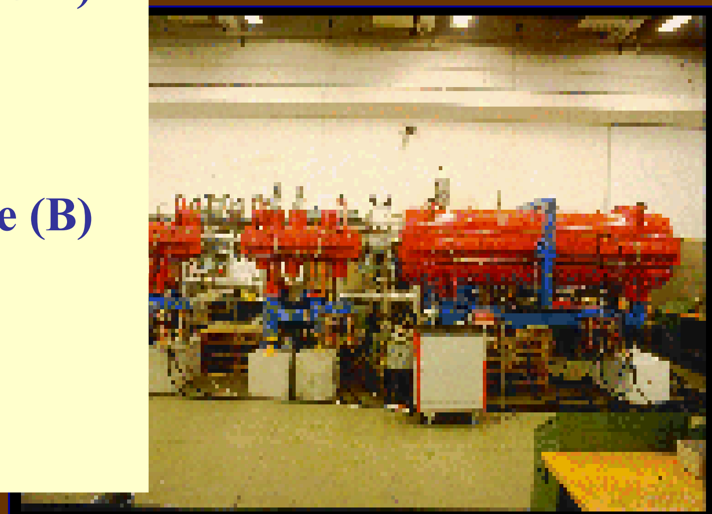


Christina Trautmann, Darmstadt, Germany

Accelerator facility for MeV – GeV ion beams







Heavy ion accelerator facilities for materials science

10-1000	MeV/u	linear & synchrotron	Darmstadt (Ger)
1-100	MeV/u	cyclotron	Ganil, Caen (F)
25	MeV/u	cyclotron	Dubna (Ru)
5	MeV/u	cyclotron	Berlin (Ger)
1-30	MeV/u	cyclotron	Louvain La Neuve (B)

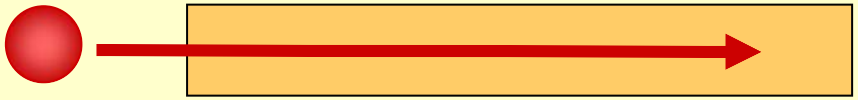
China: Lanzhou

India: Nuclear Science Center Delhi

Japan: Tokai, Riken, Takasaki, Chiba

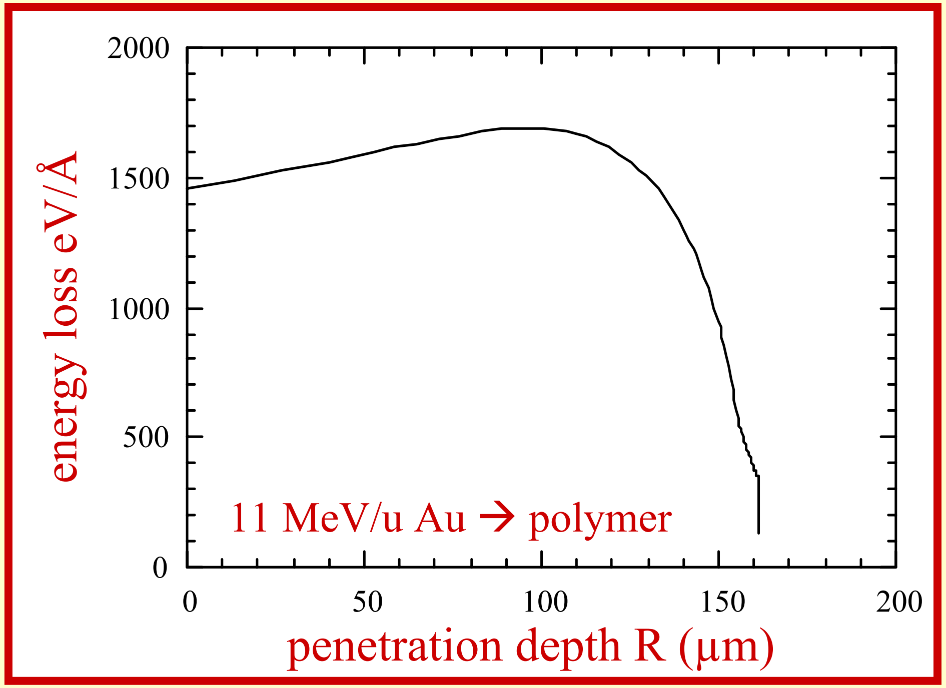
USA: AGS -Brookhaven, Argonne Nat. Lab

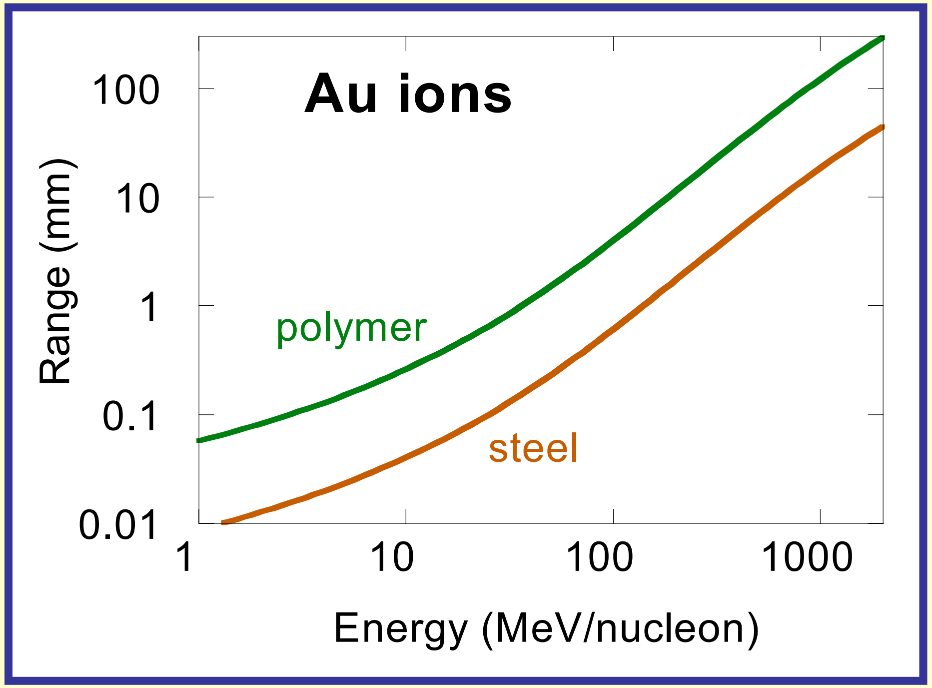
ion range versus beam energy



energy loss versus depth

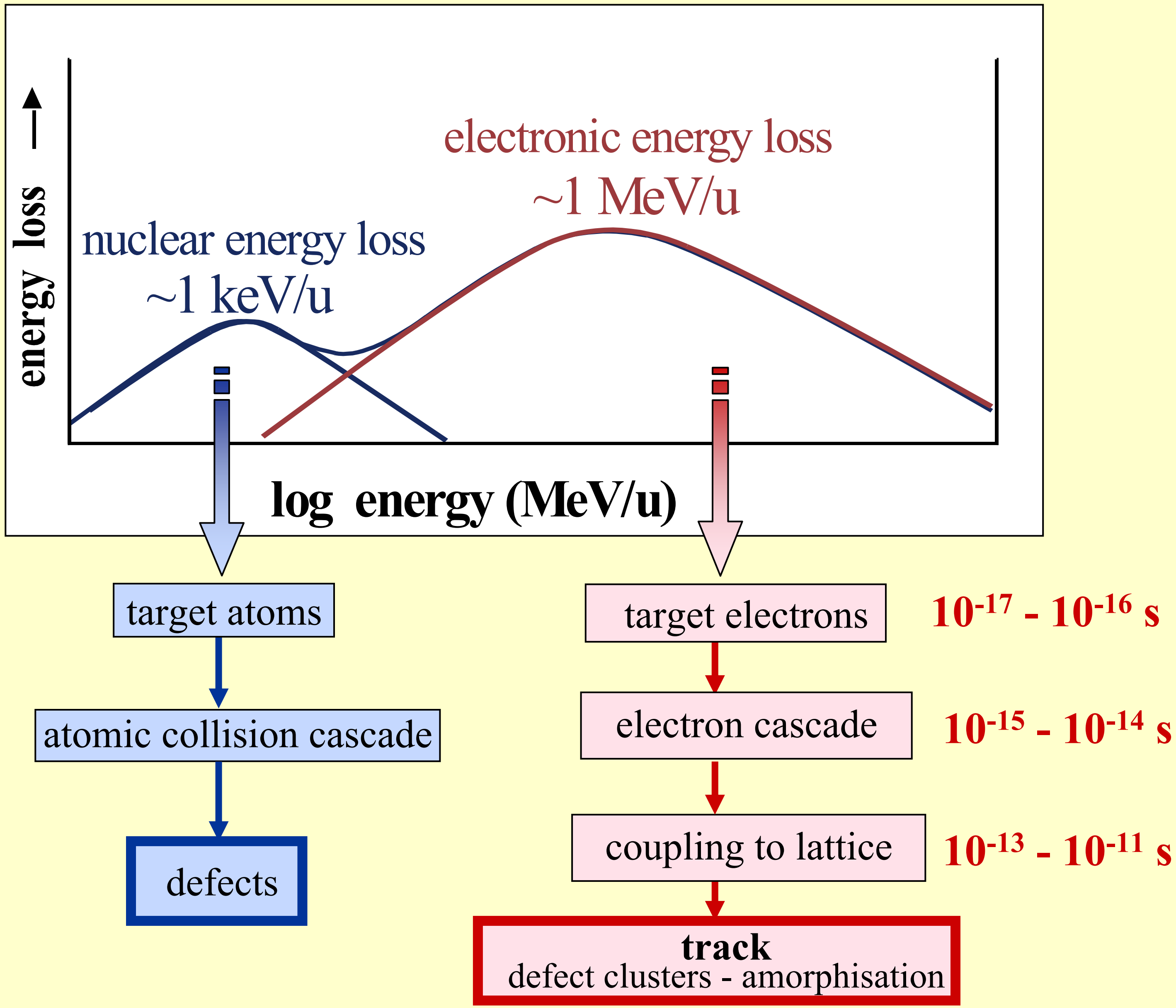
$$Range = \int_0^E \left(-\frac{dE}{dx} \right)^{-1} dE$$



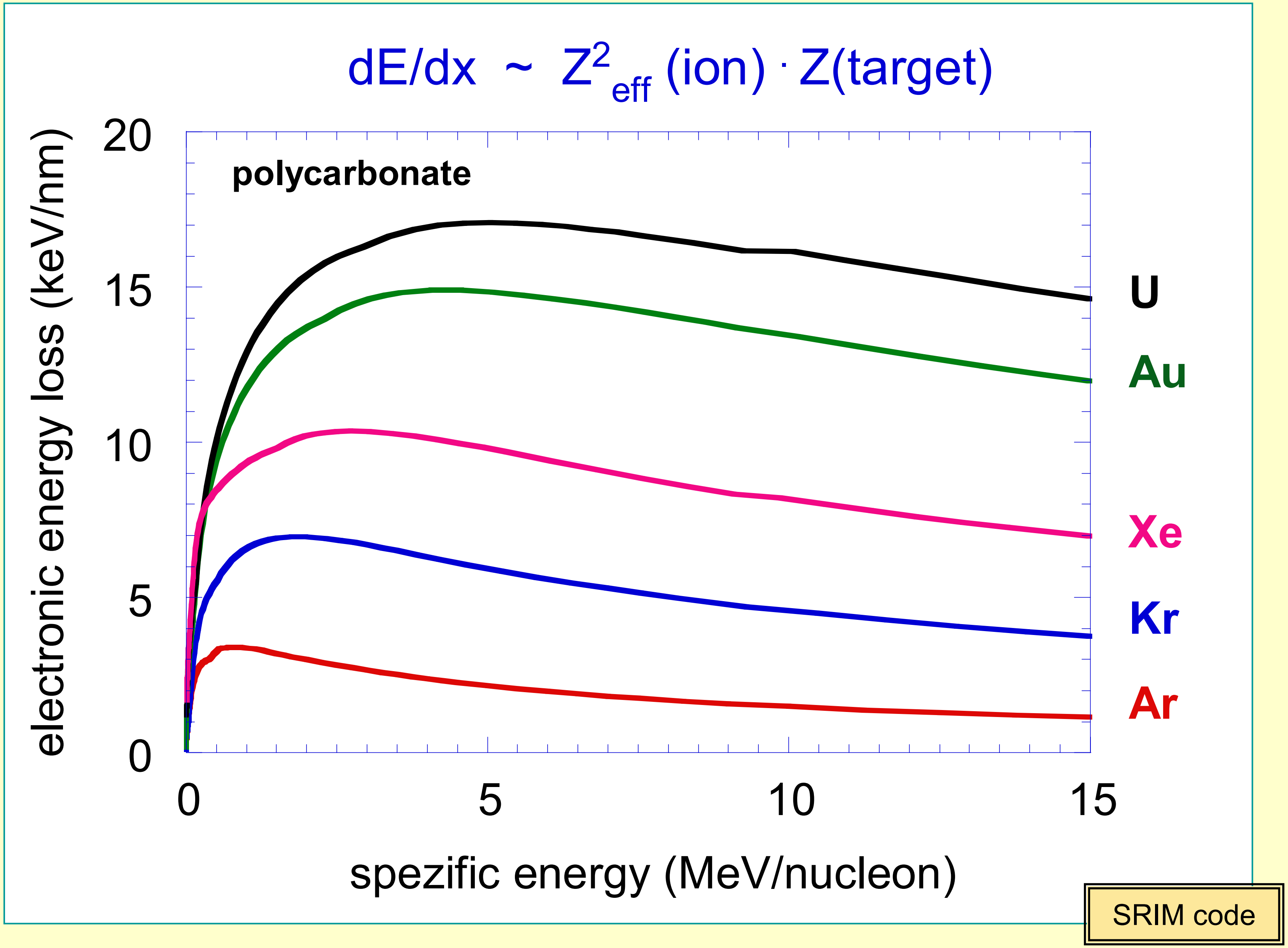


e.g. 11 MeV/u: ^{40}Ar → 11 x 40 = 440 MeV
^{238}U → 11 x 238 = 2.6 GeV

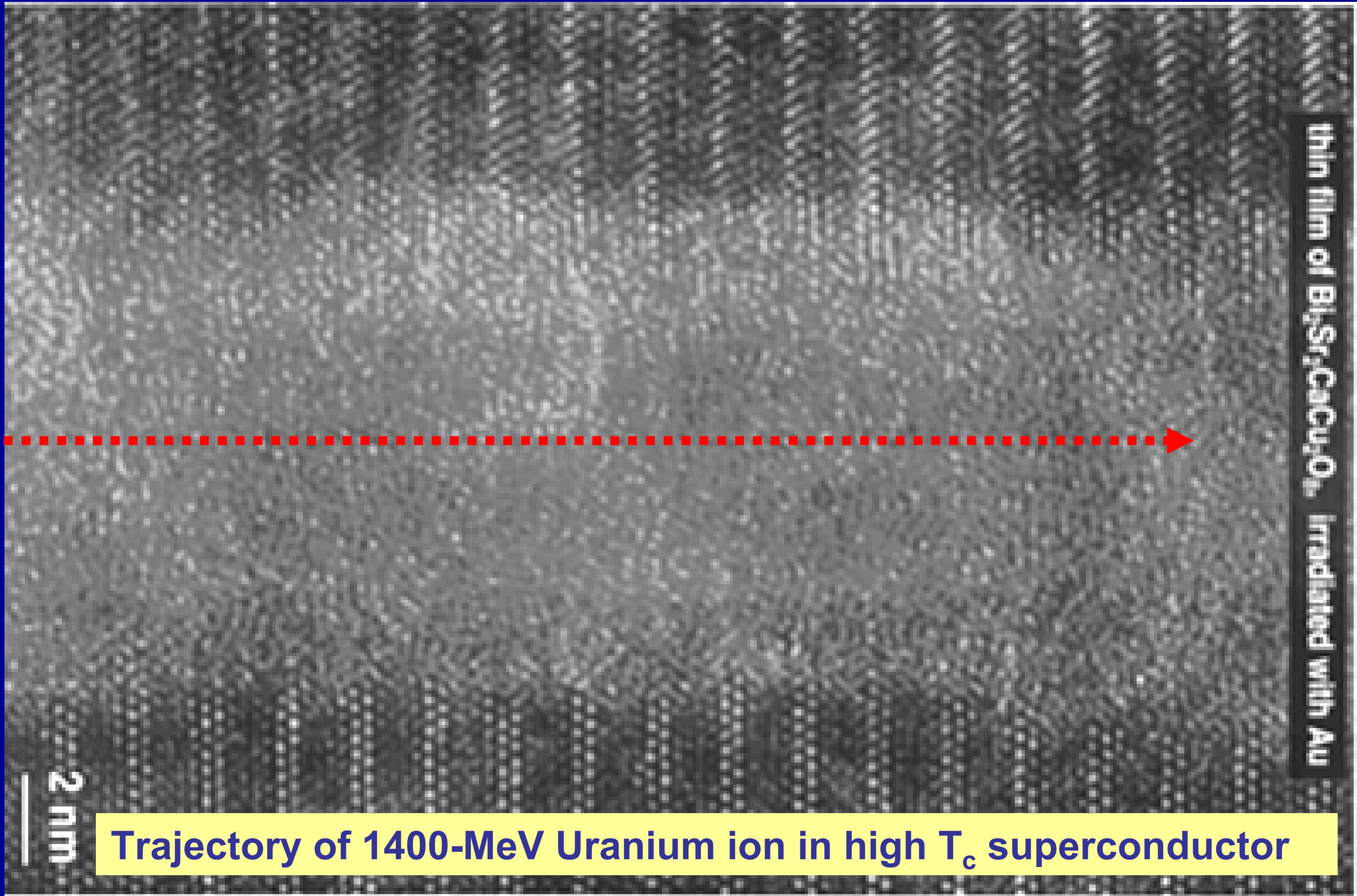
Energy deposition process



electronic energy loss – stopping power



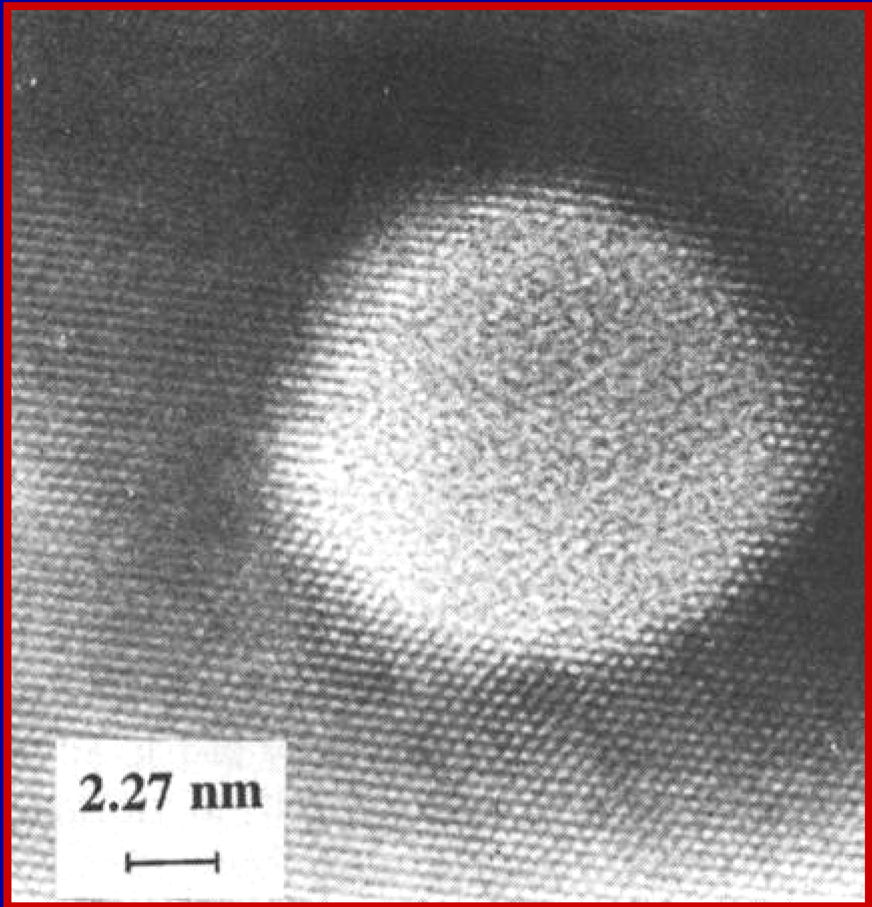
High resolution transmission electron microscopy



Trajectory of 1400-MeV Uranium ion in high T_c superconductor

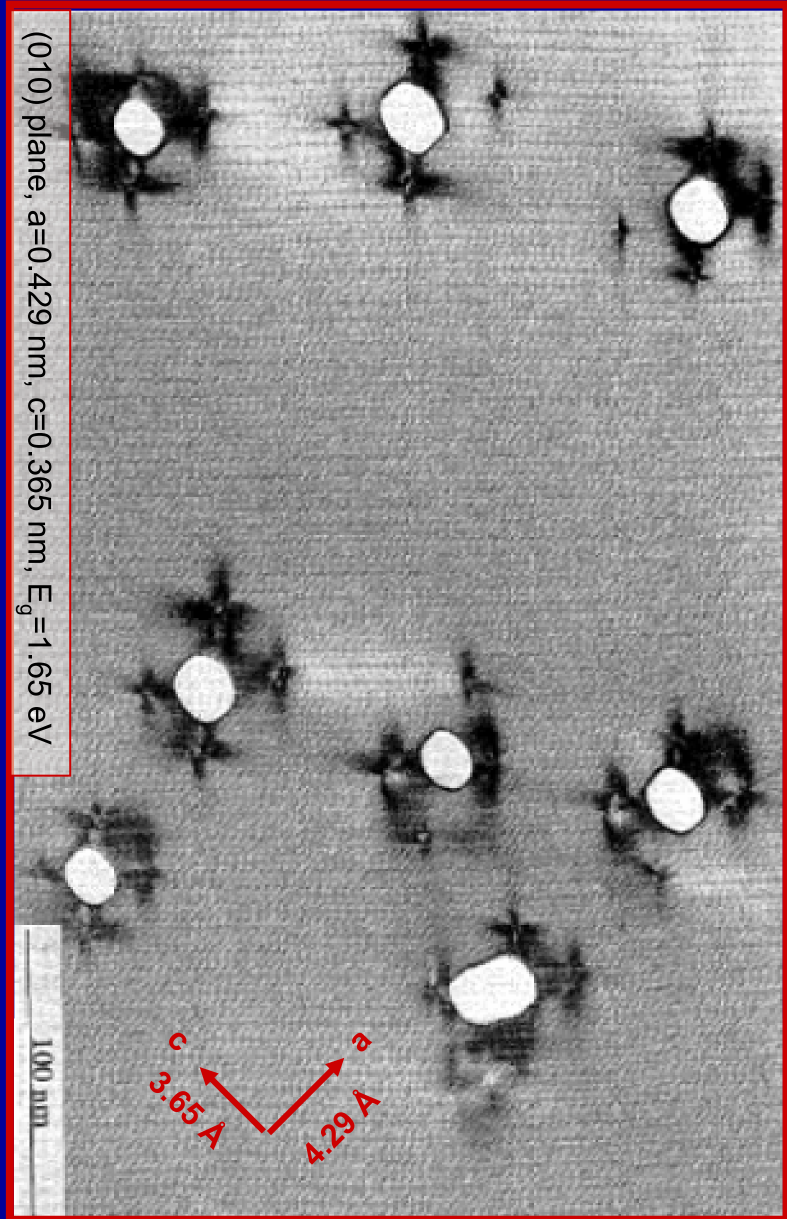
Wiesner et al., Physica C 268 (1996) 161

Tracks in amorphisable material



62 MeV Pb-ions → SiO_2 quartz

2.7 GeV U-ions → GeS

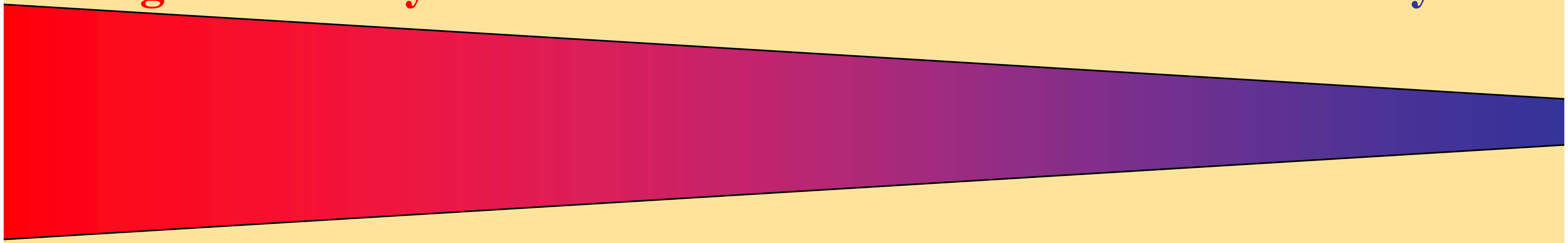


Meftah et al., Phys. Rev B 49 (1994) 12457

Vetter et al., NIMB 91(1994) 129

Material sensitivity

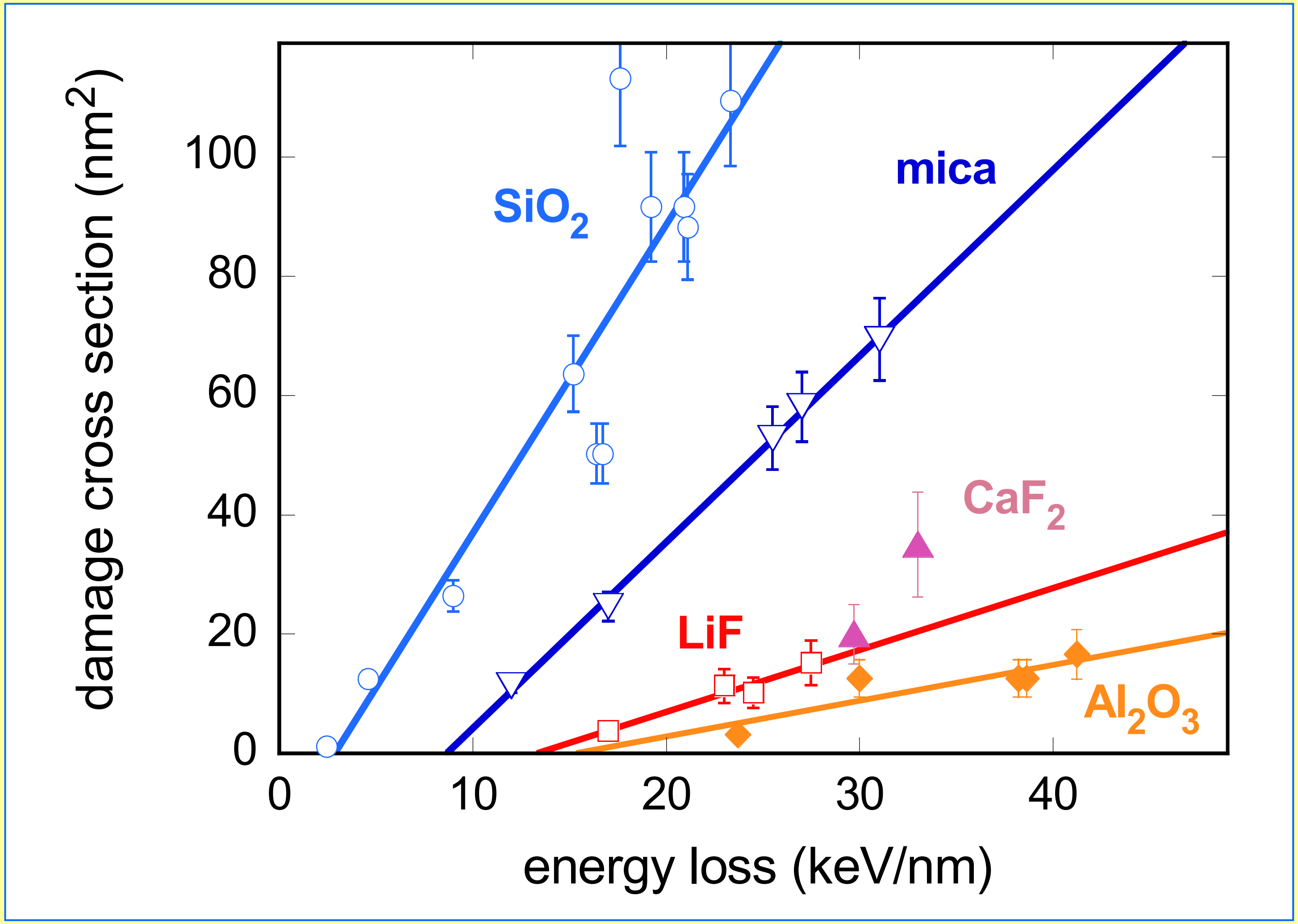
high sensitivity — low sensitivity



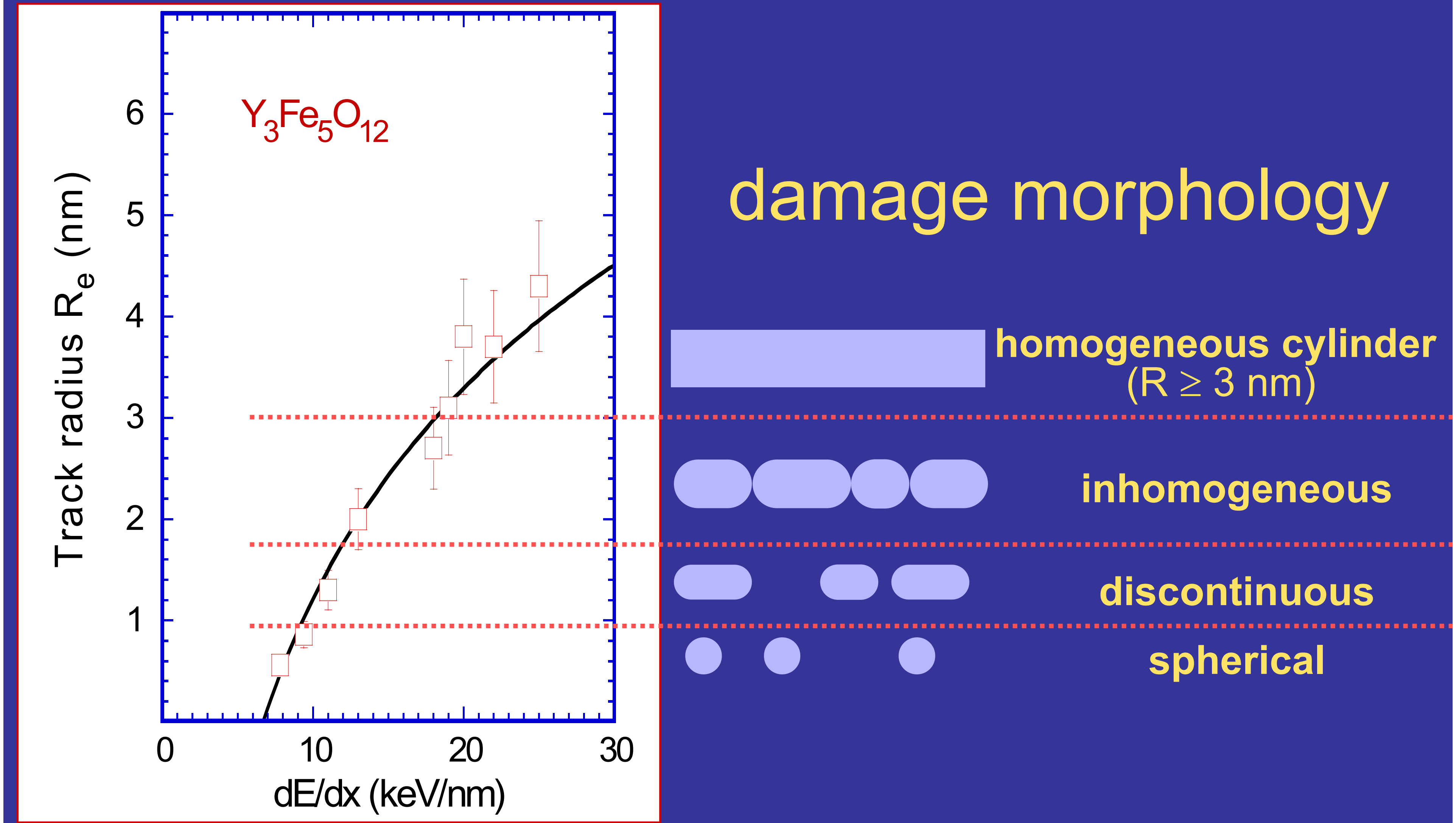
dE/dx threshold: ~1 keV/u — ~20 keV/u — ~50 keV/u

insulators	semi-conductors	metals
☺ oxides, spinels	☺ amorphous Si	☺ amorphous alloys
☺ ionic crystals	☺ GeS, InP, $Si_{1-x}Ge_x$	😐 Fe, Bi, Ti, Co, Zr
☺ polymers	☹ Si, Ge	☹ Au, Cu, Ag…

Track formation threshold

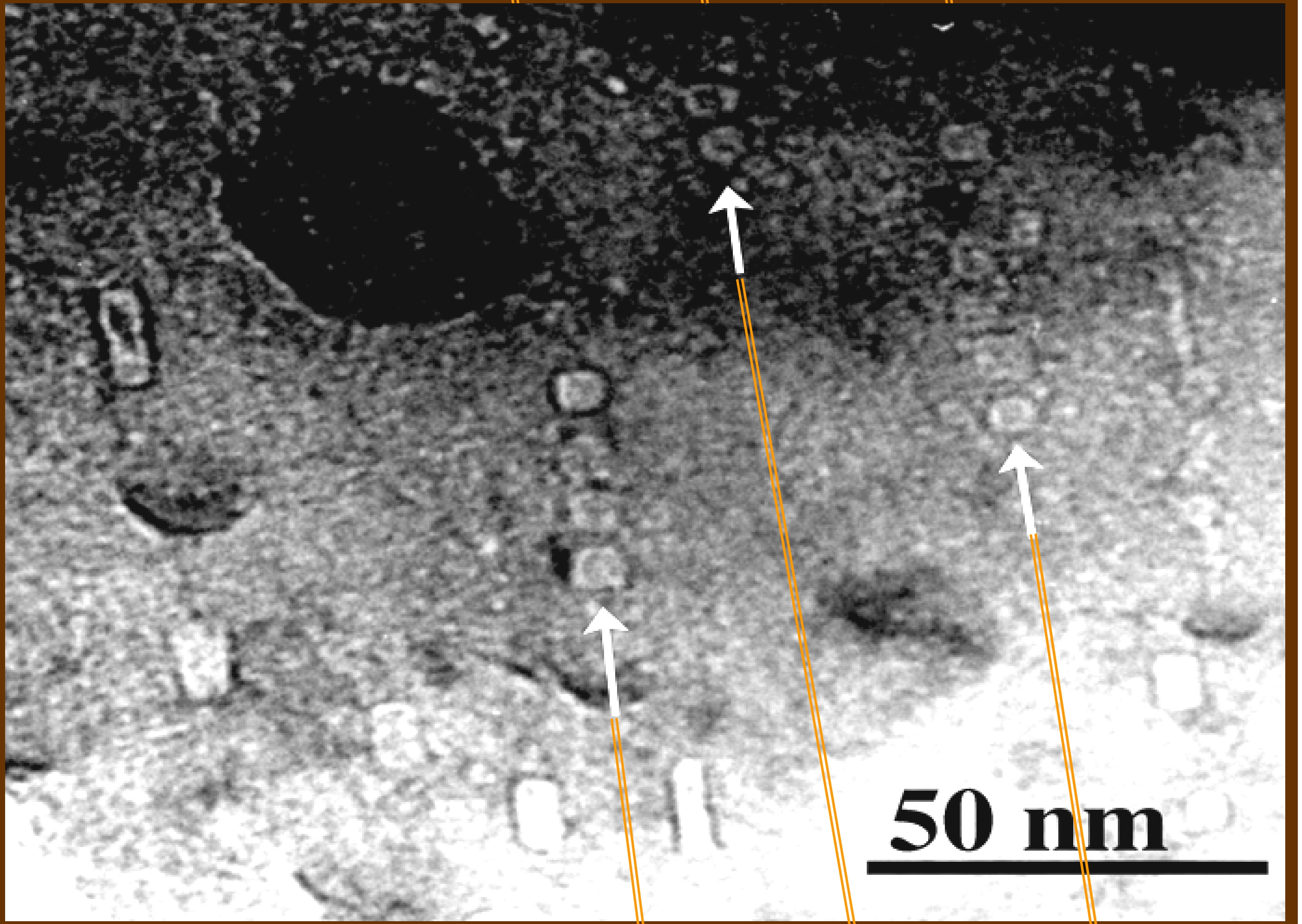


Track size versus energy loss



Toulemonde et al., Sol. State Phen. 30/31 (1993) 477

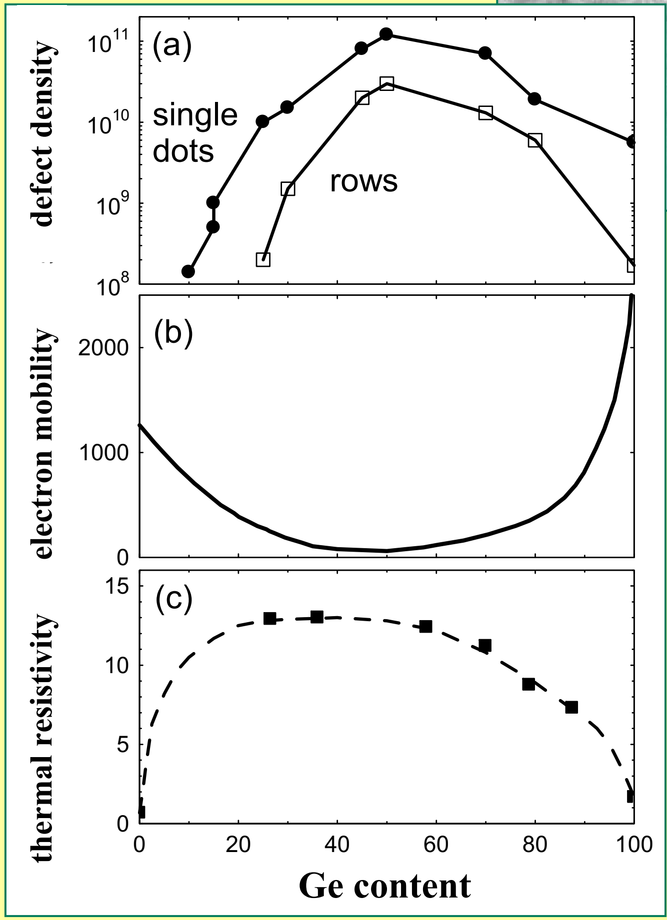
11.1 MeV/u Bi → CaF_2



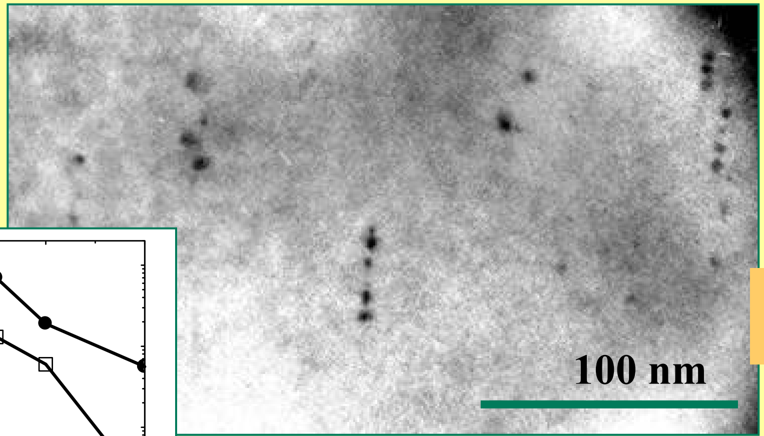
Khalfaoui et al, NIMB 240 (2005) 819

discontinuous tracks in semiconducting compounds

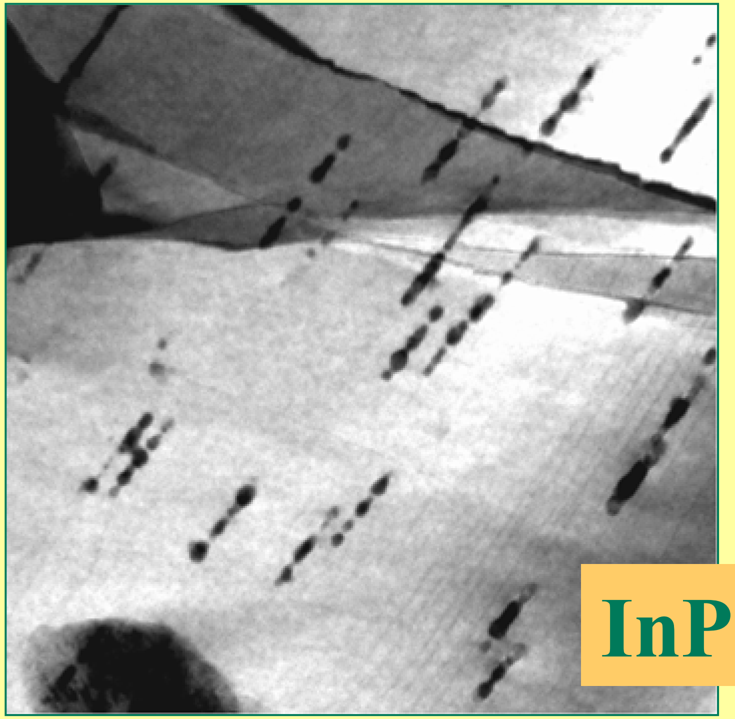
Si_xGe_{1-x}



Gaiduk et al, PRB 66 (2002) 045316
Physica B 340 (2003) 808



$Si_{50}Ge_{50}$

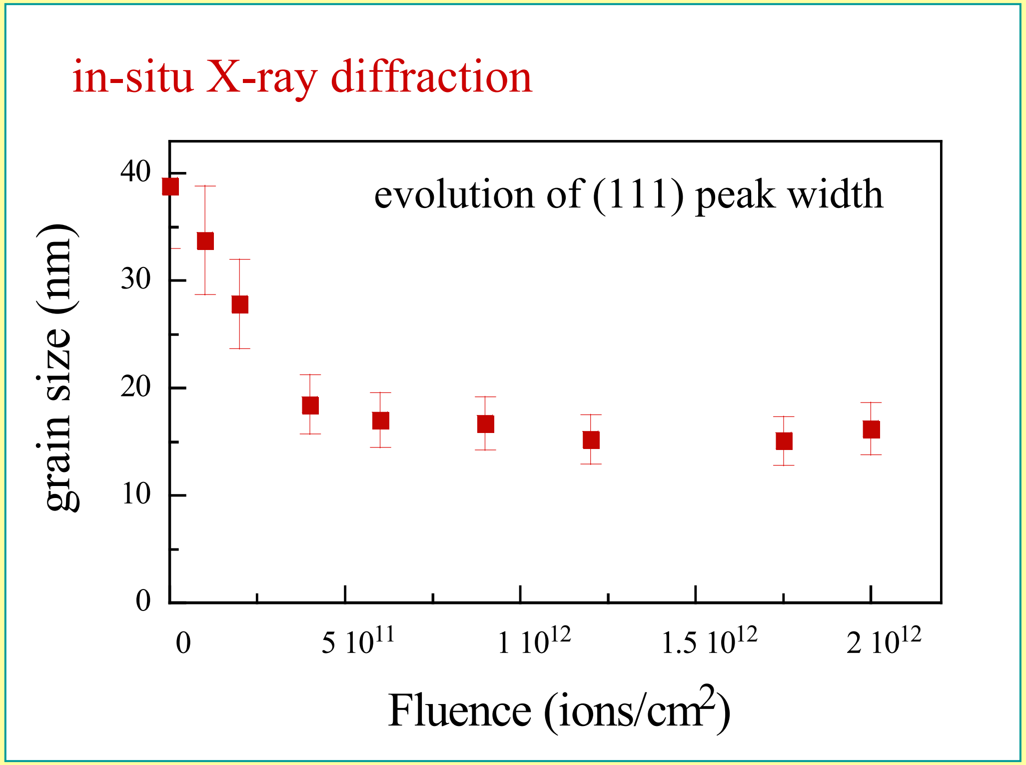


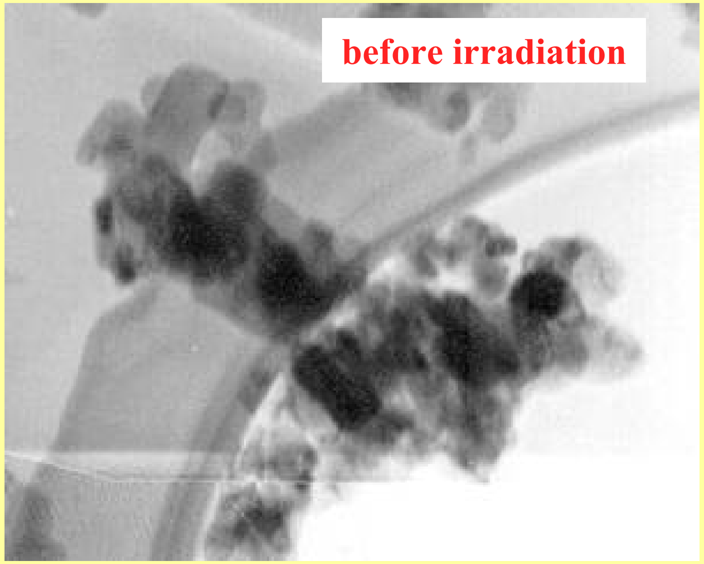
InP

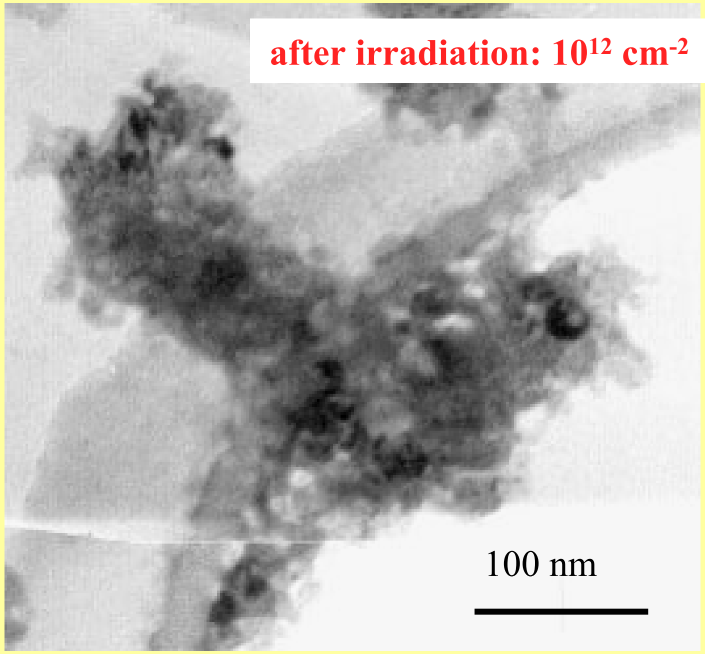
L. Chadderton

Beam-induced grain breaking

4 MeV/u Pb → CaF_2 powder





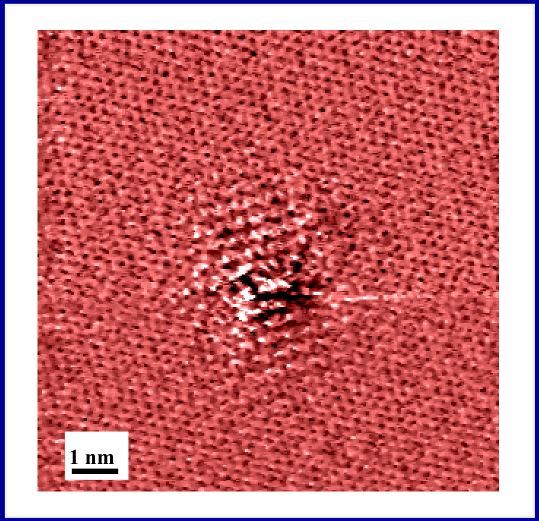


40 nm → 20 nm grains

Boccanfuso, PhD thesis, Caen, (2001)
Boccanfuso et al. NIMB 175-177 (2001) 590
NIMB 191 (2002) 301

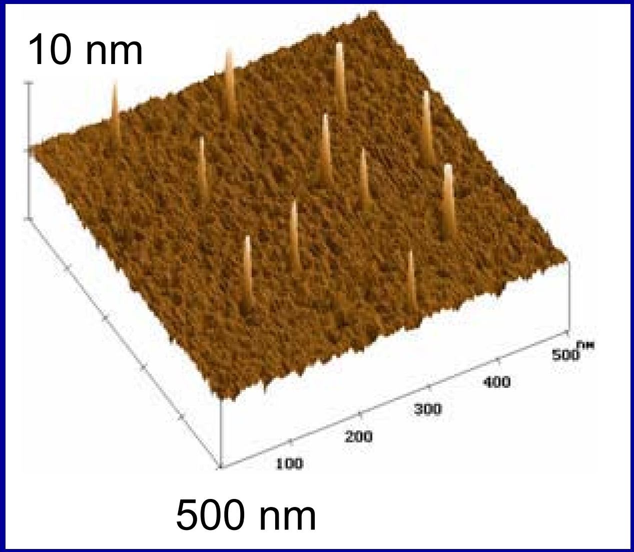
Tracks at sample surface

graphite (HOPG)



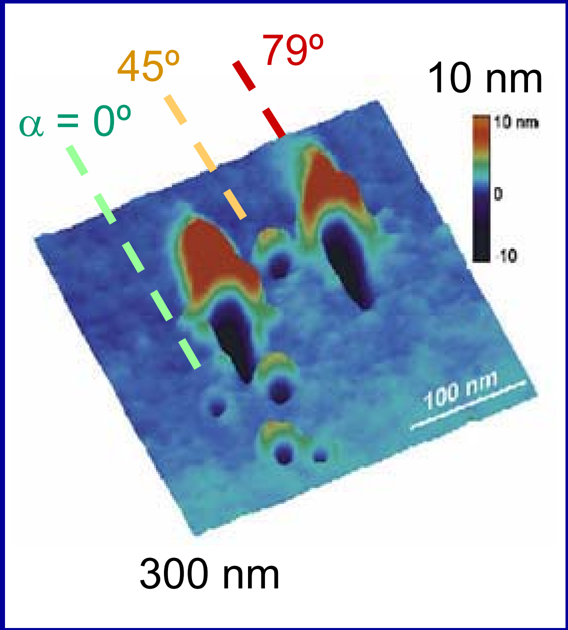
Liu, PRB 64 (2001)

ionic crystal CaF_2



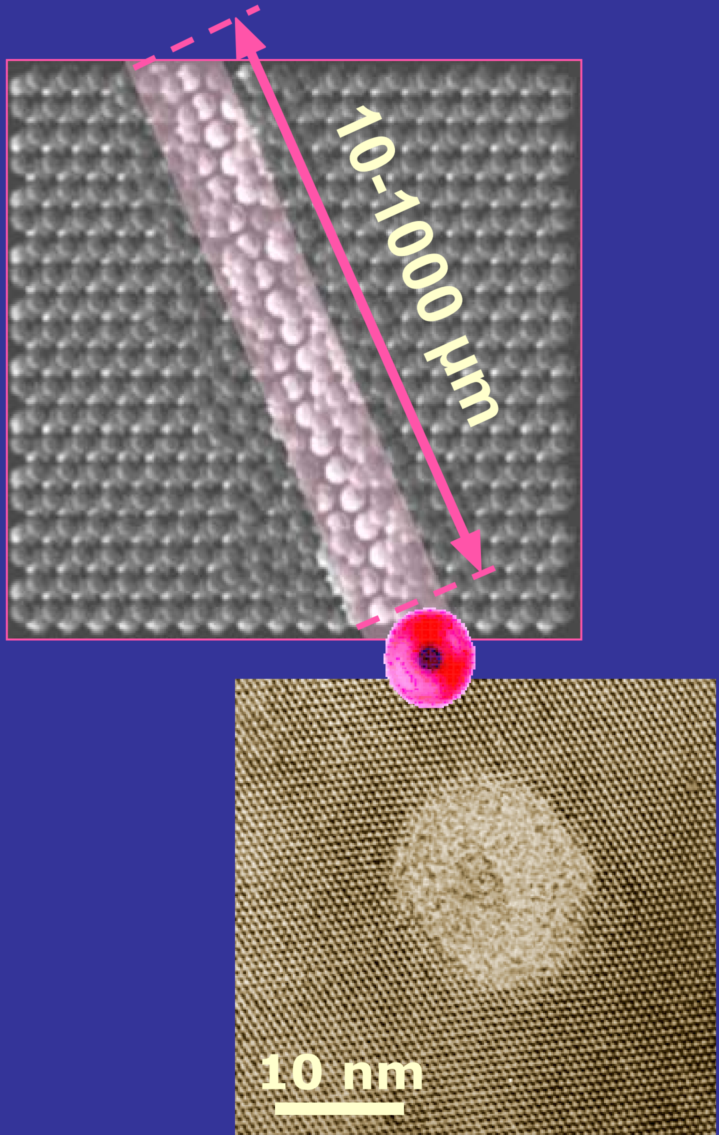
Khalfaoui NIMB 240 (2005)

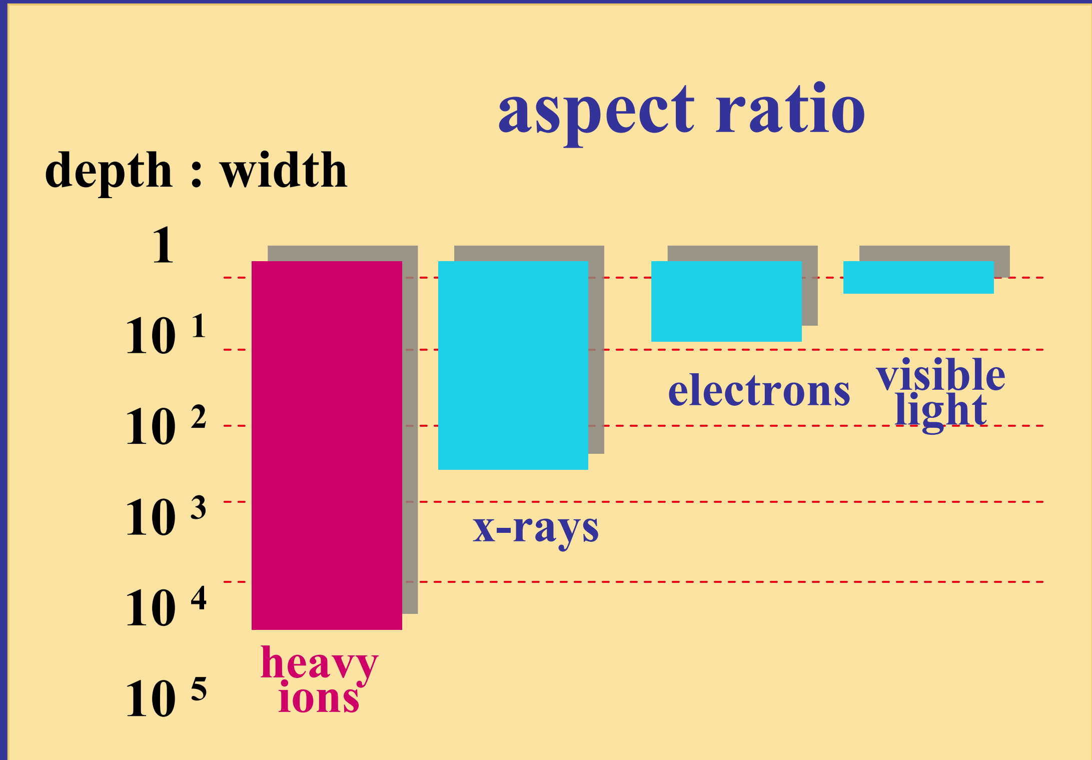
polymer (PMMA)



Papaléo, NIMB 206 (2001)

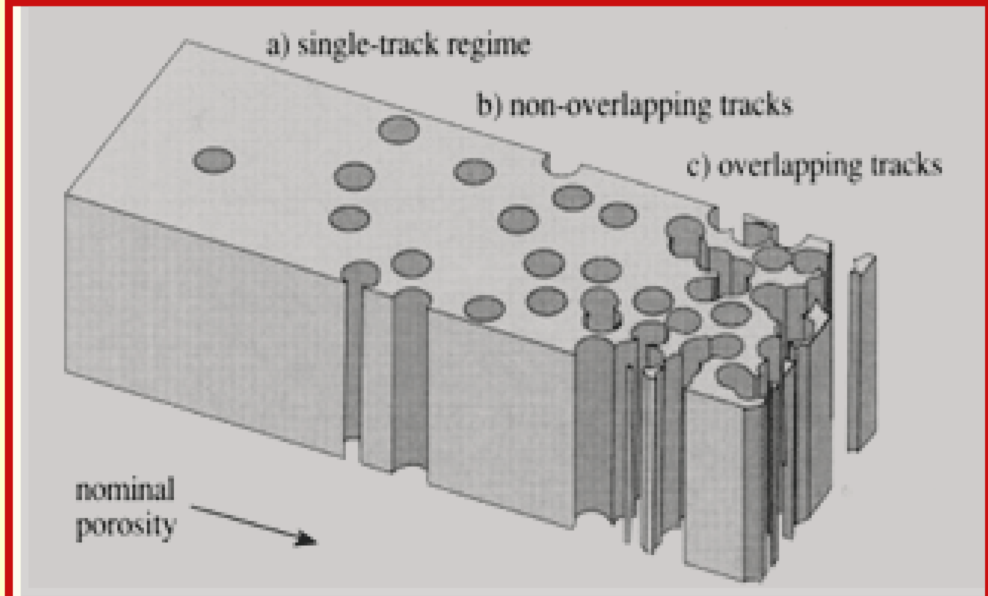
MeV-GeV ions as structuring tool





Vetter et al., NIMB 141 (1998) 747

Irradiation Parameters

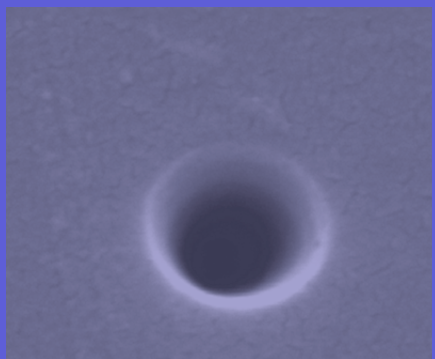


ion species ..C…Xe...U

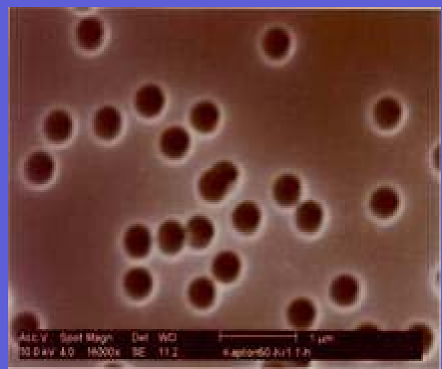
energy: 1 – 10 MeV/u

fluence: 1 ... 10^{13} ions/cm^2

single ion



random

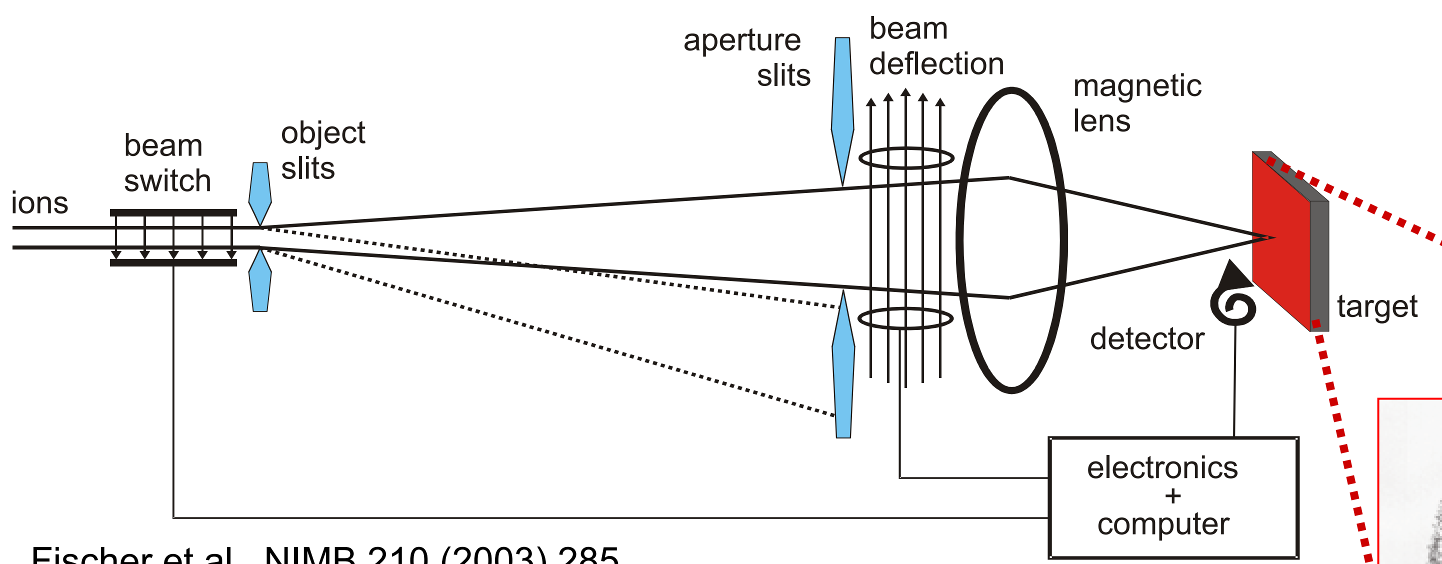


ordered

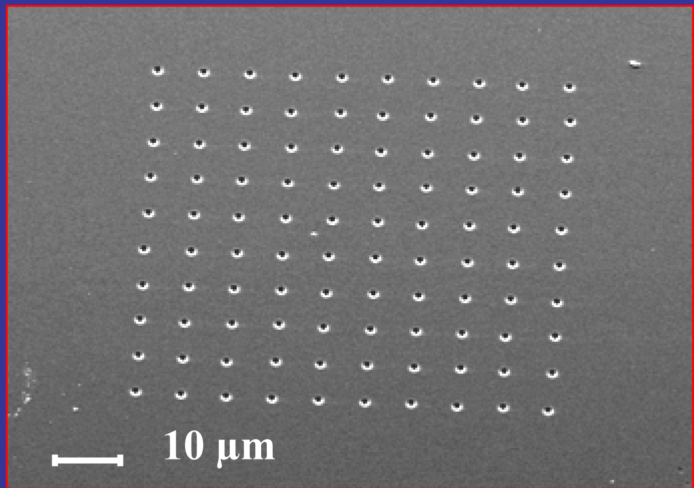
micro probe

Heavy-ion microprobe

Positioning of single ions

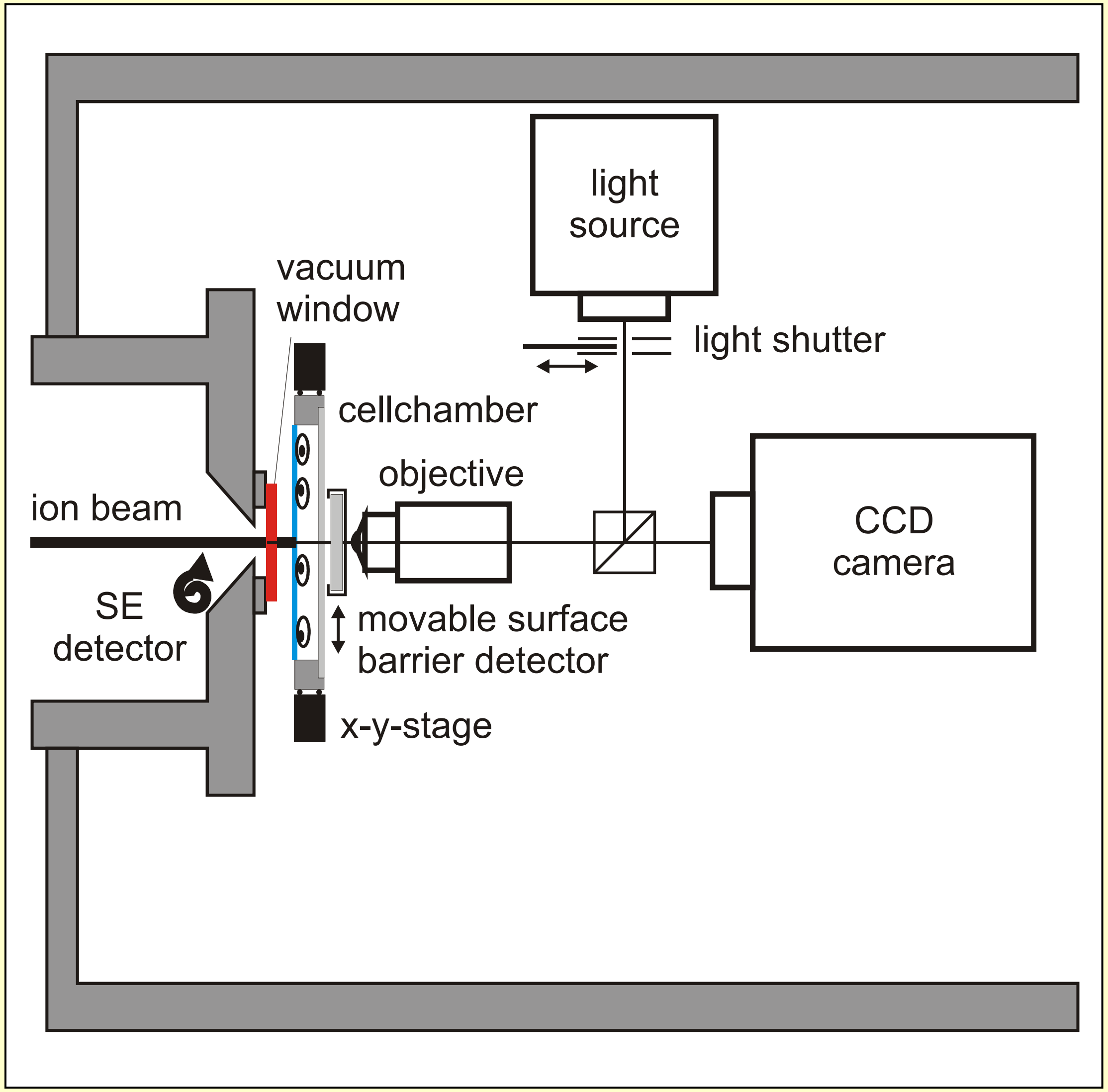


Fischer et al., NIMB 210 (2003) 285



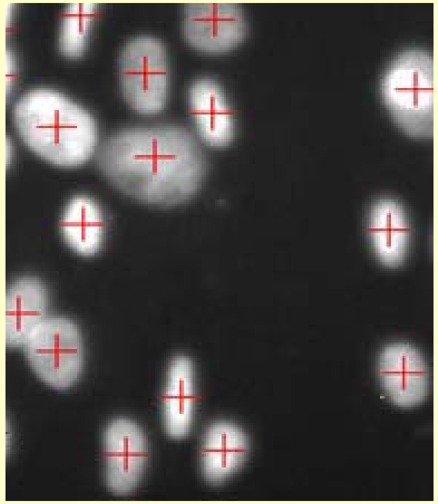
Fischer et al. NIMB 158 (1999) 245

Irradiation setup for cell iradiation

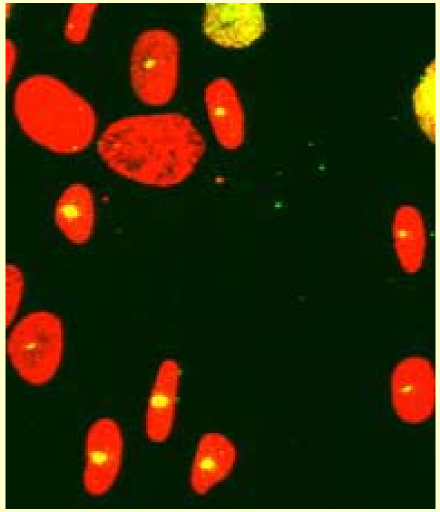


Heiss, PhD Thesis, Darmstadt (2004)
Radiation Research 165 (2006) 231

- stained cell nuclei automatically indexed by microscope and CCD camera

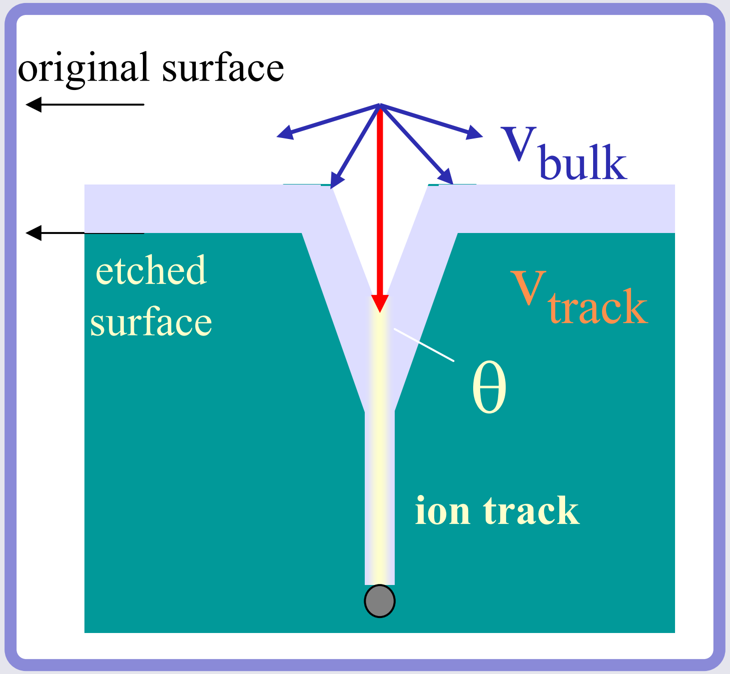


- ion irradiation with microprobe
- ion hits made visible by immuno staining

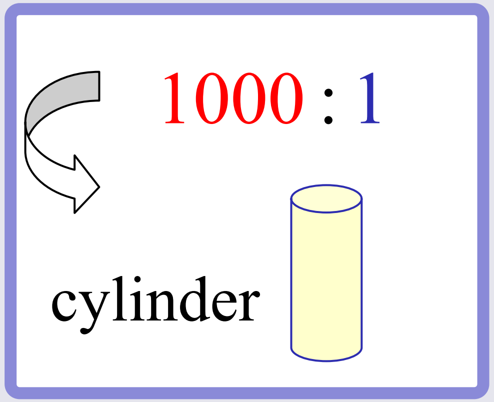


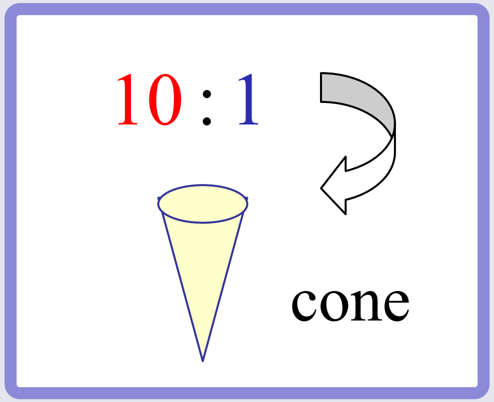
Control of pore geometry

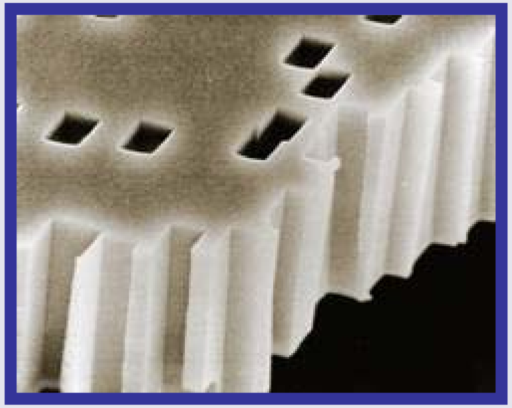
$v_{track} : v_{bulk} = \sin\theta$ ➔ pore geometry



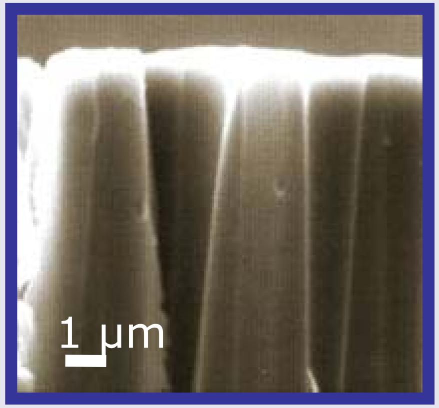
chemical etchant
(e.g., NaOH, NaOCl, H_2SO_4)



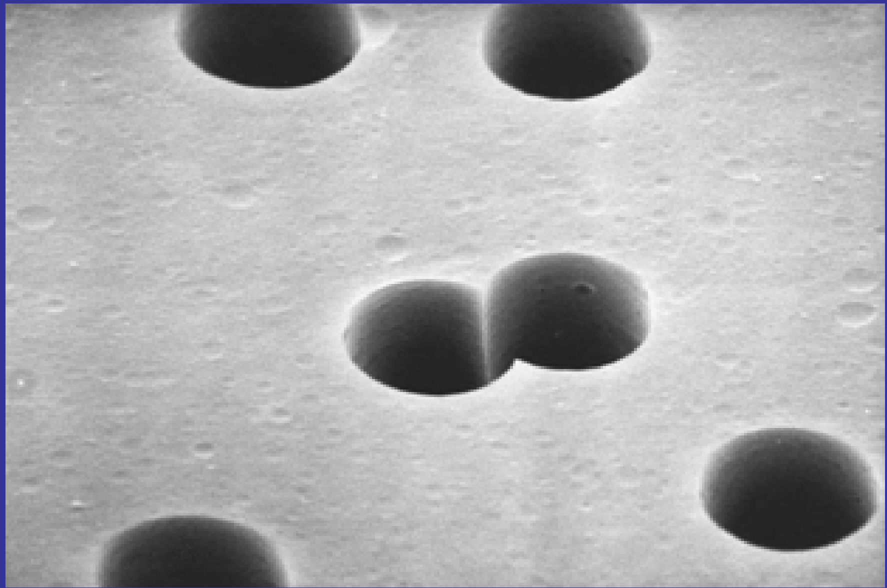


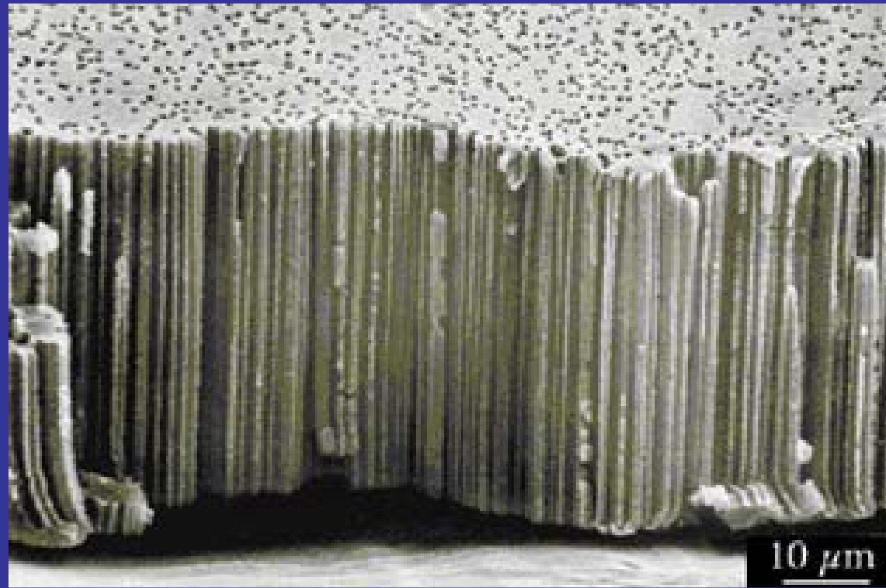


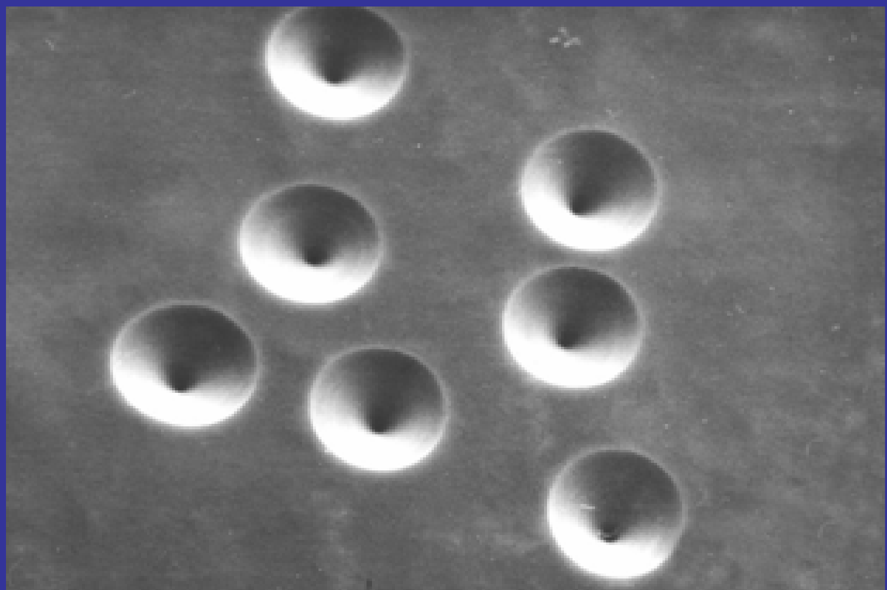
mica

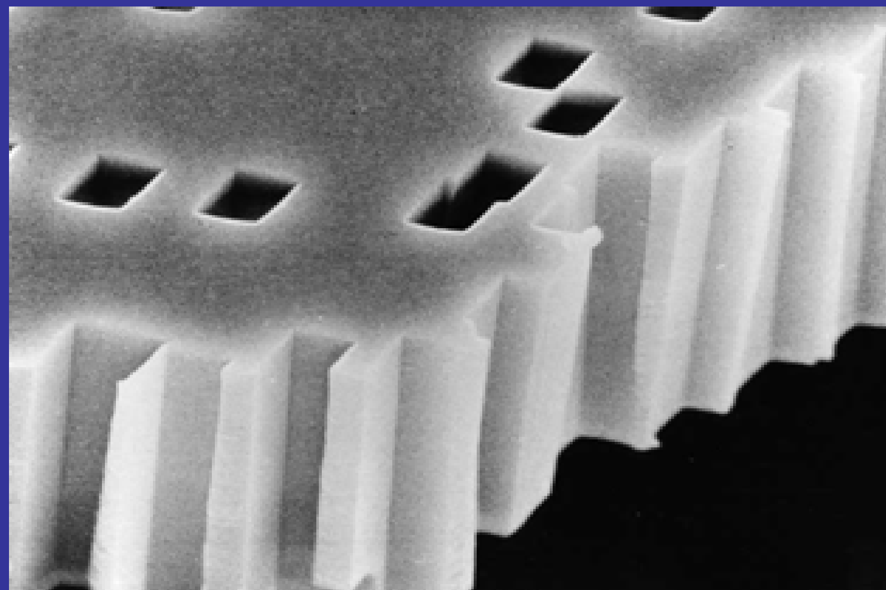


Kapton

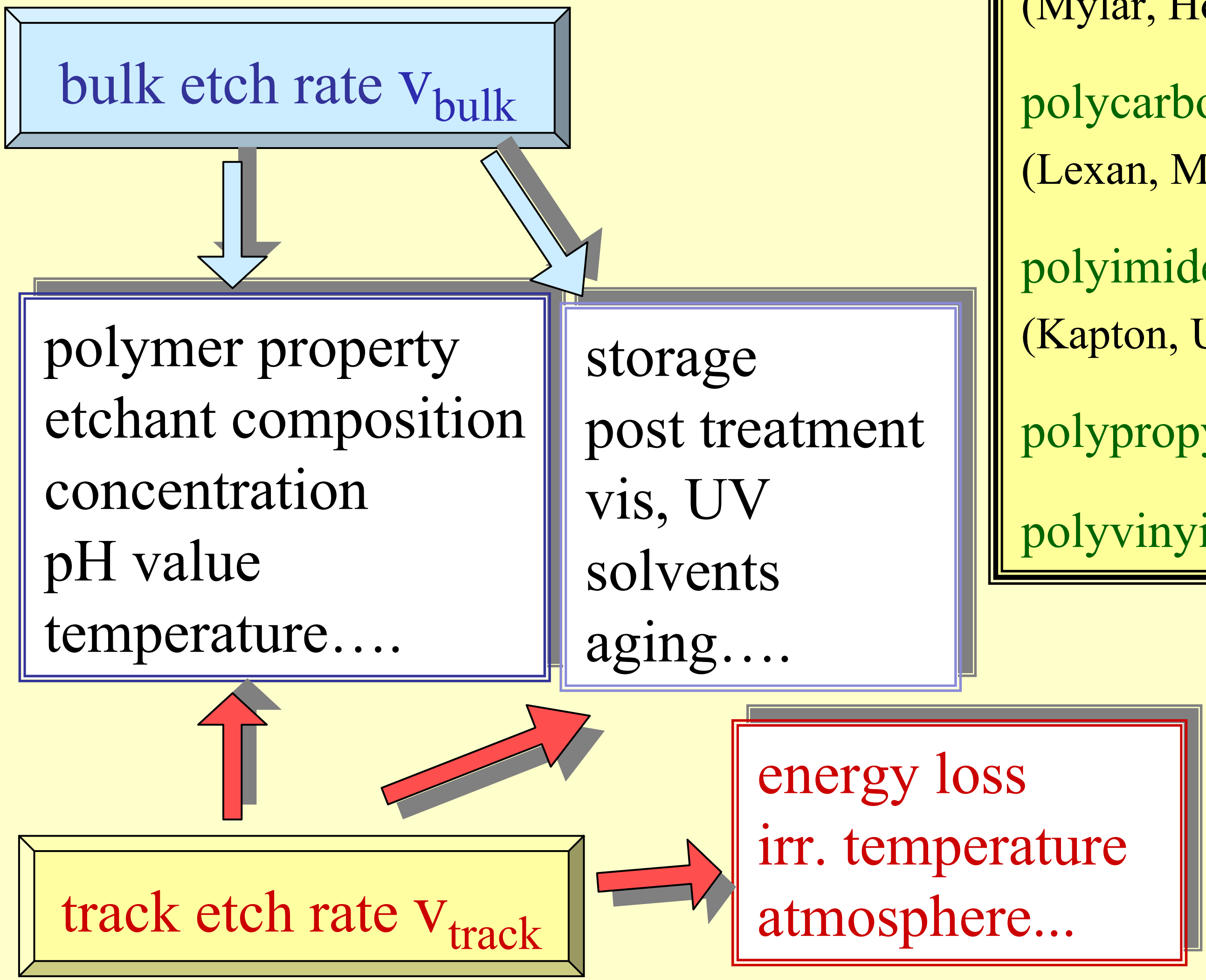



10 μm





Track etching process



POLYMERS

polyethylene terephthalate **(PET)**
(Mylar, Hostaphan)

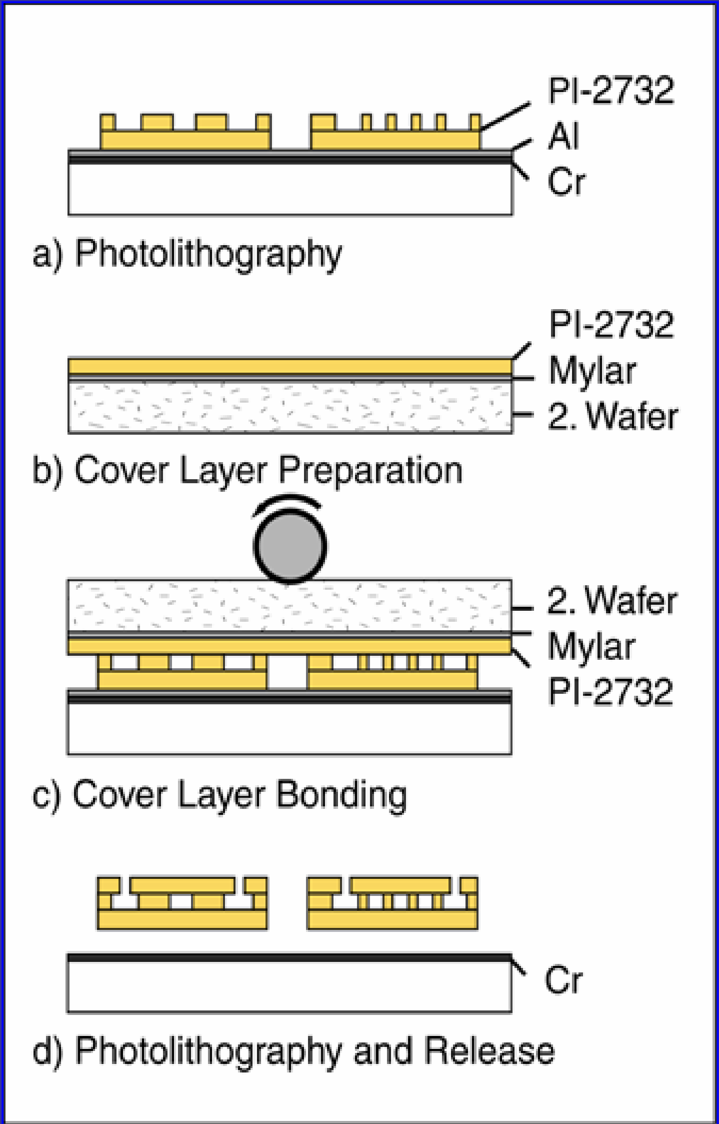
polycarbonate **(PC)**
(Lexan, Makrofol, CR39)

polyimide **(PI)**
(Kapton, Upilex)

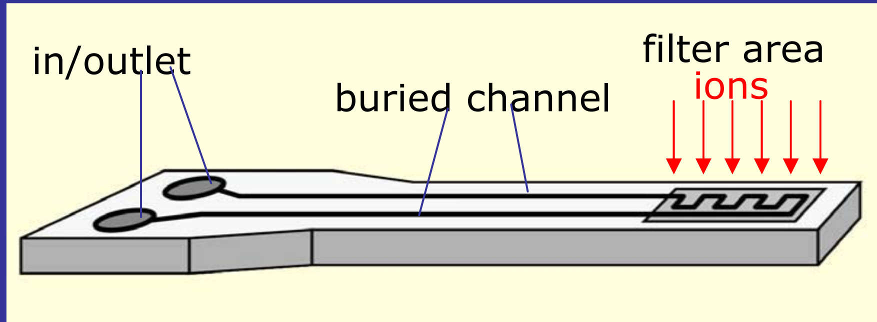
polypropylene **(PP)**

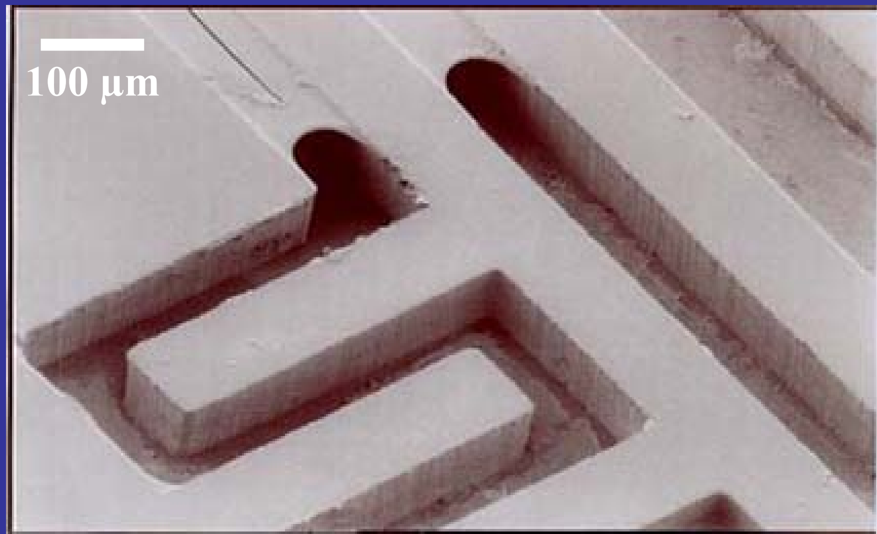
polyvinyidene fluoride **(PVDF)**

Ion track technology & microfluidic systems



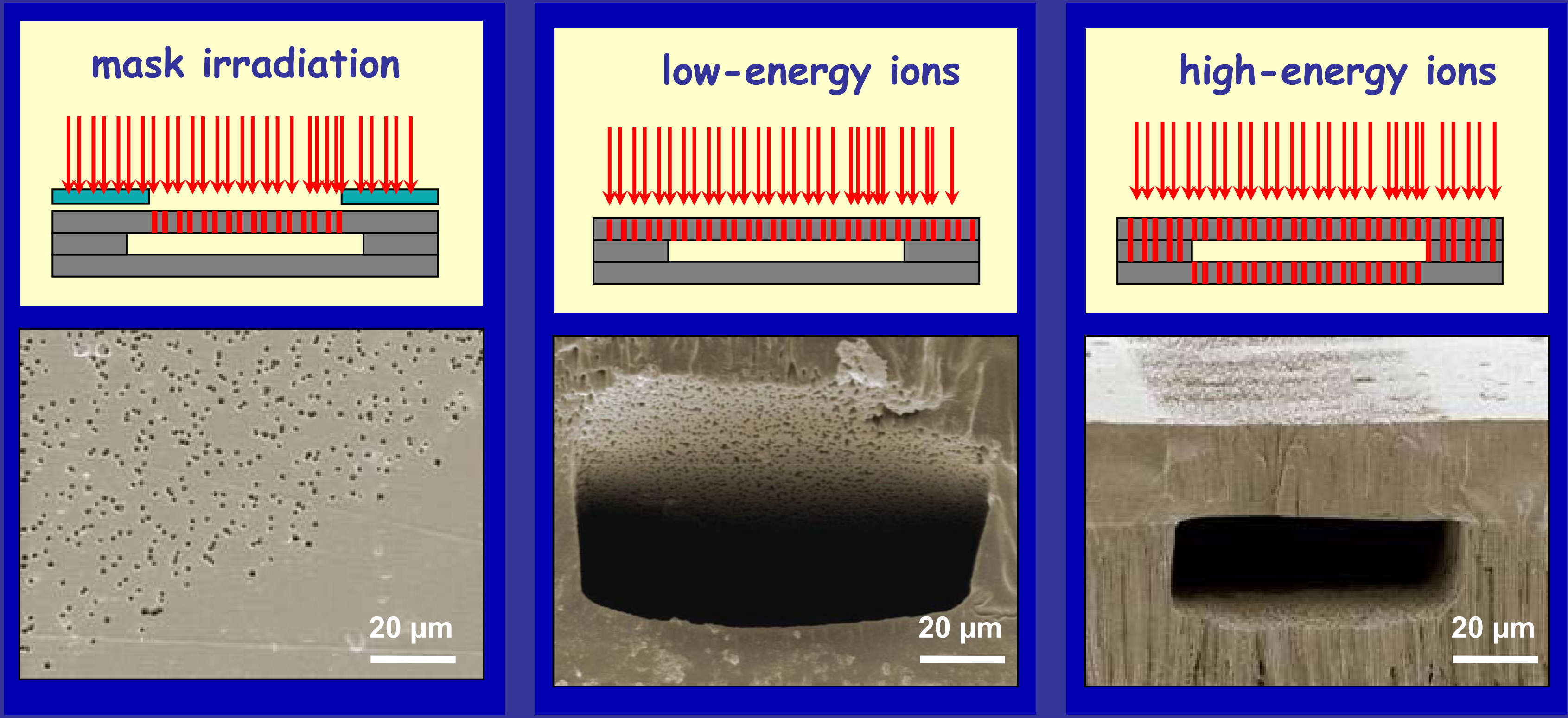
fabricated by photolithography, bonding, and annealing





S. Metz, PhD thesis, EPFL Lausanne, 2003

Integration of microporous membrane

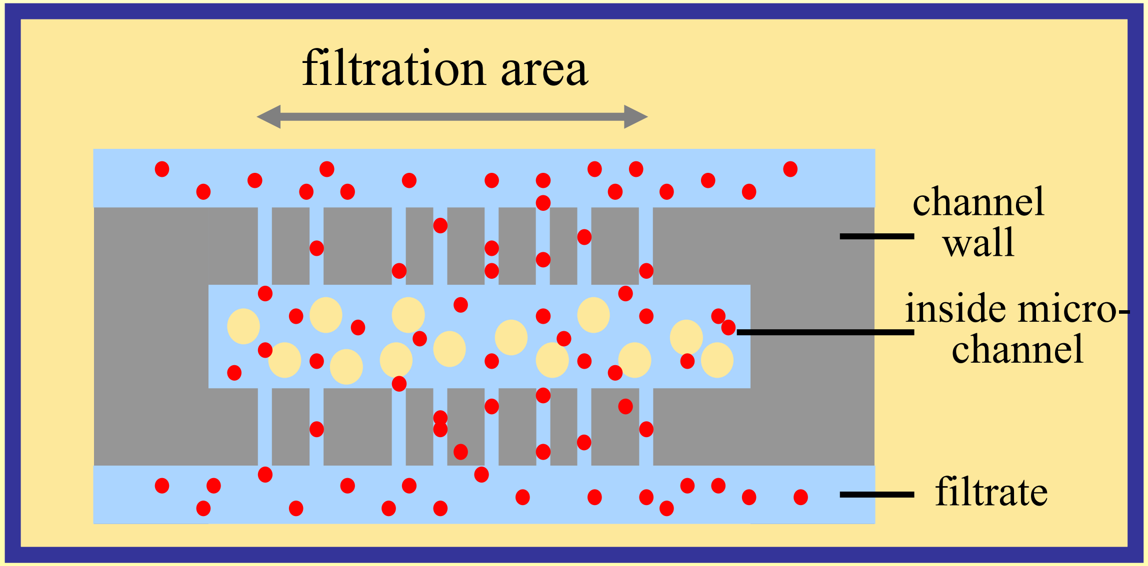


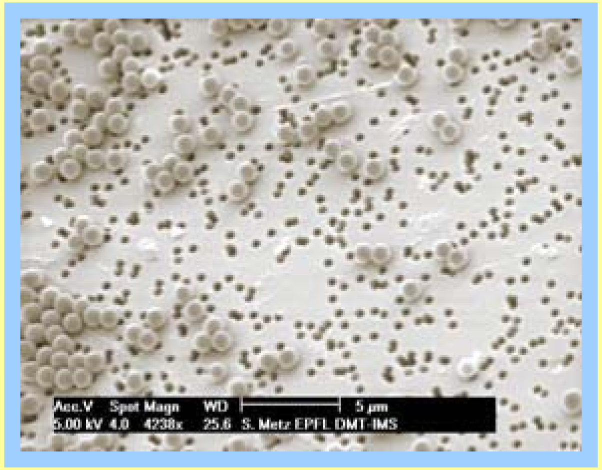
control parameters

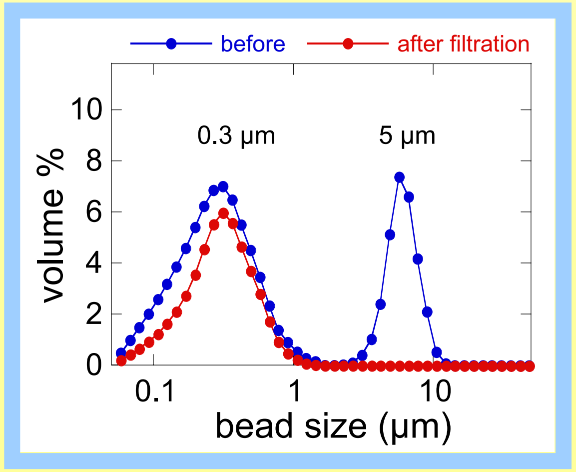
mask	→	filter area
ion energy	→	structural depth
ion fluence	→	pore density
etch time	→	pore size

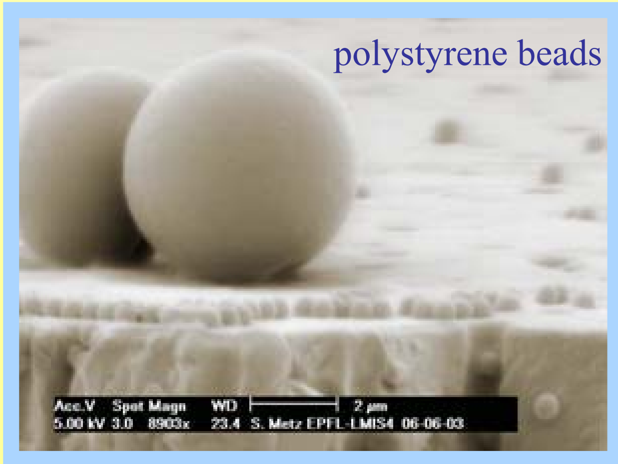
Metz et al. J. Micromech. & Microeng. 14 (2004) 324

Microfluid filtration with nanopores

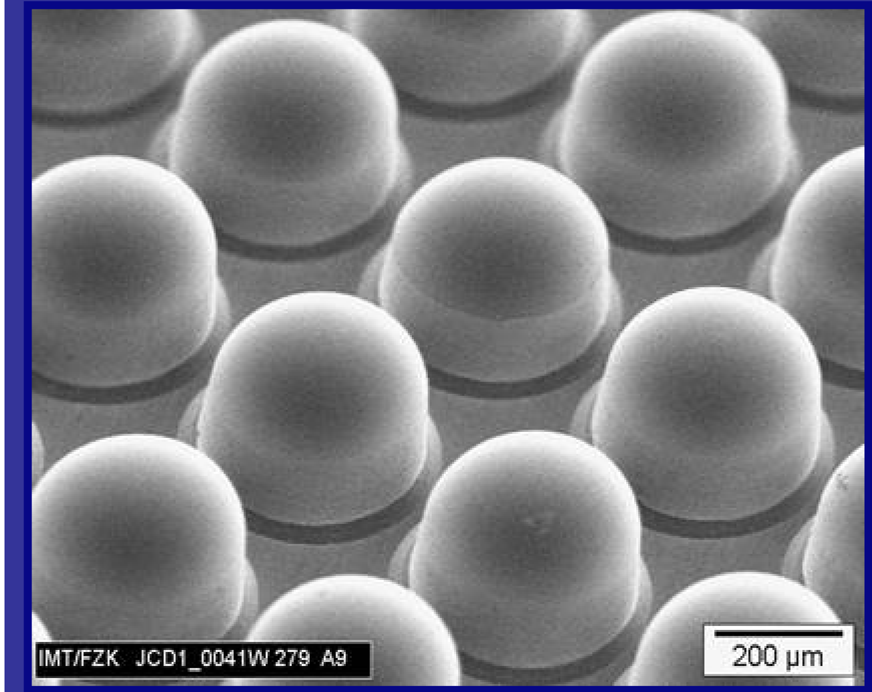


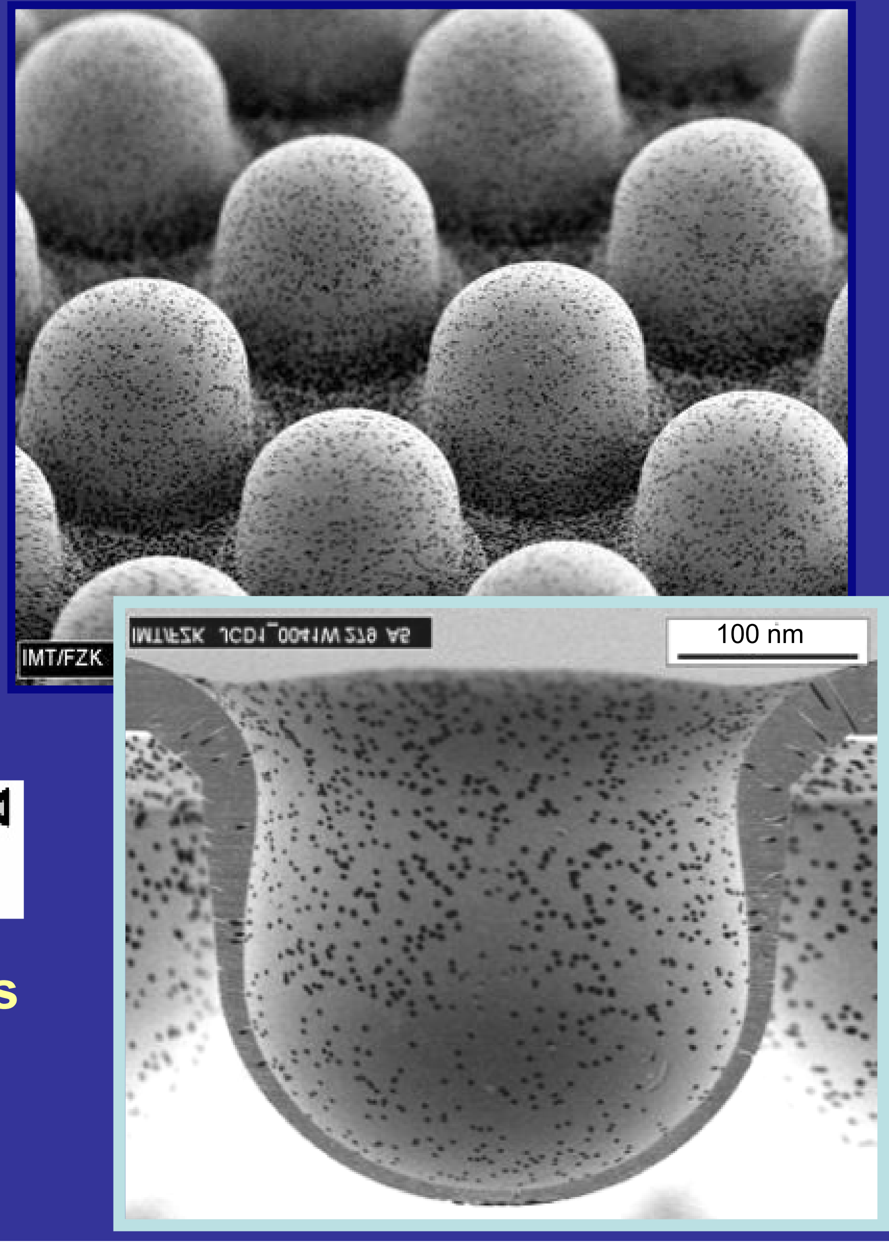


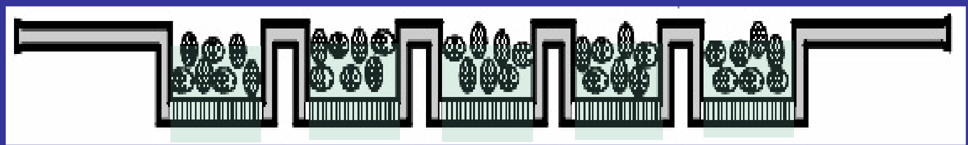




Perforation of thermoformed microcontainers





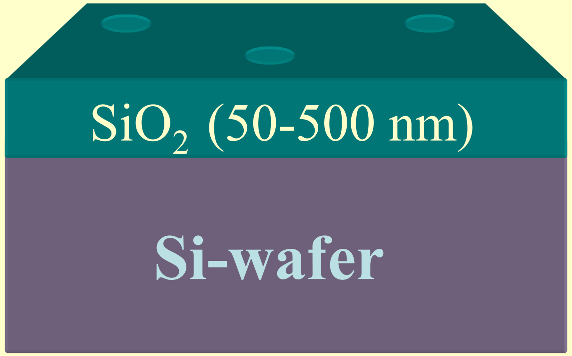


drainage during growth of cell cultures in liquid medium

Giselbrecht, PhD thesis Karlsruhe 2006
IEE Proc. Nanobiotechnology 151 (2004) 151

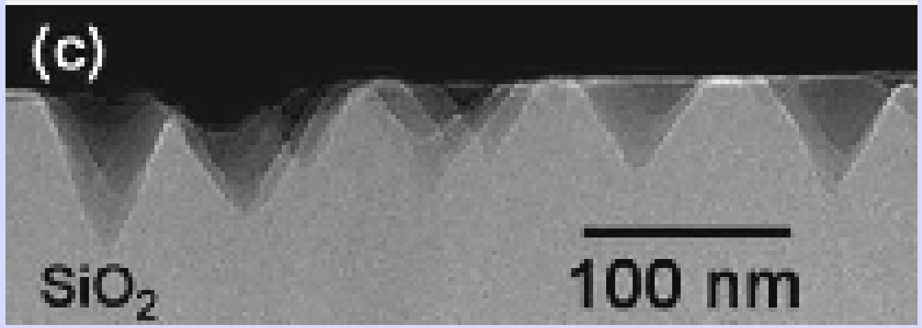
Compatibility of silicon and ion-beam technology

SiO_2 / Si



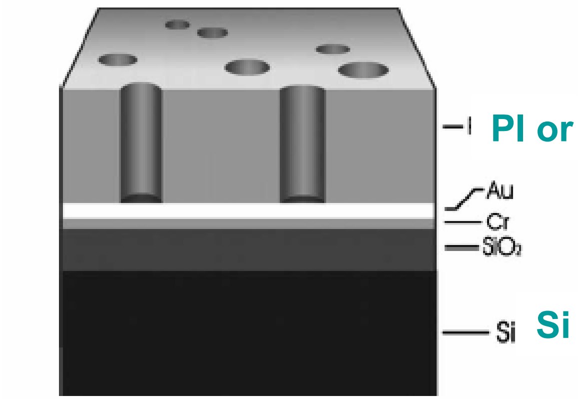
irradiated with 20 MeV Au

cross section of etched ion tracks in SiO_2 film

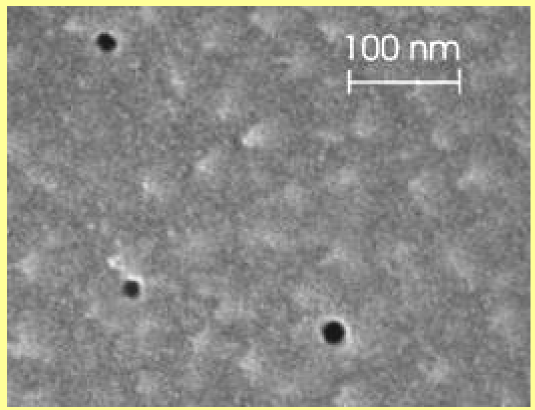


Milanez Silva et al. NIM B 206 (2003) 486

Xe ions (1075 MeV) → polymer resist / Si



etched ion tracks in resist (~10 nm)

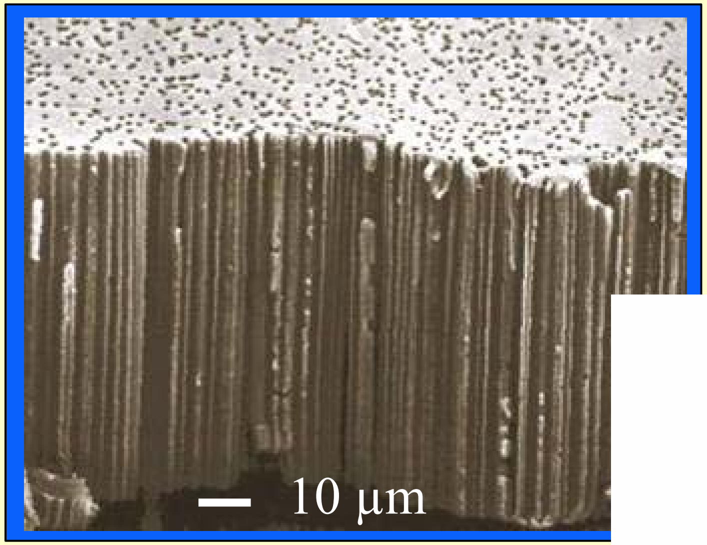


Dauginet-De Pra et al.NIMB 196 (2002) 81

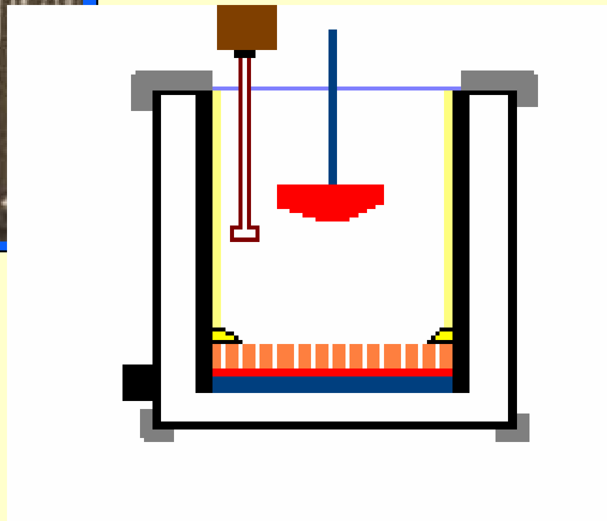
Skupinski et al. NIMB240 (2005) 681

Ion track membranes as templates

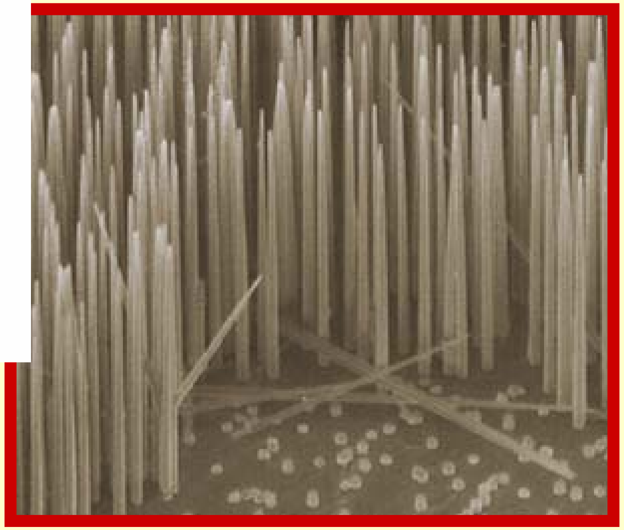
..... from pores to wires ......



etched ion track membrane



filling of pores in galvanic cell



free-standing metal needles

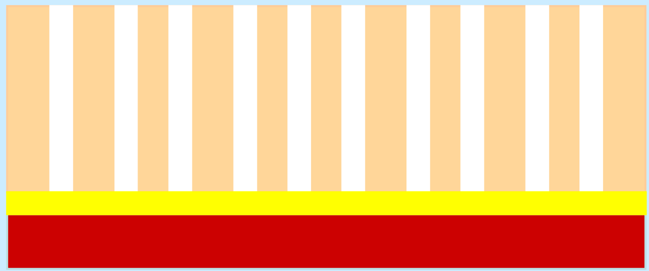
Dobrev et al. J. Vac. Sci. Technol. B 19 (2001) 1385

Template method

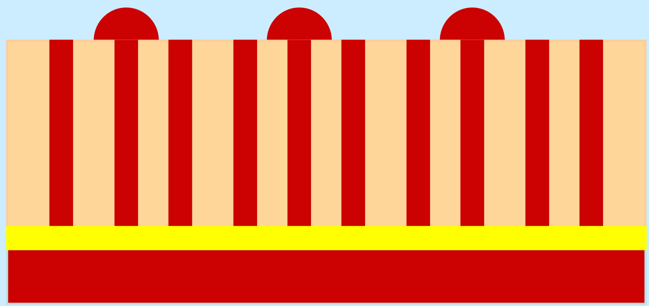
Electrochemical deposition in etched ion track membranes

1. Membrane

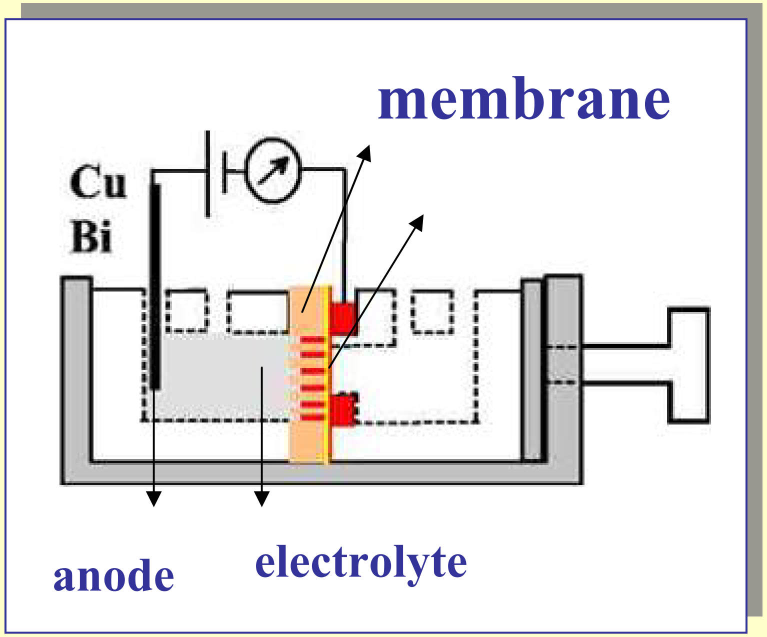
2. Au + Cu layer



3. Wires and caps



electrochemical deposition process

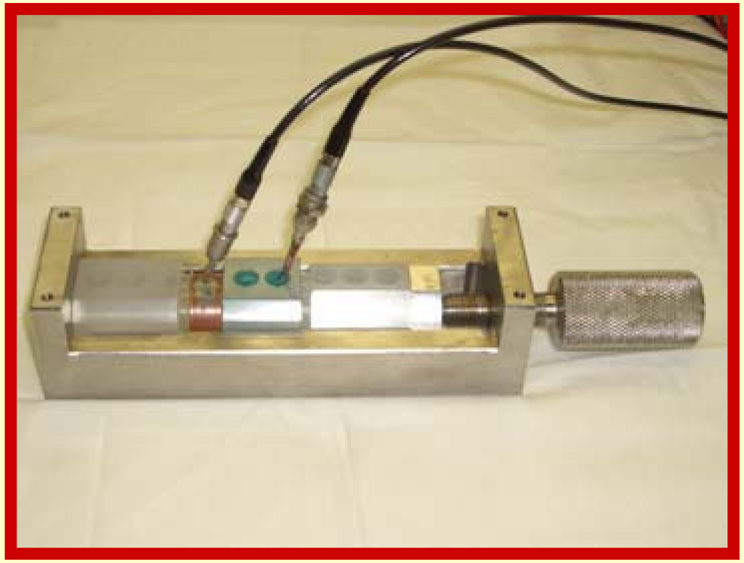


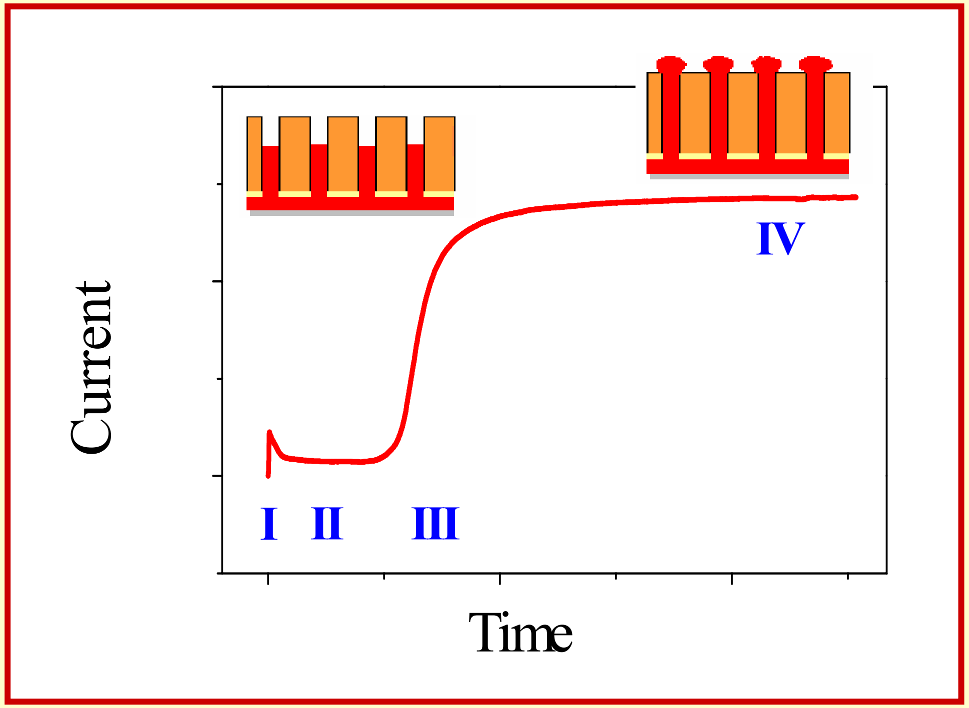
metals: Cu, Au, Ni, Fe

multilayers: Cu/Co, Cd/Te

semimetals: Bi

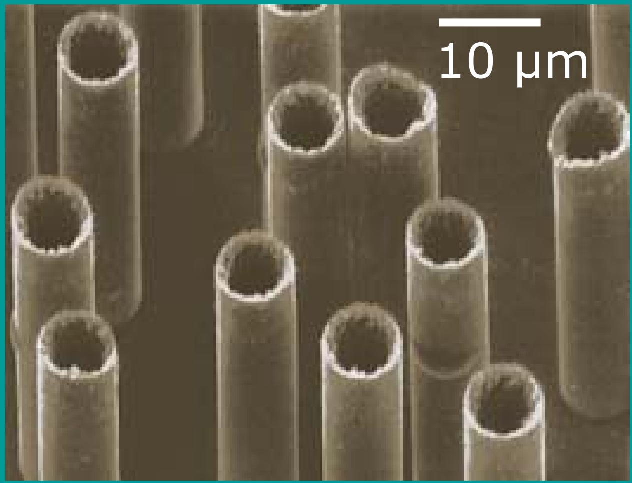
semiconductor: CdTe, CdS





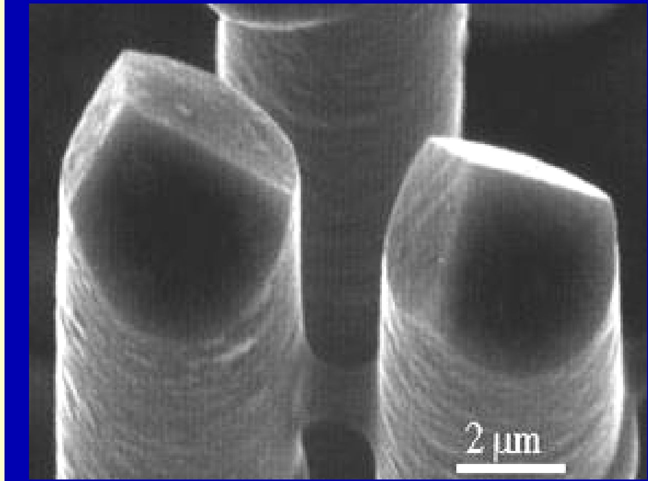
Microneedles and nanowires

metallic micro-tubes



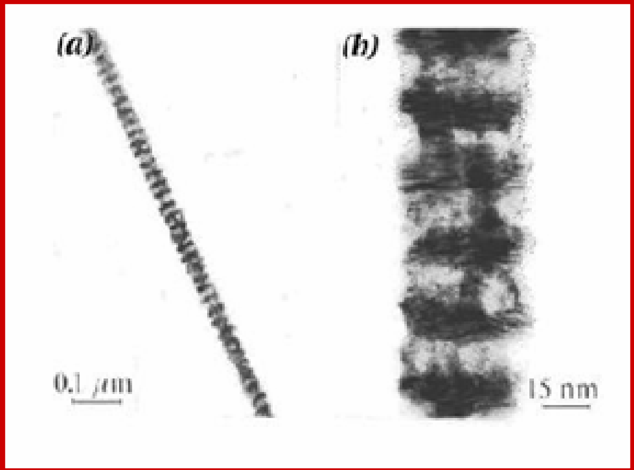
D. Dobrev et al. (GSI)

single-crystalline Cu needles



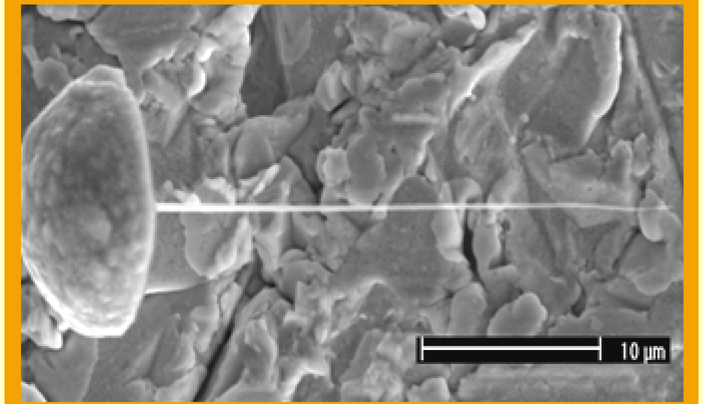
E. Toimil et al. Adv. Mater. 13 (2001) 62

10-nm thick multilayers of Co / Cu



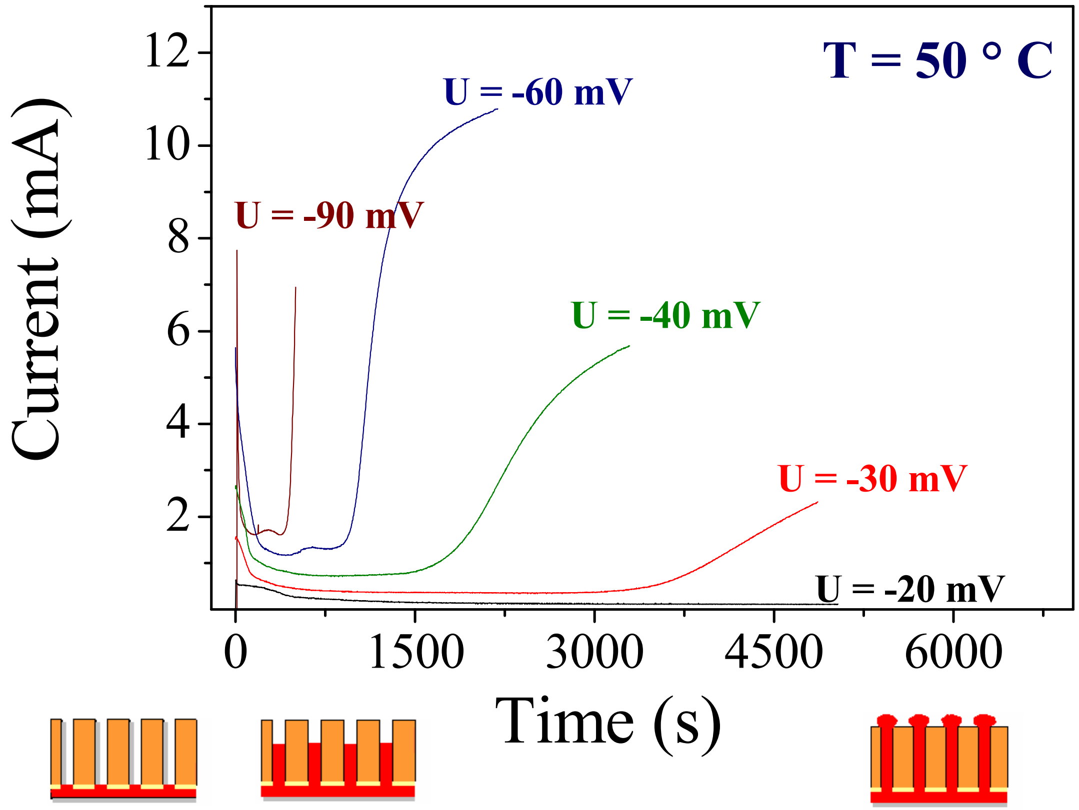
L. Piraux et al., Louvain-la-Neuve

28-nm Co / 14-nm Cu



I.Enculescu et. al. (2004)

Deposition parameters

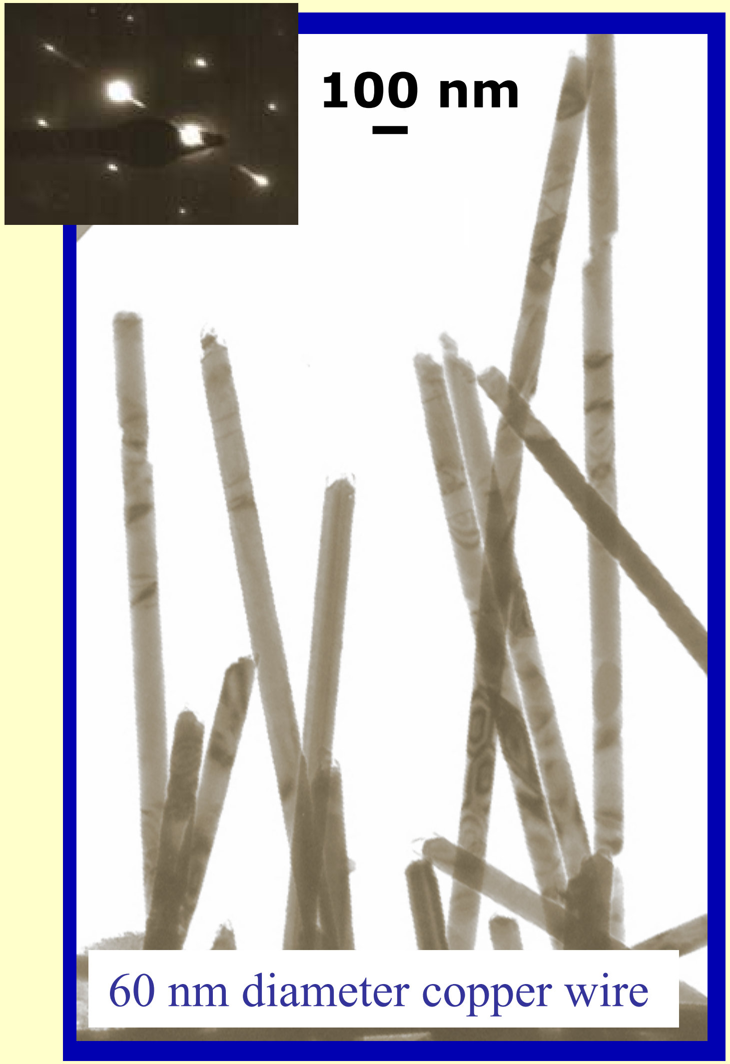


temperature
over-voltage
electrolyte

crystallinity

- ✓ **T = 50°C & j < 100 mA/cm²: single-crystalline**
- ✓ **T = 25°C & j > 100 mA/cm²: poly-crystalline**

Single-crystalline nanowires



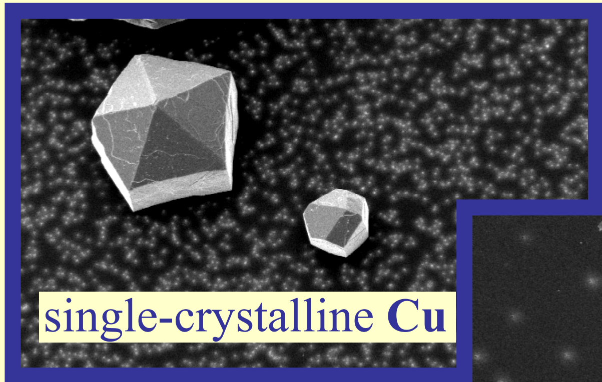
60 nm diameter copper wire

Toimil, PhD thesis, Heidelberg (2001)

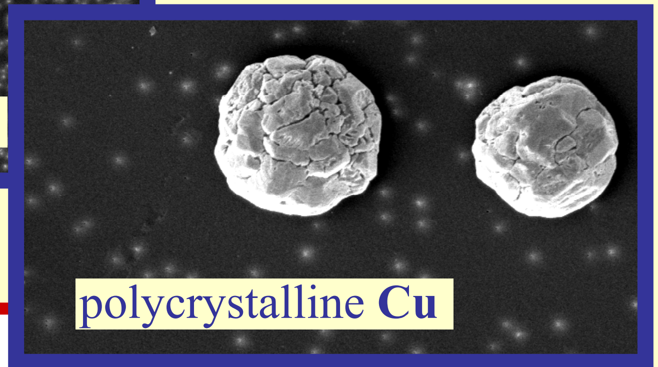
low over-voltage & high temperature

high crystallinity

different cap morphology

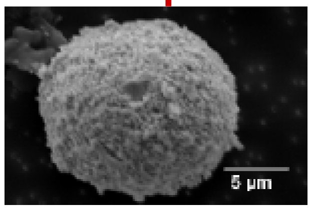


single-crystalline **Cu**

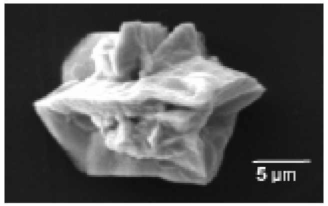


polycrystalline **Cu**

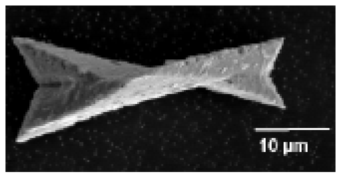
Bi caps



-40 mV, RT



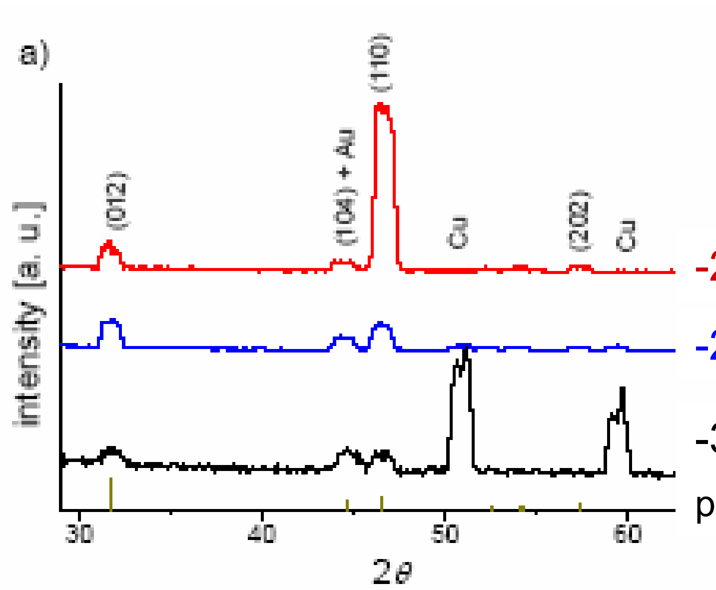
-40 mV, 60°C



-20 mV, 60°C

Cornelius et al., Nanotechn. 16 (2005) S246

Growth of textured nanowires



depends on deposition conditions

texture coefficient

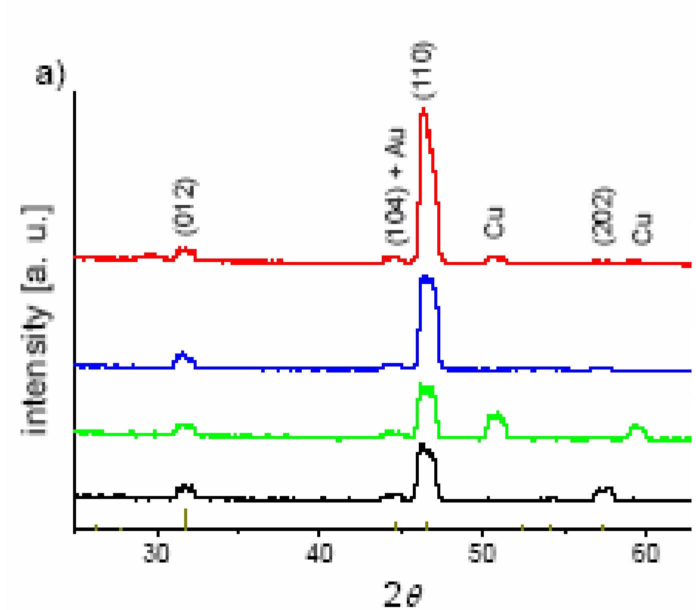
-20 mV, 60°C TC(110) = 4.2

-20 mV, 50°C TC(110) = 1.8

-30 mV, 60°C TC(110) = 1.3

powder sample

Bi wires
∅ 80 – 100 nm



depends on wire diameter

texture coefficient

40 nm TC(110) = 4.5

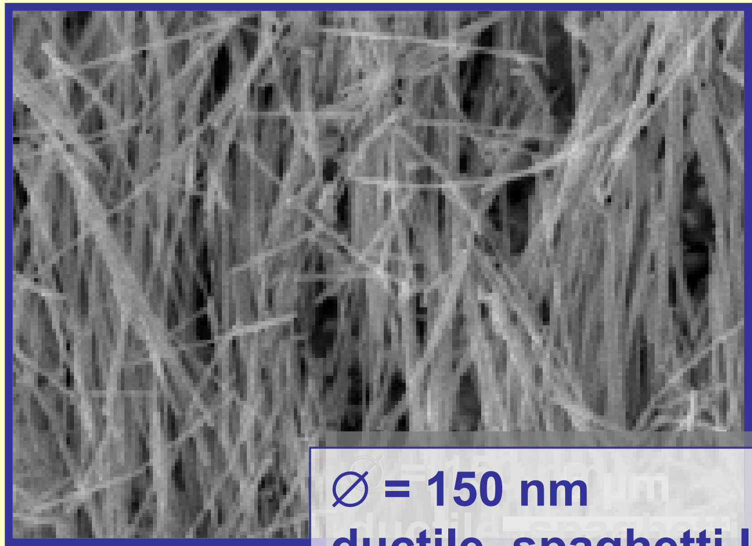
80 nm TC(110) = 4.2

120 nm TC(110) = 3.8

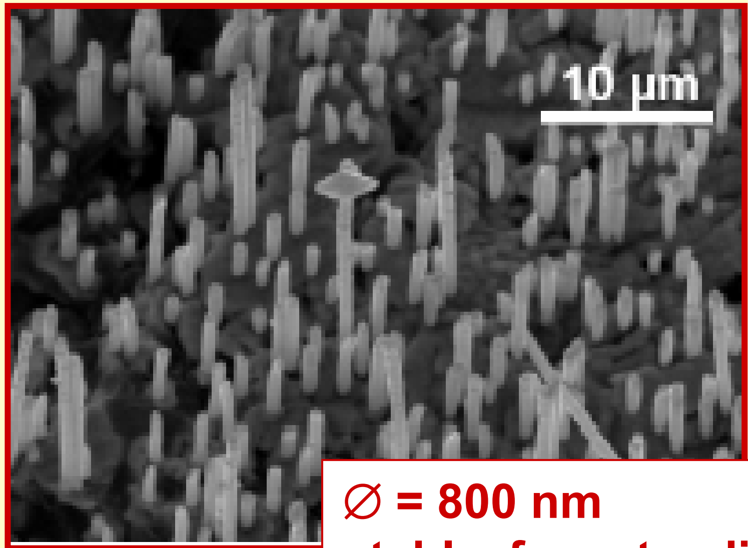
160 nm TC(110) = 2.8

deposition
-20 mV, 60°C

nanowires as cold field emitters



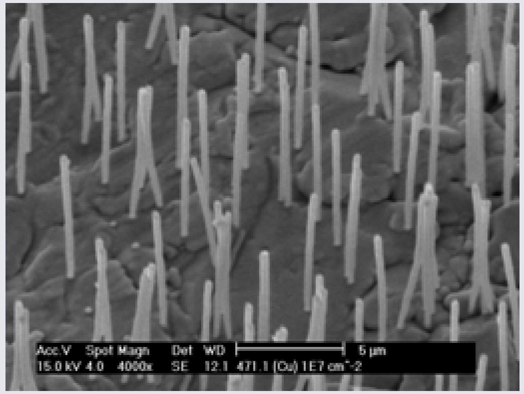
∅ = 150 nm
ductile, spaghetti like

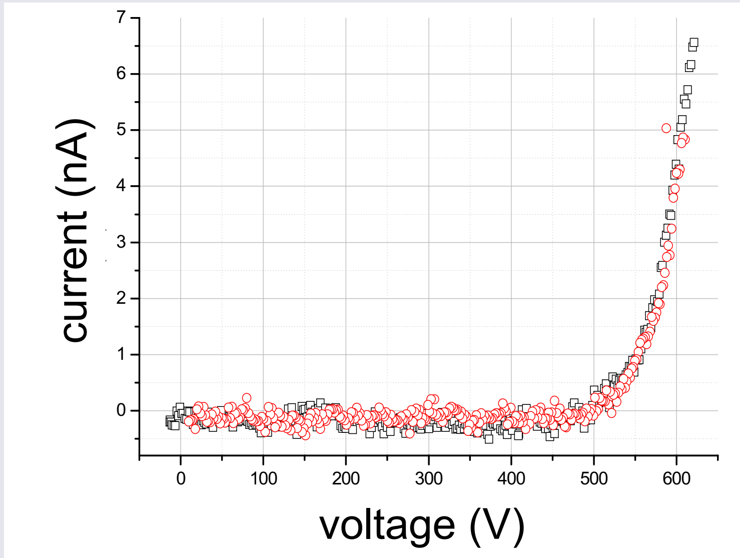


∅ = 800 nm
stable, free standing

Cornelius PhD thesis, Heidelberg (2006)

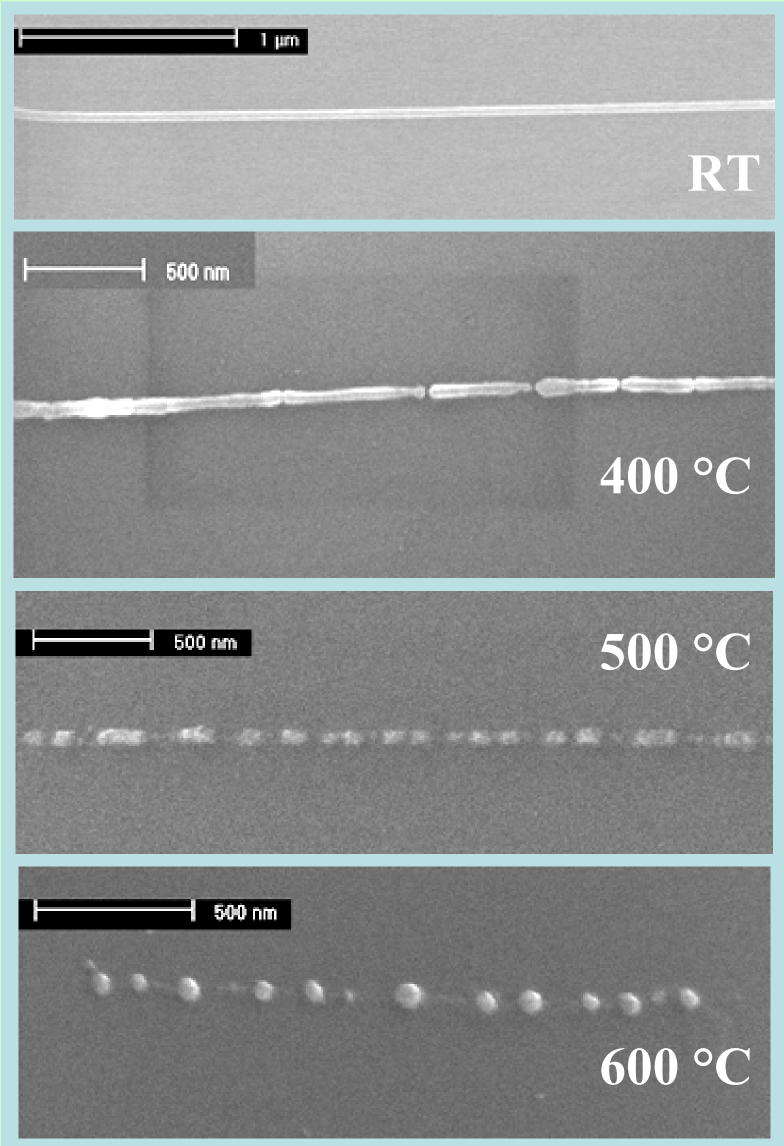
'cold' field emitters





Maurer et al NIMB 245 (2006)

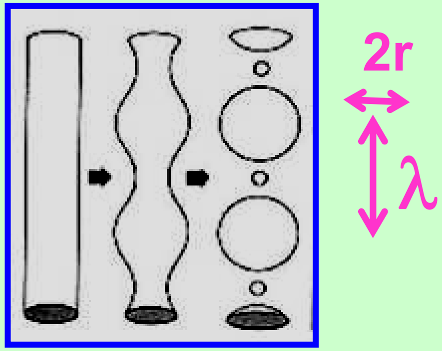
Thermal stability of Cu nanowires



30-nm Cu nanowire
on SiO_2 substrate
annealed in vacuum, 30 min

Rayleigh Instability

- Liquid cylinder → spherical droplets
- Surface decrease lowers energy for
  $\lambda > 2\pi r$
- For solid cylinders with radius r under surface diffusion:
  $\lambda = 8.89r$ and $d_s = 3.78\ r$

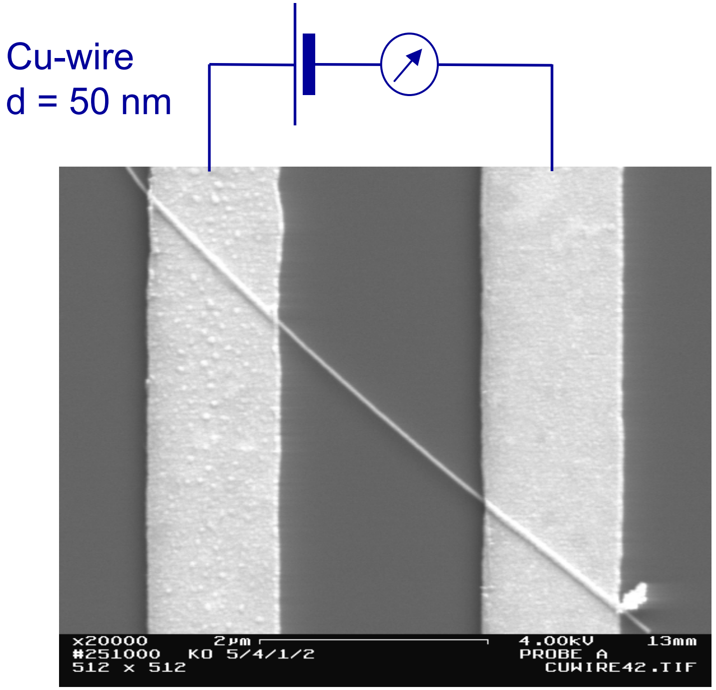


T_{fragm}(400°C) << T_{melt} (1083°C)

Toimil-Molares et al., APL 85 (2004)

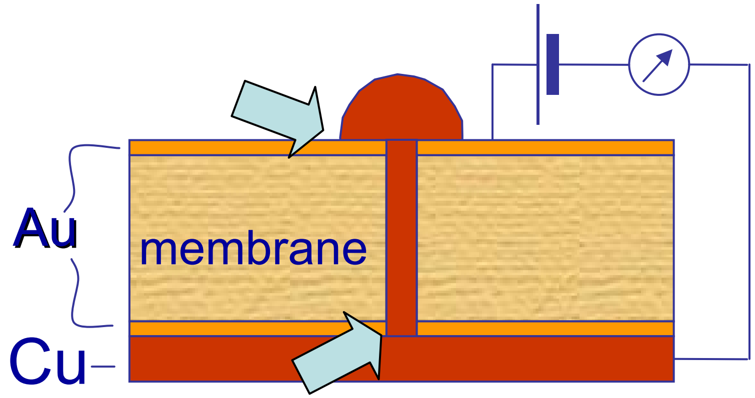
electric transport properties of nanowires

lithographic contacts



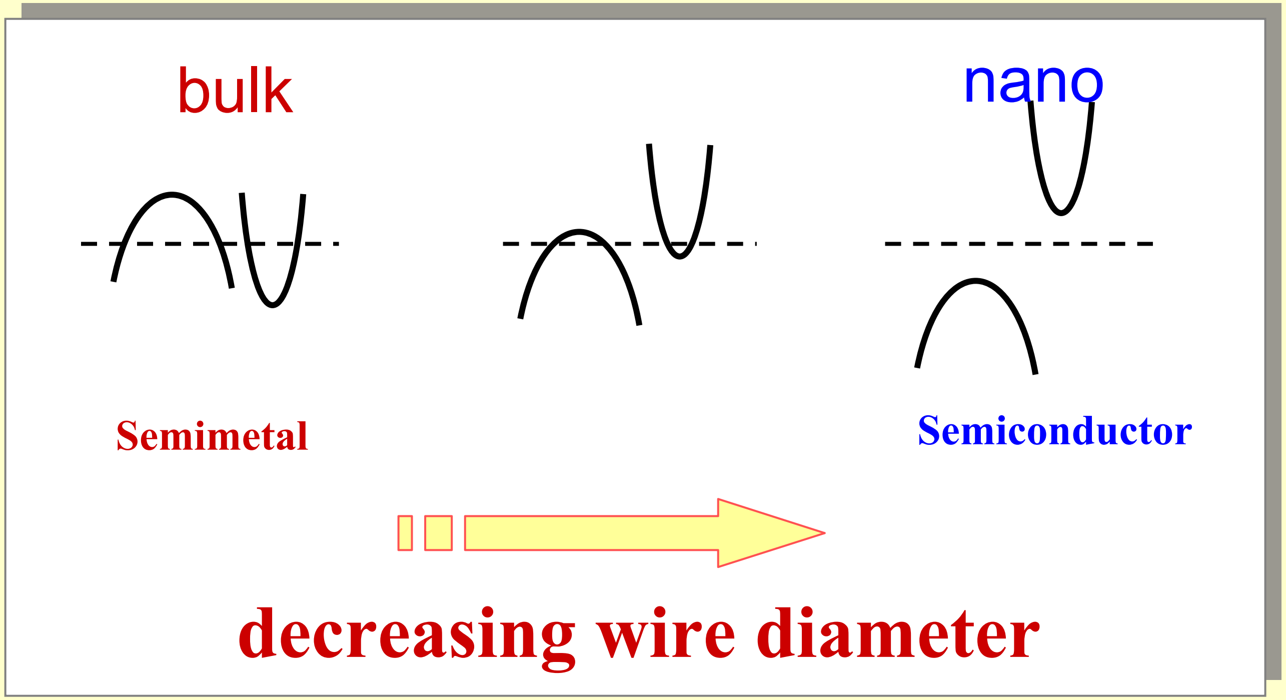
Toimil et al., APL 82 (2003) 2139

selfdefined contacts



Enculescu et al., Appl. Phys. A, 77 (2003) 751

Material: Bismuth



Bulk Bi

conduction band overlaps with the valence band by 38 meV

Bi nanowires (~50 nm)

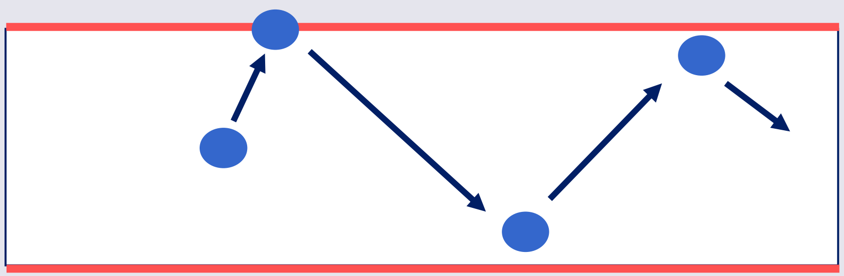
transition to semiconductor due to quantum confinement

Surface & Grain boundary scattering

If the diameter of the wire ~ electron mean free path λ, additional scattering processes come into play

Surface scattering

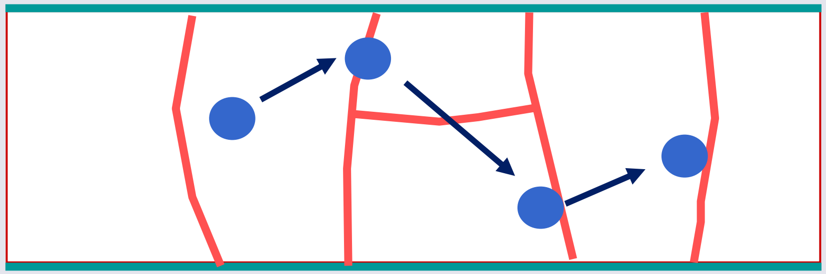
Dingle et al., Proc. R. Soc. A 201, 545 (1950)



$$\frac{\rho}{\rho_0} = \mathrm{f}\left(\frac{D_{\mathrm{wire}}}{\lambda}\right)$$

Grain boundary scattering

Mayadas et al., Phys. Rev. B 1, 1382 (1970)

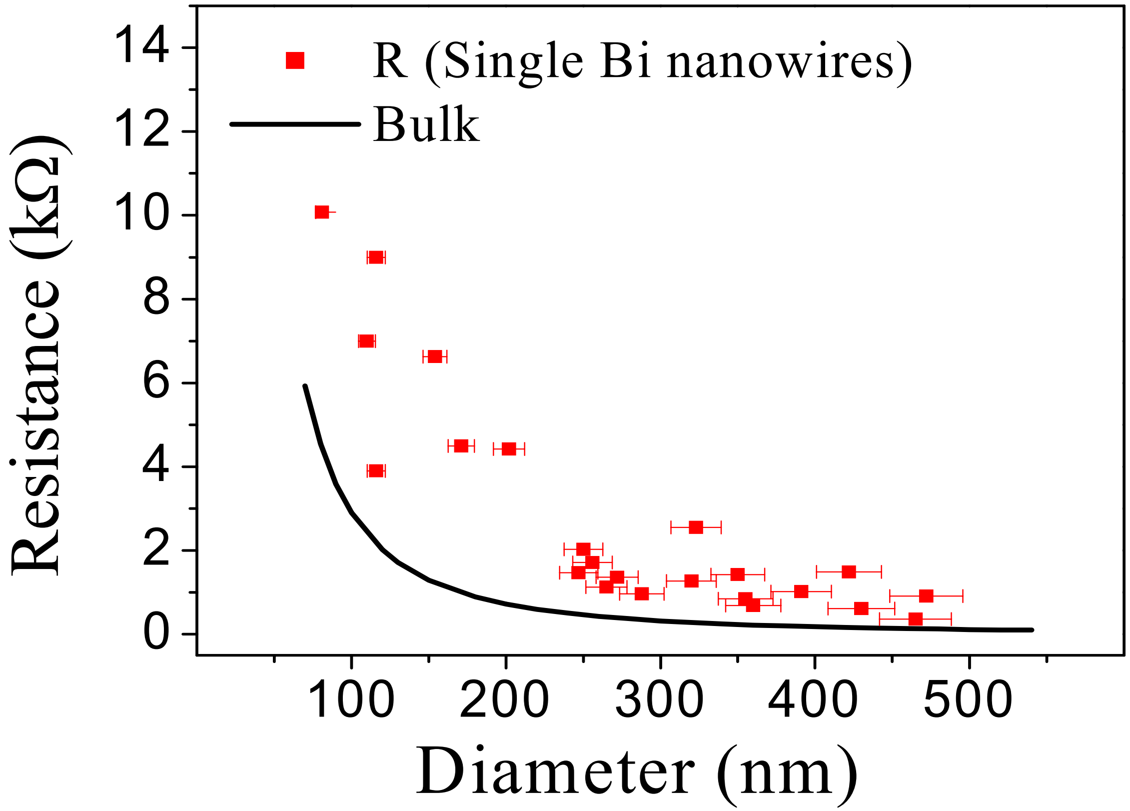


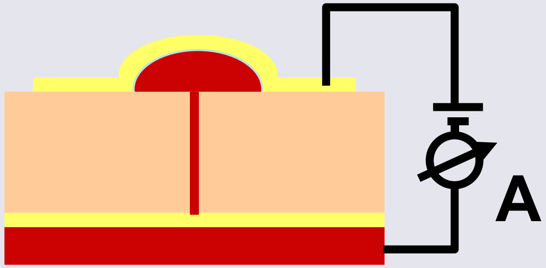
$$\frac{\rho}{\rho_0} = \mathrm{f}\left(\frac{\lambda}{d}\frac{R}{1-R}\right)$$

d = mean grain size

R = reflexion coefficient

resistance of single Bi nanowires





T = 50 °C
U = 20 - 40 mV

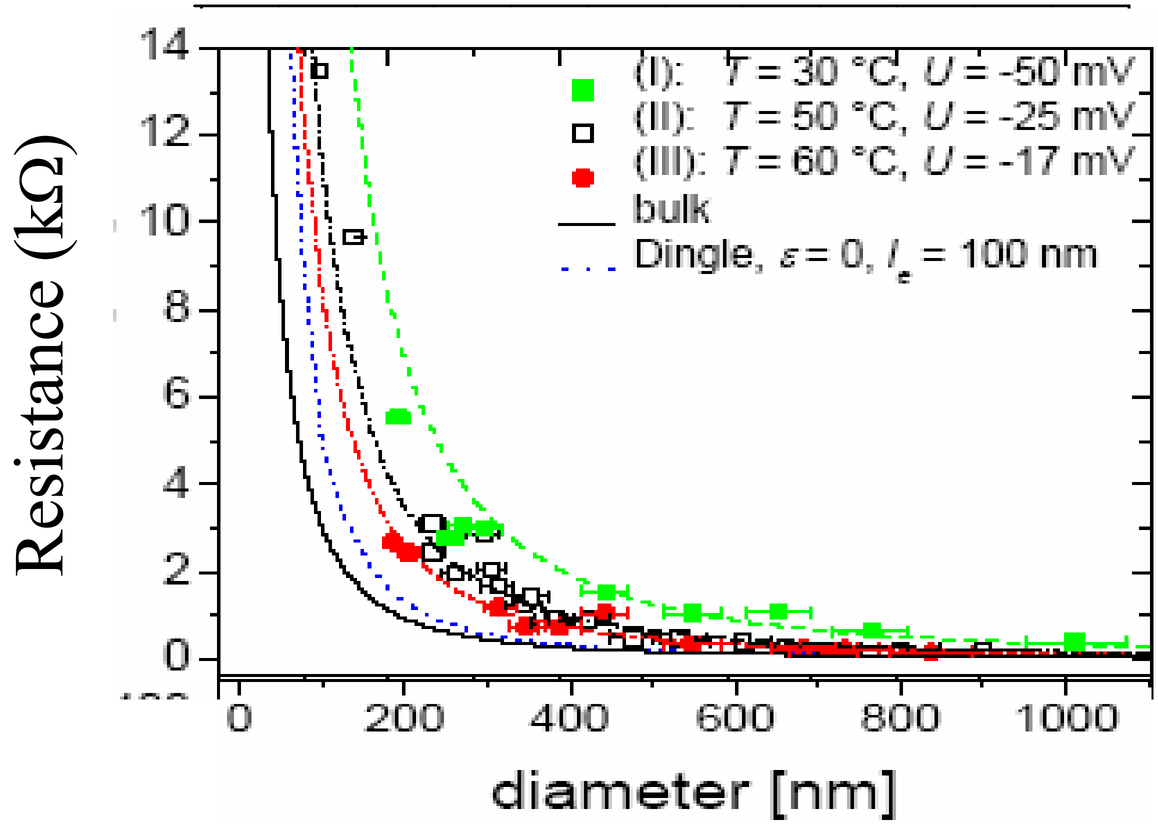
different crystallinity

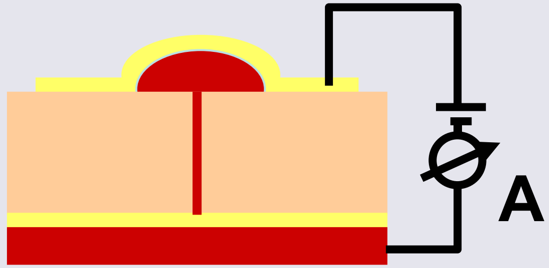
different grain boundary scattering

- ✓ resistance values higher than expected for bulk resistivity
- ✓ different resistances for wires of similar diameter

Cornelius PhD thesis, Heidelberg 2006

resistance of single Bi nanowires





T = 50 °C
U = 20 - 40 mV

different crystallinity

different grain boundary scattering

- ✓ resistance values higher than expected for bulk resistivity
- ✓ different resistances for wires of similar diameter
- ✓ resistance depends on crystallinity

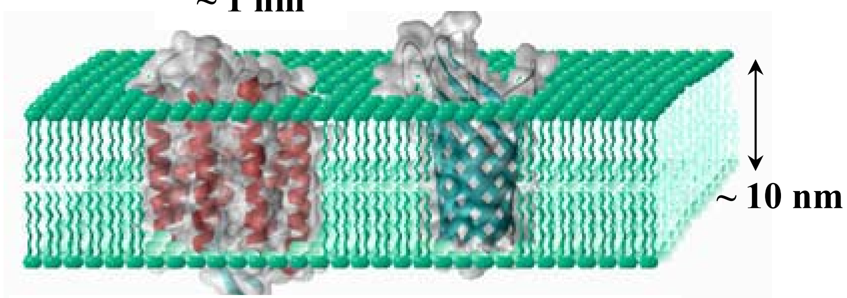
Applications of nanopores

etched ion track
in polymer

- **biosensors**
- **DNA detection**
- **synthetic model pores**

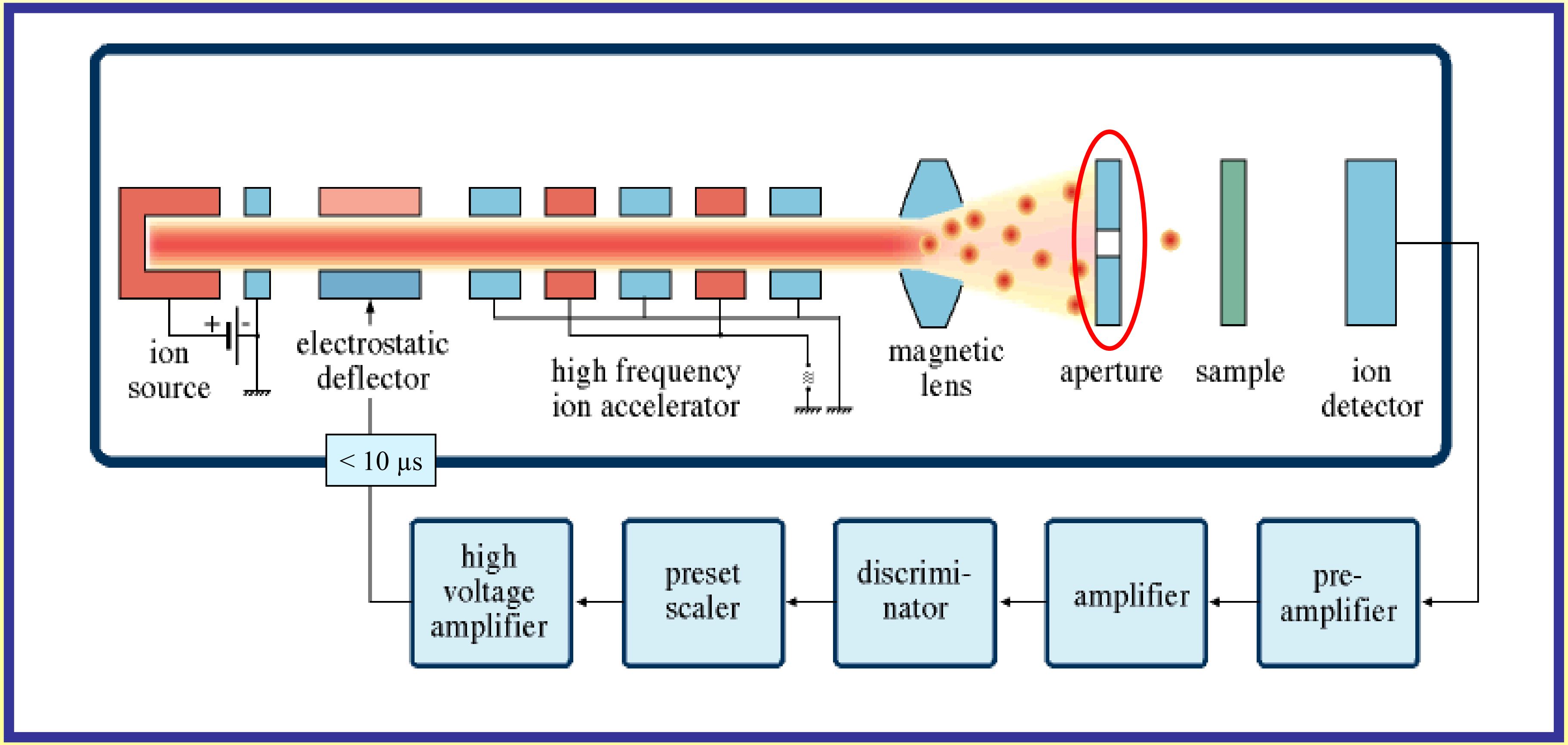
  control of pore size and shape
  less fragile

Bio-pore (α-hemolysin)

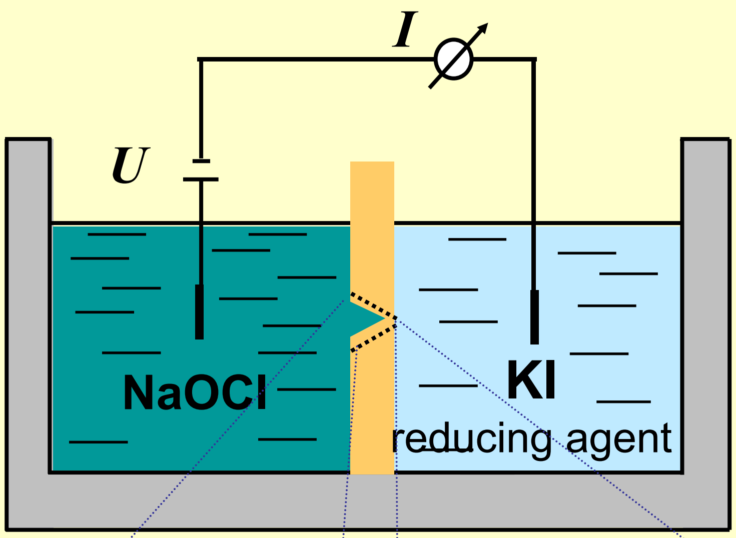


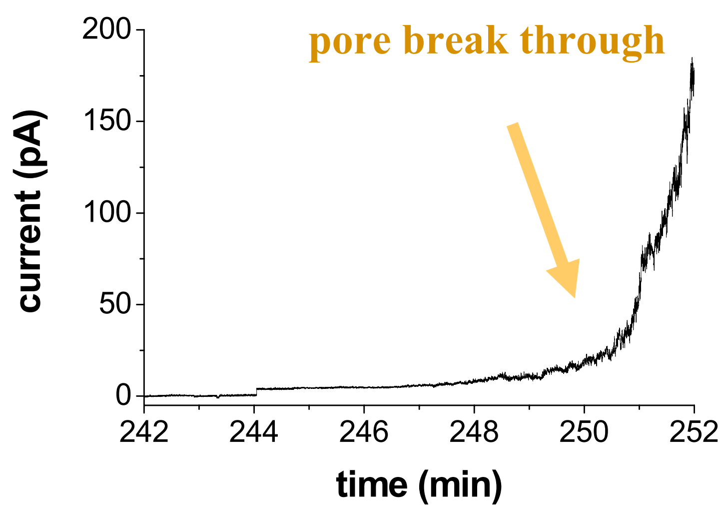
Science **175** (23) (1972) 720

Single ion irradiation

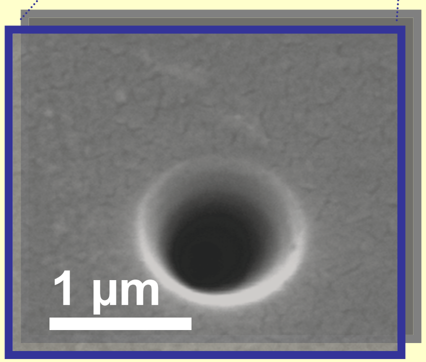


Single nanopores by electro-stopping

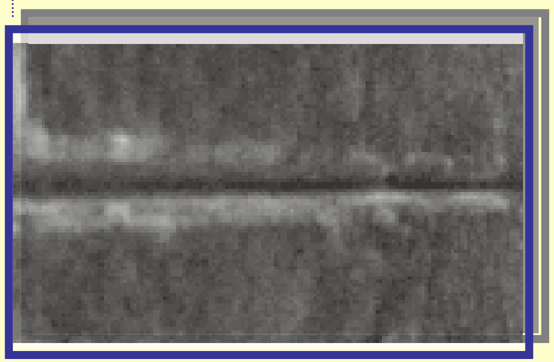




Kapton:etch stop: $OCl^- + 2\,H^+ + 2\,I^- \rightarrow I_2 + Cl^- + H_2O$



large opening



small opening

d ≈ 2 nm

$$R = 4\,L / \pi\,\kappa\,D\,d$$

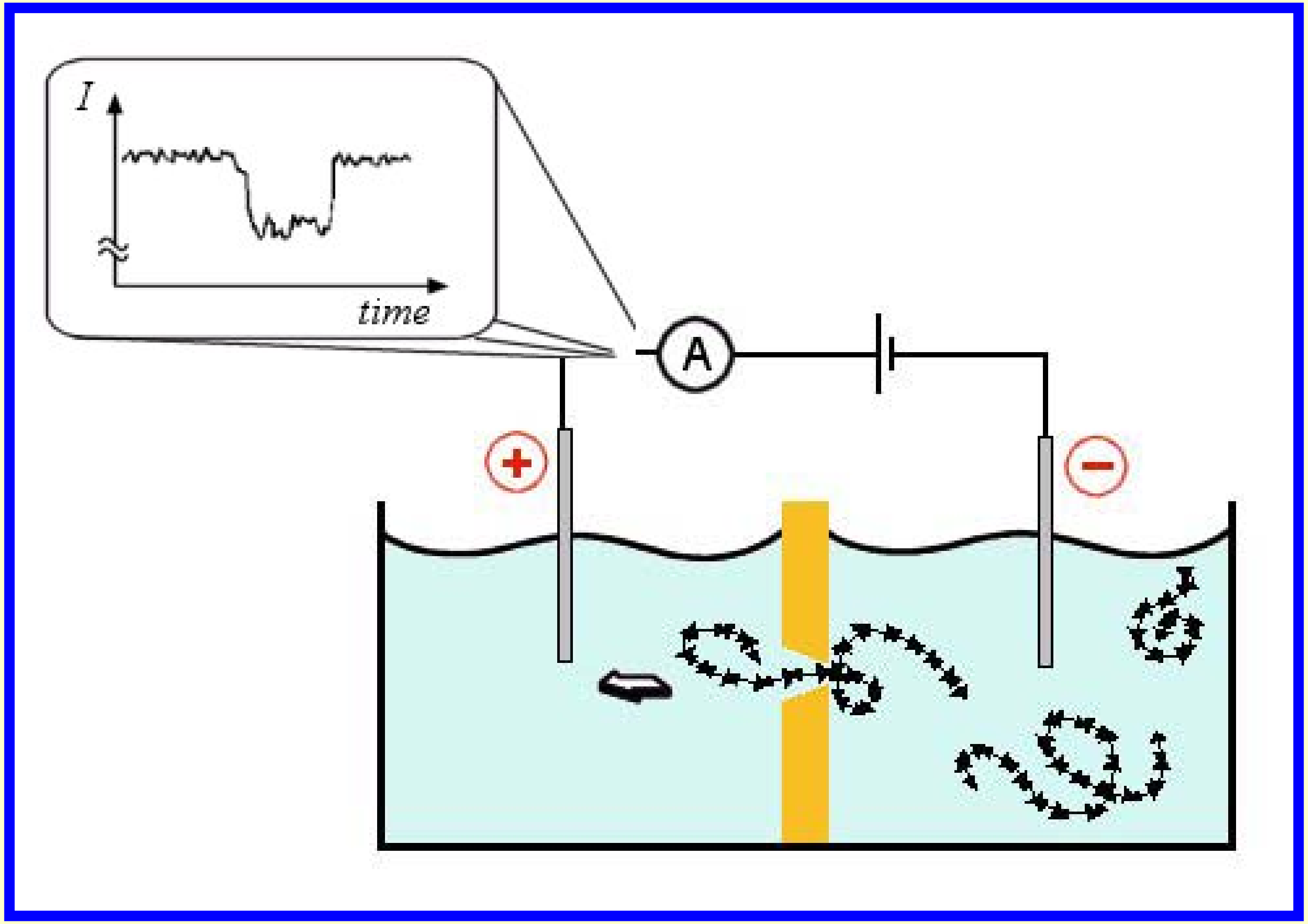
R resistance

κ conductivity of KCl

L length of the pore

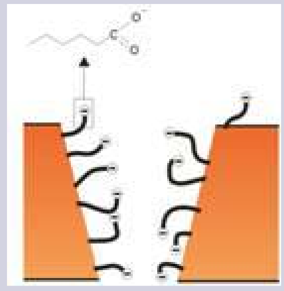
Siwy et al., Appl. Phys. A 76 (2003)

Single nanopores as bio-sensors

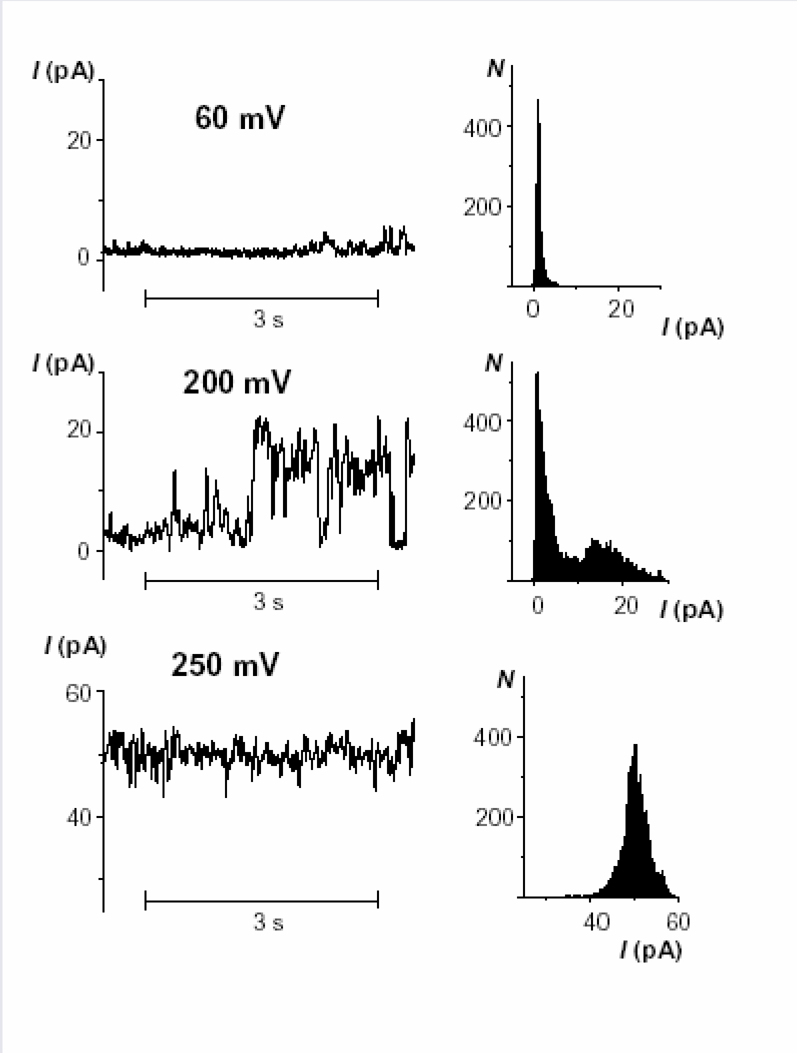


Mara et al., Nano Lett. 4 (2004) 497
Schiedt et al., NIMB 236 (2005) 109

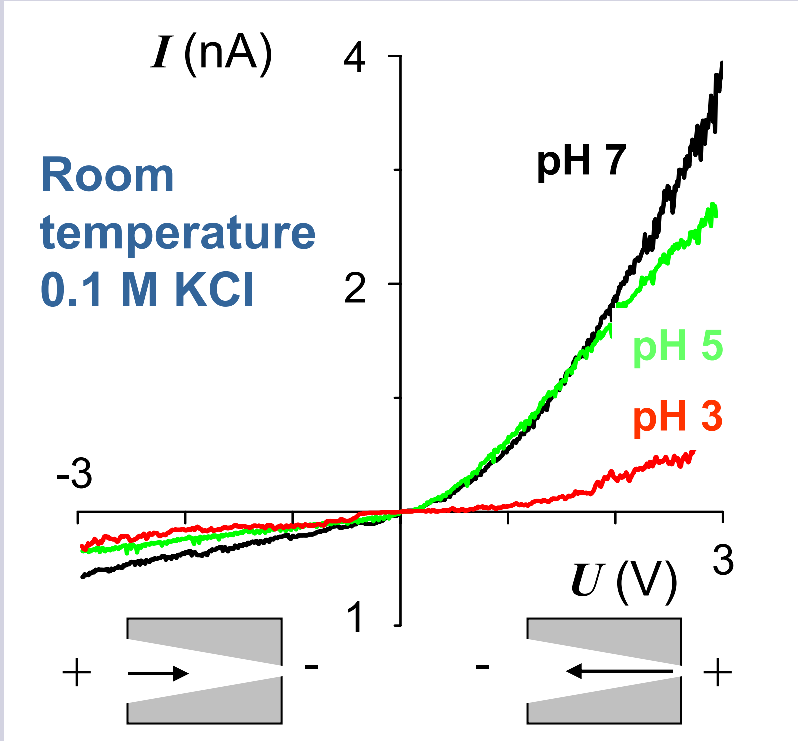
… in the case of single pores in PET …



Ion currents also switches between discrete levels



Ion currents are also rectified



Cervera et al. Europhys. Lett., **71** (2005) 35
J. Chem. Phys. **124** (2006) 104706

Conclusions

- Energetic ions produce tracks of few nanometers in diameter and high aspect ratio (>>1000)
- Track etching in insulators (e.g., polymers, mica SiO_2) allows the controlled production of nanoporous membranes
- Combination with micro-mechanical systems, lithography and Si technology possible
- Ion tack membranes most suitable as template for fabrication of nanowires (electrical, thermal, structural etc. properties)
- Single nanopores suitable as model for bio-pores and as biosensors