Ion irradiation of carbon nanotubes

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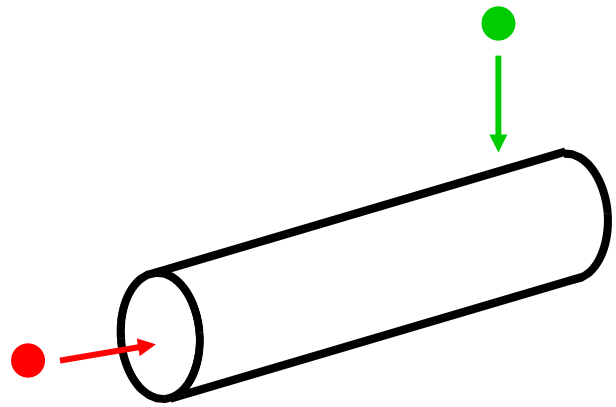
Support: NSERC & PREA

Outline

- Properties and applications of carbon nanotubes
- Irradiation of carbon nanotubes by ion beams
  - Some experiments
  - MD simulations
- Ion channelling through carbon nanotubes
  - High energies
  - Medium energies
  - Low energies
  - Experimental facts
- Outlook

(High energies, Medium energies, Low energies: } Theory & simulation)

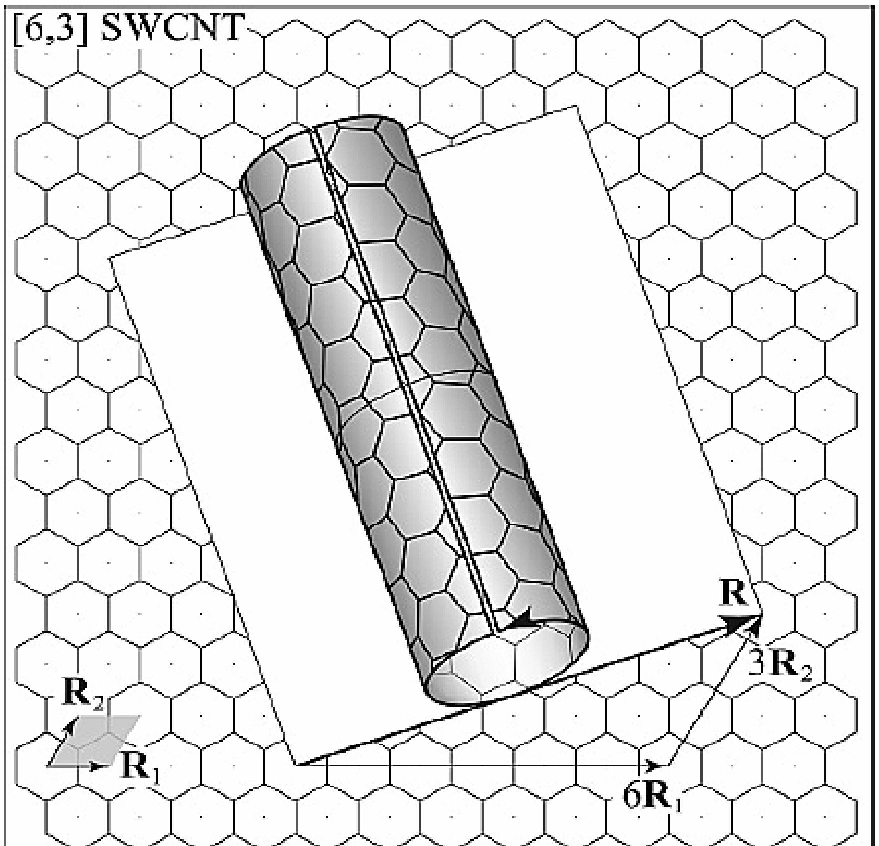


Carbon nanotubes (diameter ~ 1 nm, length ~ 1 mm)

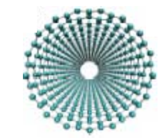
- Exceptional electrical, mechanical and thermal properties
- Dependent on structural and chemical modifications

C. Gómez-Navarro *et al.*, *Nature Mat.* 4 (2005) 534.

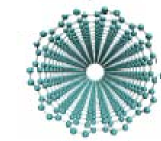
Rolling single graphene sheet:



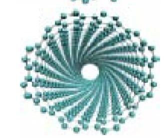
a) zig-zag

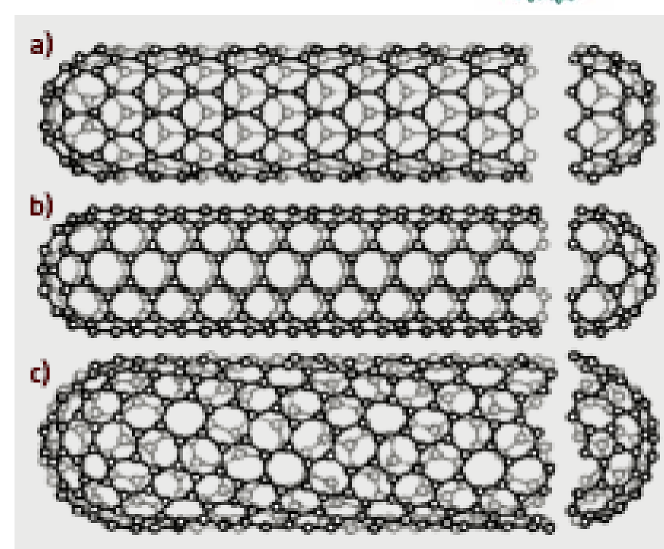


b) Armchair



c) chiral



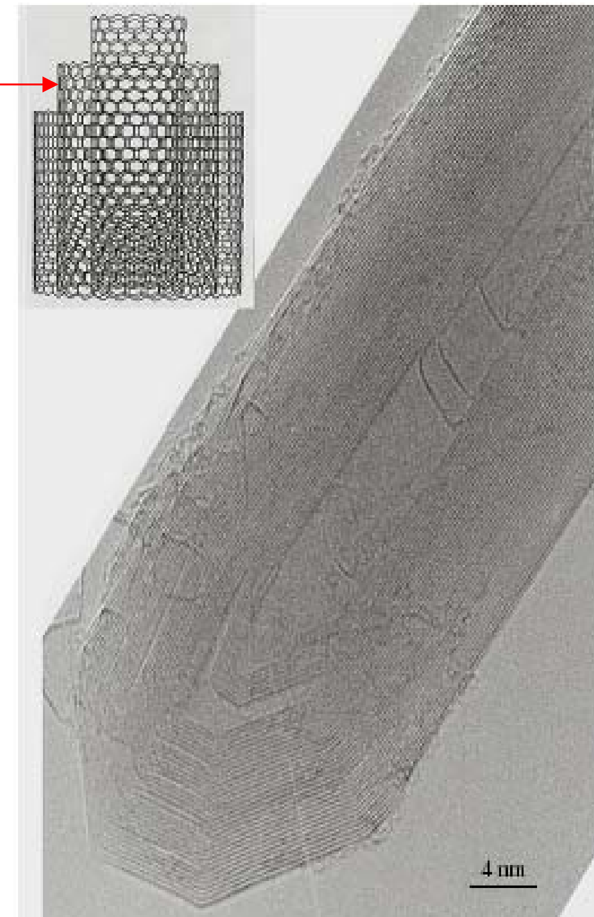


Ends usually closed

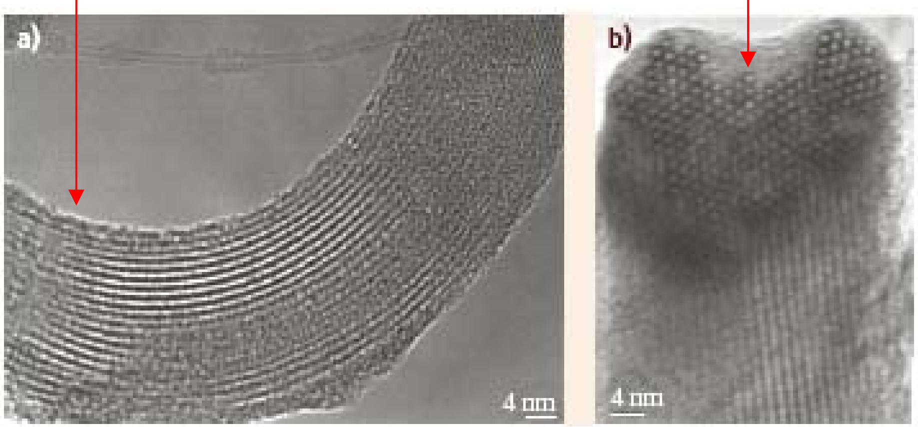
- Nanotube properties:
  - Electrical, mechanical, thermal
  - Dependent on: molecular structure, geometric confinement, local modification
- Applications:
  - Nanoelectronic devices
  - New composite materials
  - Sensitive chemical detectors
  - Ion storage (H, Li)
  - Field emission displays
  - Nanoelectromechanical systems (NEMS)

Stacking of nanotubes by van der Waals forces with inter-wall separations ~ 0.34 nm

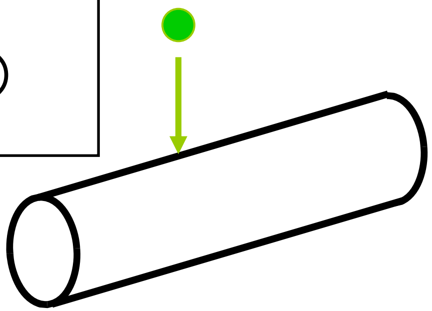
Multi-wall carbon nanotube (MWNT)



Ropes of SWNTs arranged in hexagonal superlattice



Ion irradiation under oblique incidence ☺



- Beam characteristics:
  - Heavy and light ions
  - Energies from ~ 100 eV to ~ 100 MeV
  - Strong dependence on irradiation dose
  - Beam diameter for local modifications (FIB)
- Effects on nanotubes:
  - Creation of local defects (~ 20 eV per atom)
  - Changing electrical conductance
  - Doping, functionalization
  - Inter-tube junctions (electrical & mechanical prop.)
  - Amorphization, welding
  - Stiffening, bending, buckling

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  (High, Medium and Low energies: Theory & simulation)
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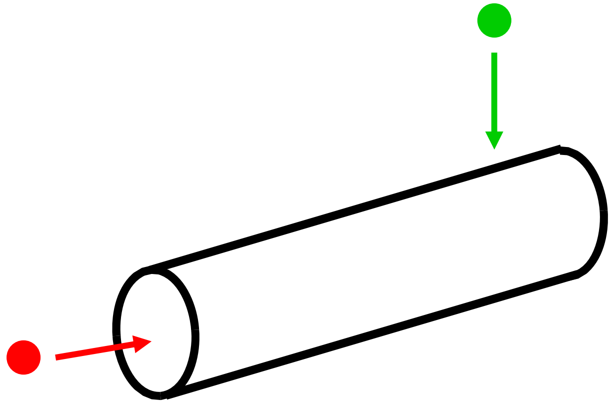
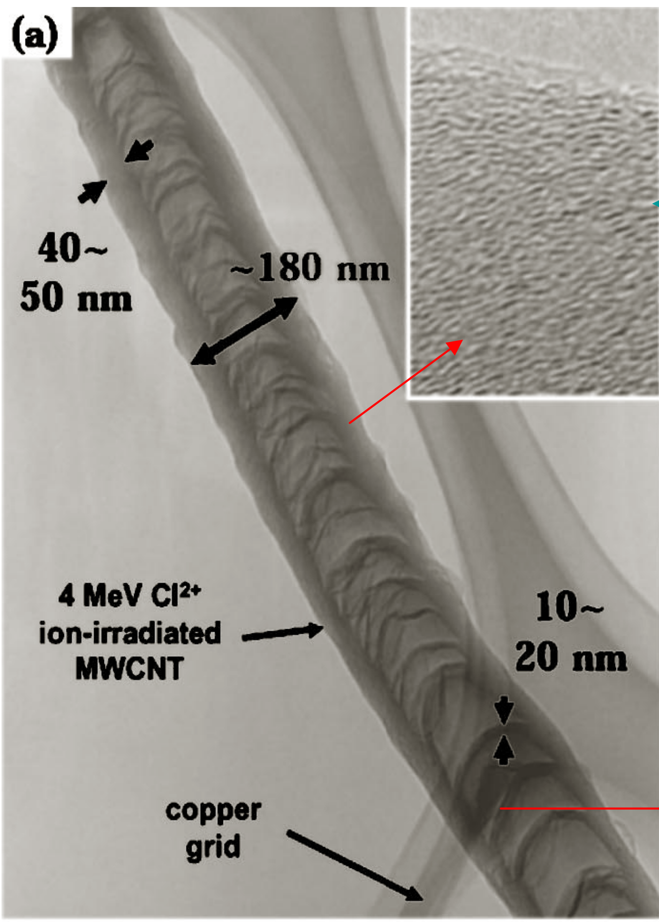


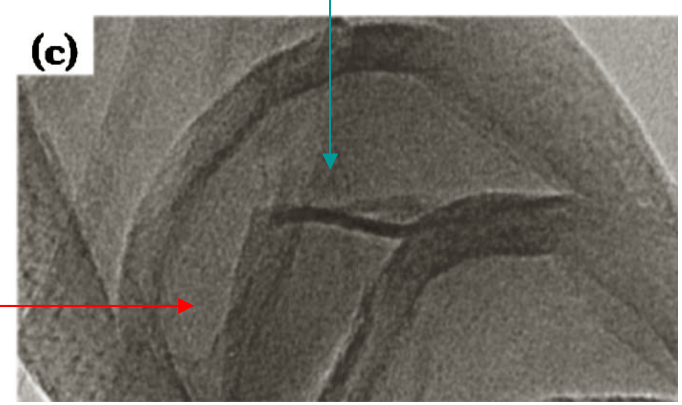
Morphological changes in multiwalled nanotubes by 4 MeV Cl^+ beams

H.M. Kim *et al., J. Appl. Phys.* 97 (2005) 26103



- ❑ Dilatation of diameter
- ❑ Amorphization of walls
- ❑ Bamboo compartments

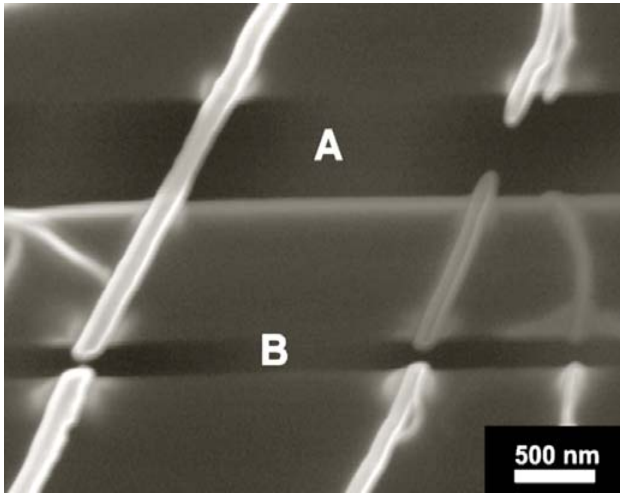
HRTEM images



Nanomachining nanotubes with 30 keV Ga^+ focused ion beams

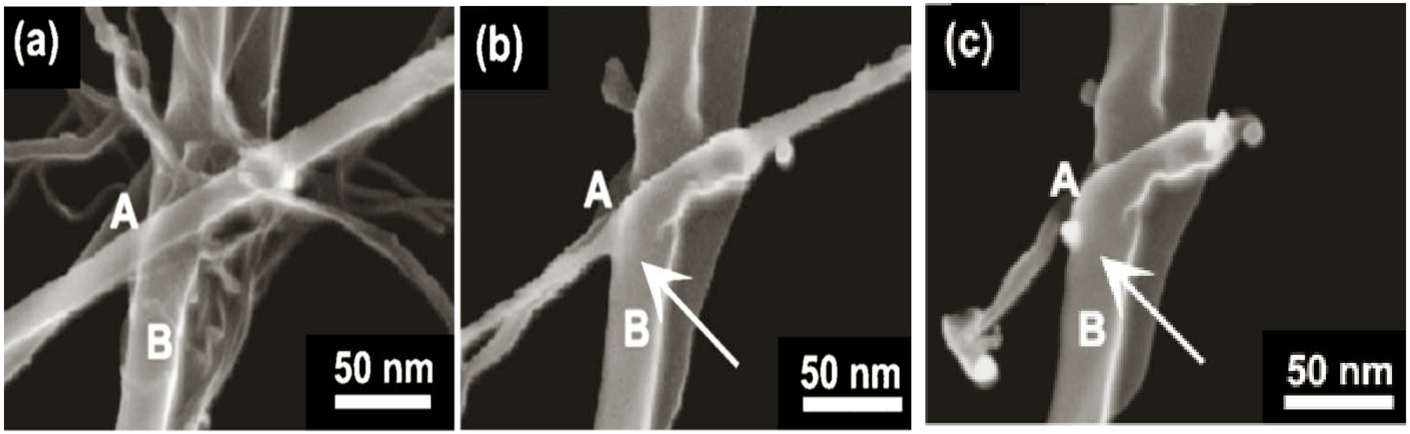
M.S. Raghuveer *et al.*, *Appl. Phys. Lett.* 84 (2004) 4484

Thinning and slicing by broad & narrow beam



Welding of crossed nanotubes and sputtering away of narrow nanotubes

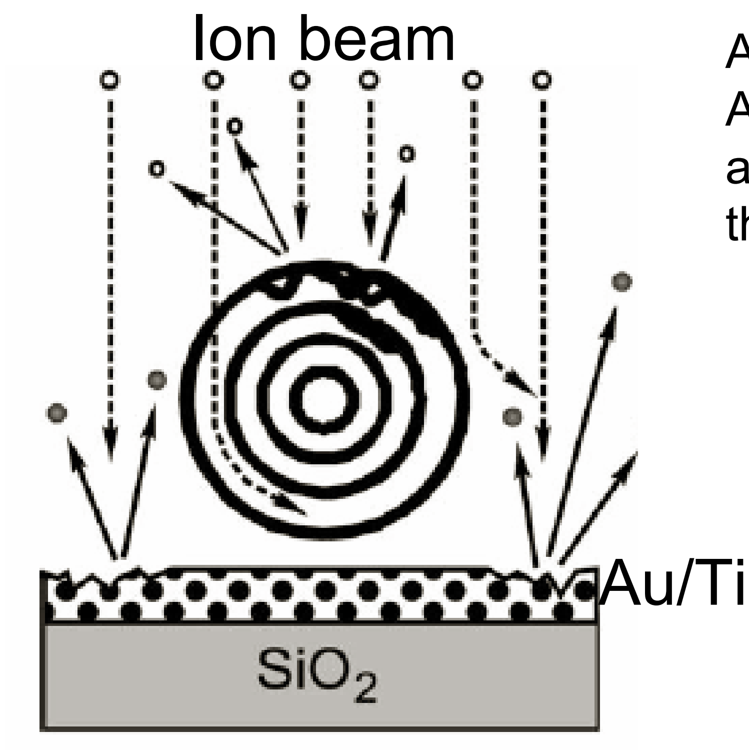
(a) before, (b) after low dose, (c) after high dose



SEM images

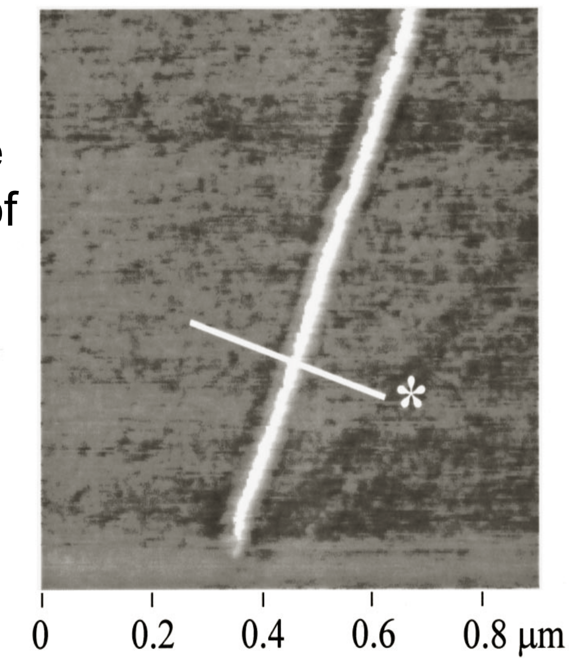
Etching metal nanowire with 300 eV Ar^+ beam using a nanotube as a mask

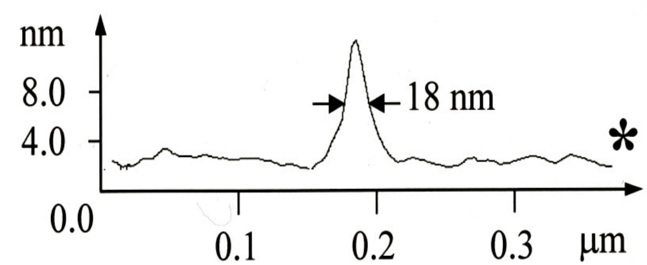
W.S. Yun *et al., J. Vac. Sci. Technol.* A 18 (2000) 1329



Au etch rate >> nanotube etch rate

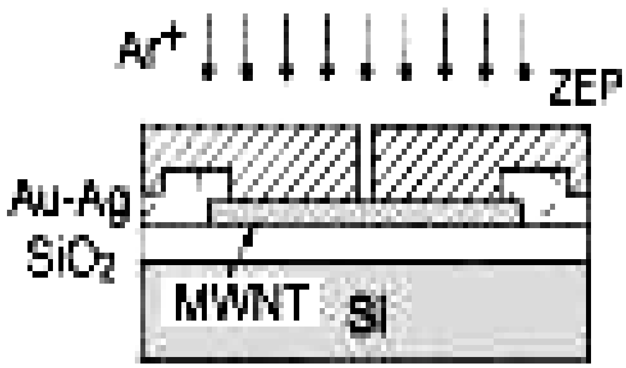
AFM image of Au/Ti nanowire after removal of the nanotube



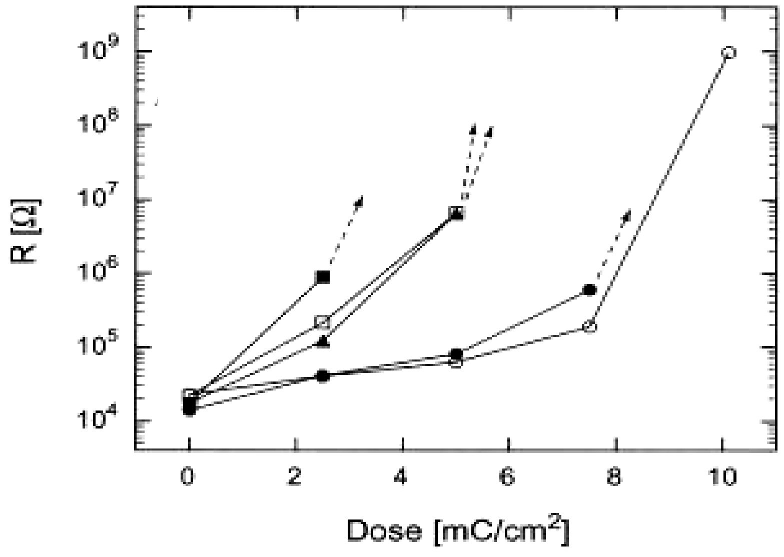


Tunnel barrier creation in a nanotube by 300 eV Ar^+ ion beam

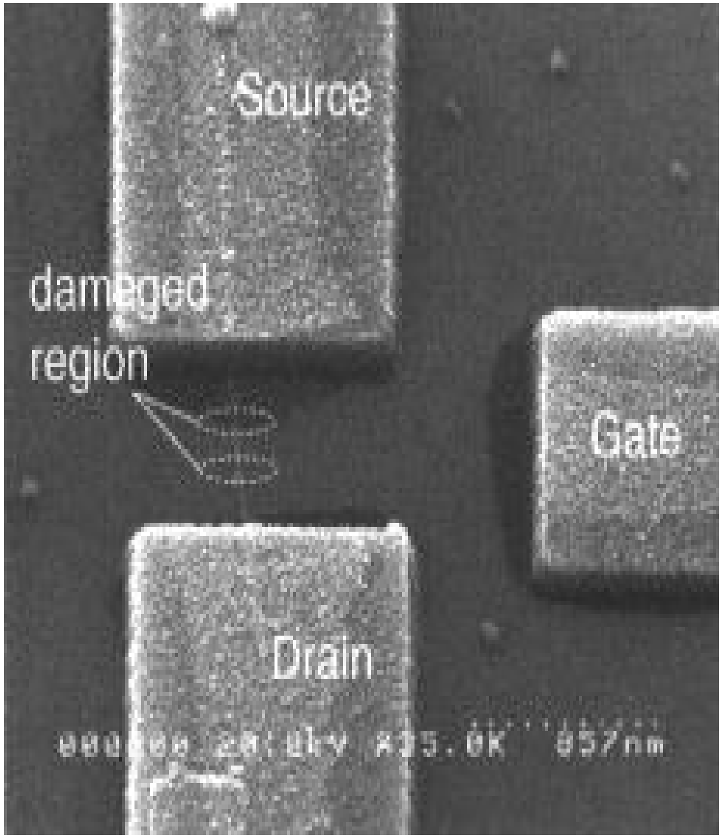
M. Suzuki *et al., Appl. Phys. Lett.* 81 (2002) 2273



Resistance vs dose



SEM image of quantum dot between double barriers



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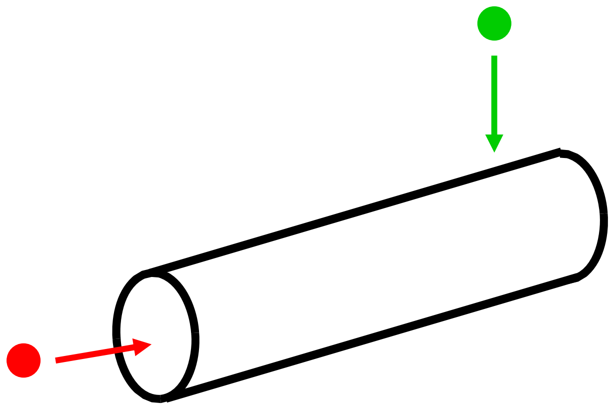
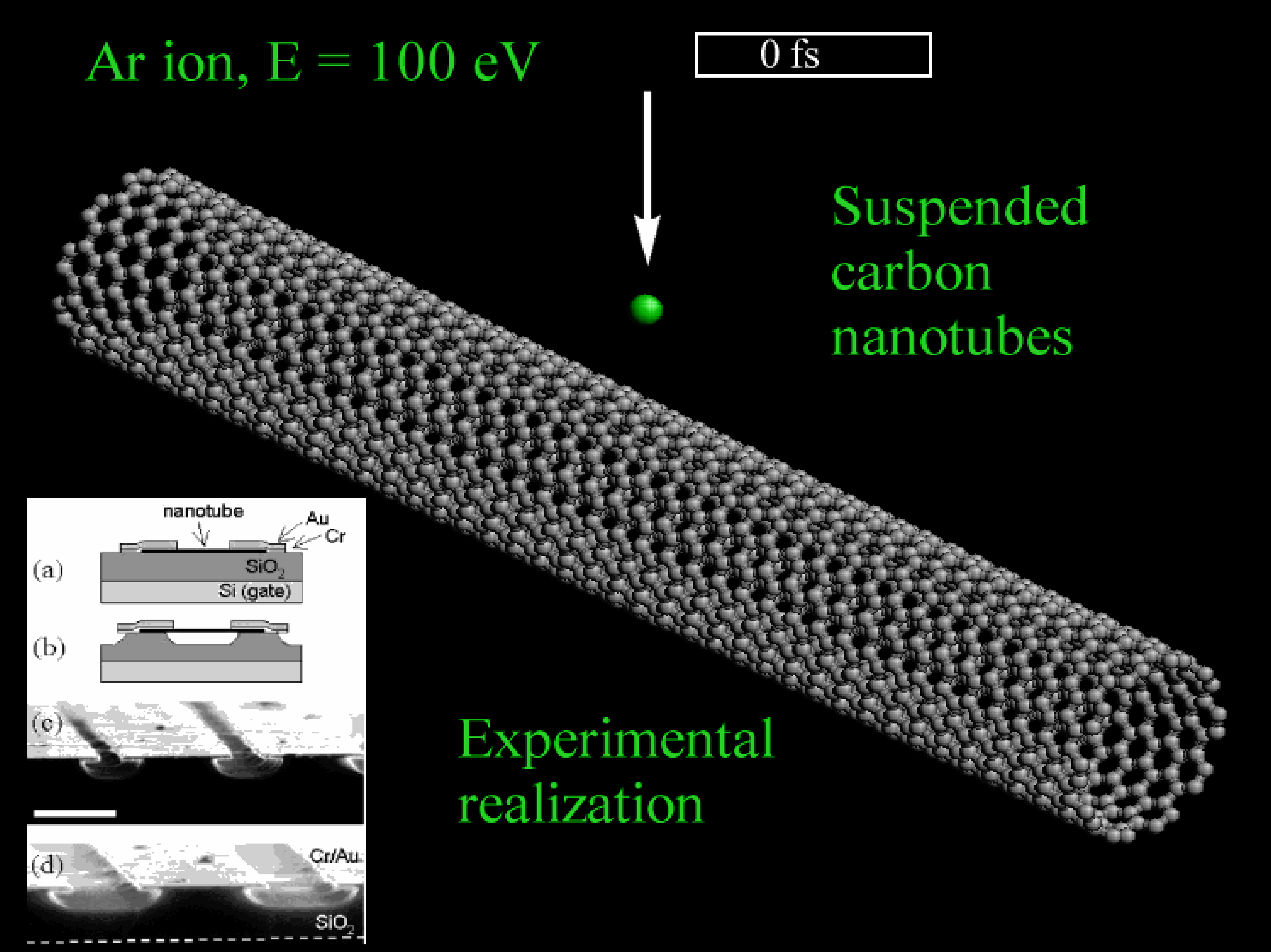
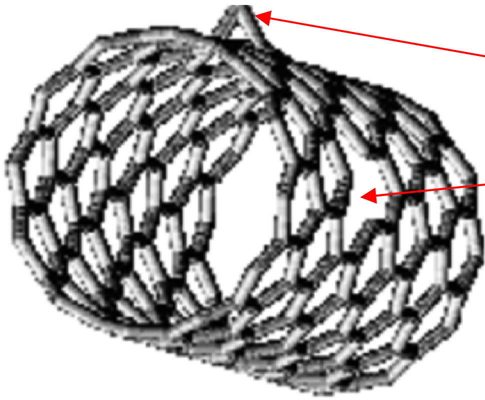



Ar ion, E = 100 eV
0 fs
Suspended carbon nanotubes
Experimental realization
nanotube
Au
Cr
(a)
SiO2
Si (gate)
(b)
(c)
(d)
Cr/Au
SiO2

MD simulations of ion irradiation-induced defects under **oblique** incidence

A.V. Krashenninkov *et al., Nucl. Instr. Meth.* B 216 (2004) 355

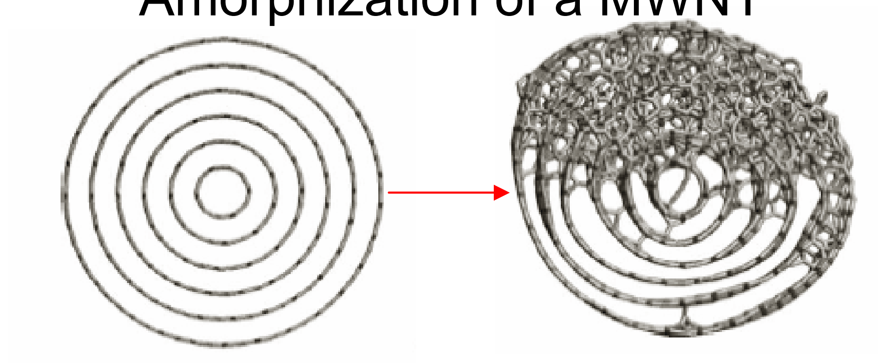
Single defect: threshold ~ 20 eV



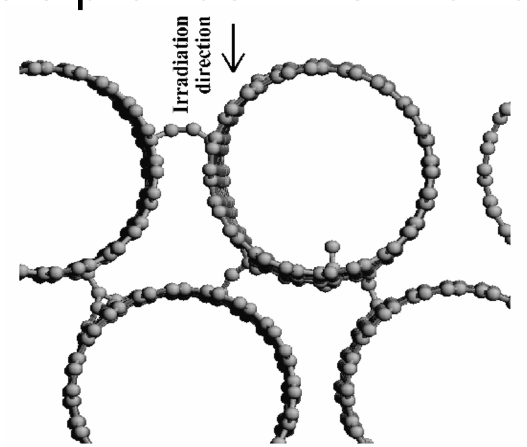
Adatom

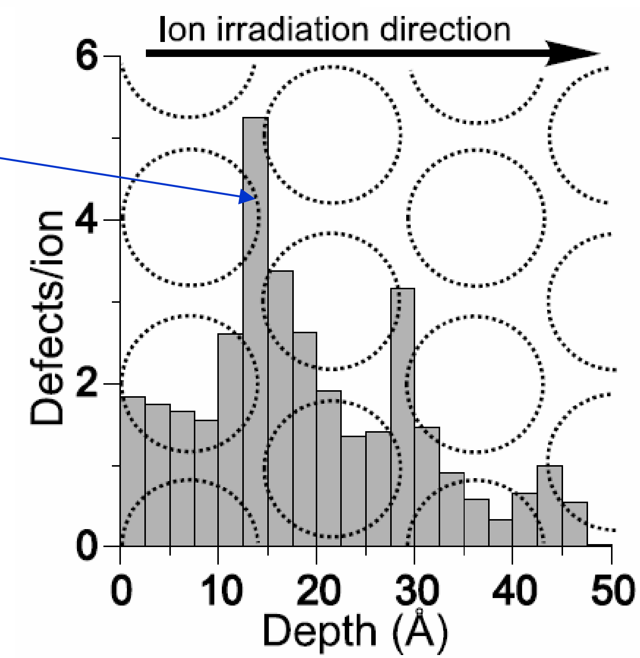
Vacancy

Amorphization of a MWNT



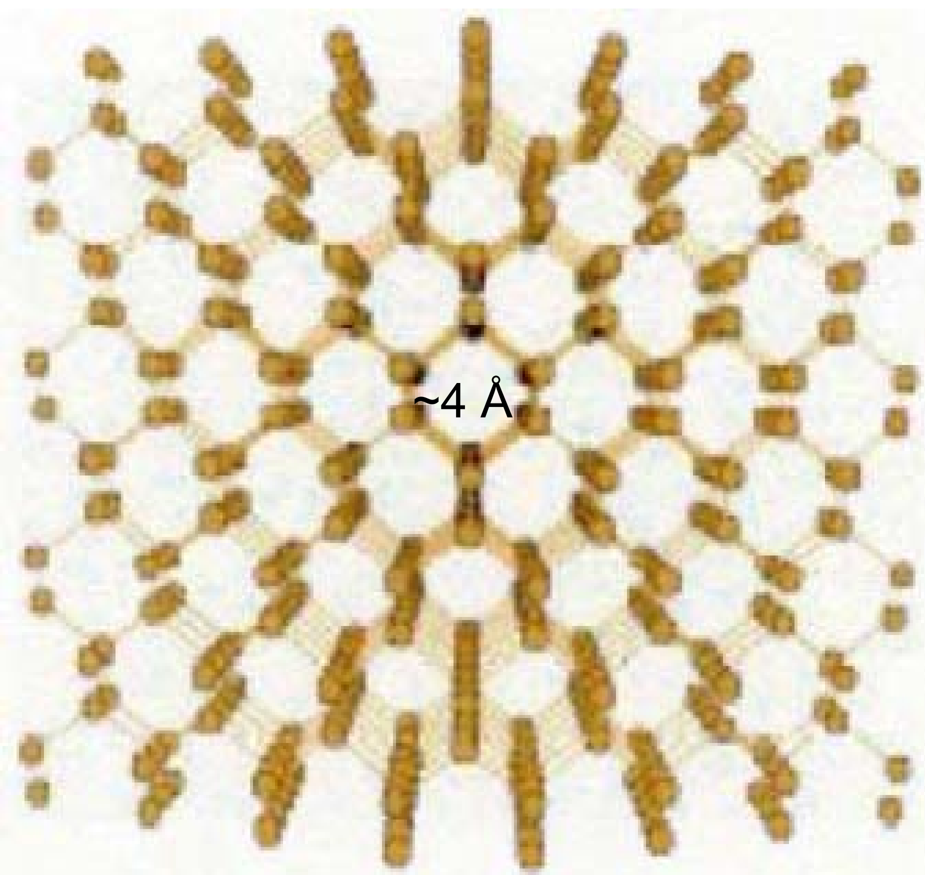
Defects provide links in a rope



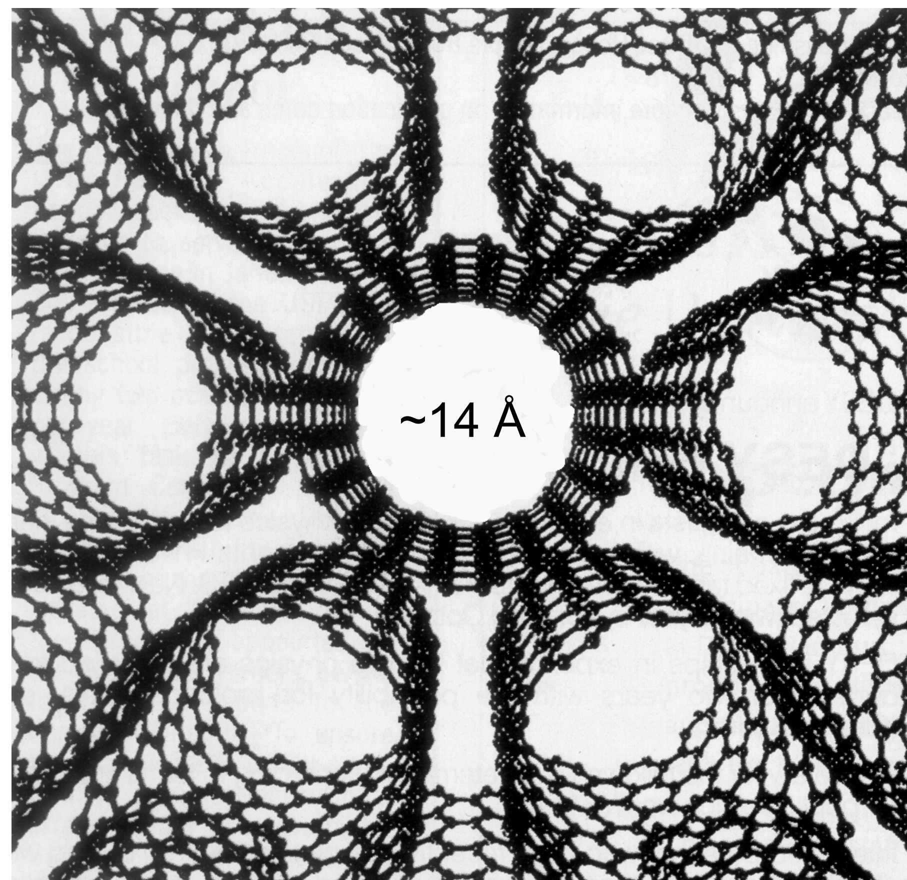


Is **ion channeling** through carbon nanotubes possible in analogy to channeling through crystals?

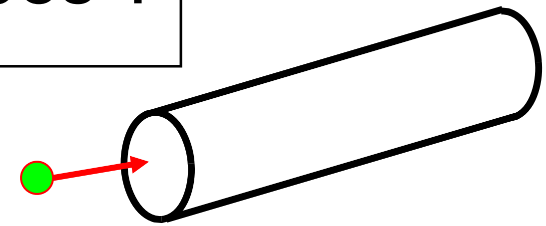
Front view of (110) channels in Si crystal



Entrance to a rope of (10,10) SWNTs



Ion channeling through carbon nanotubes ?



- Possible advantages over crystals
  - Wider channels: weaker de-channeling
  - Broader beams (using nanotube ropes)
  - Wider acceptance angles (< 0.1 rad)
  - Lower minimum ion energies (< 100 eV)
  - 3-D control of beam bending over greater lengths
- Possible applications
  - Probing the structure of nanotubes
  - Creating and transporting highly focused nano-beams
  - Nano-implantation in electronics, biology & medicine
  - Beam extraction, steering & collimation at accelerators
  - Manipulate plasma deposition, molecule transport

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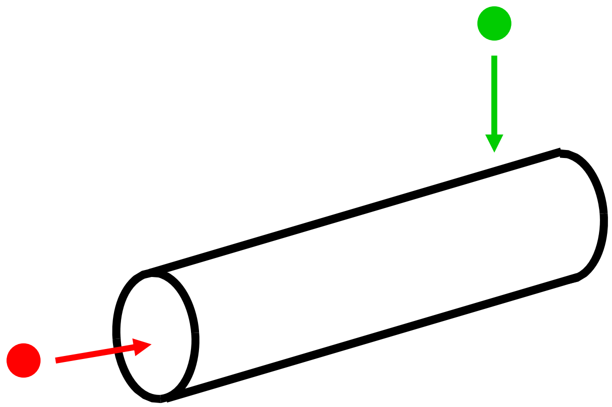
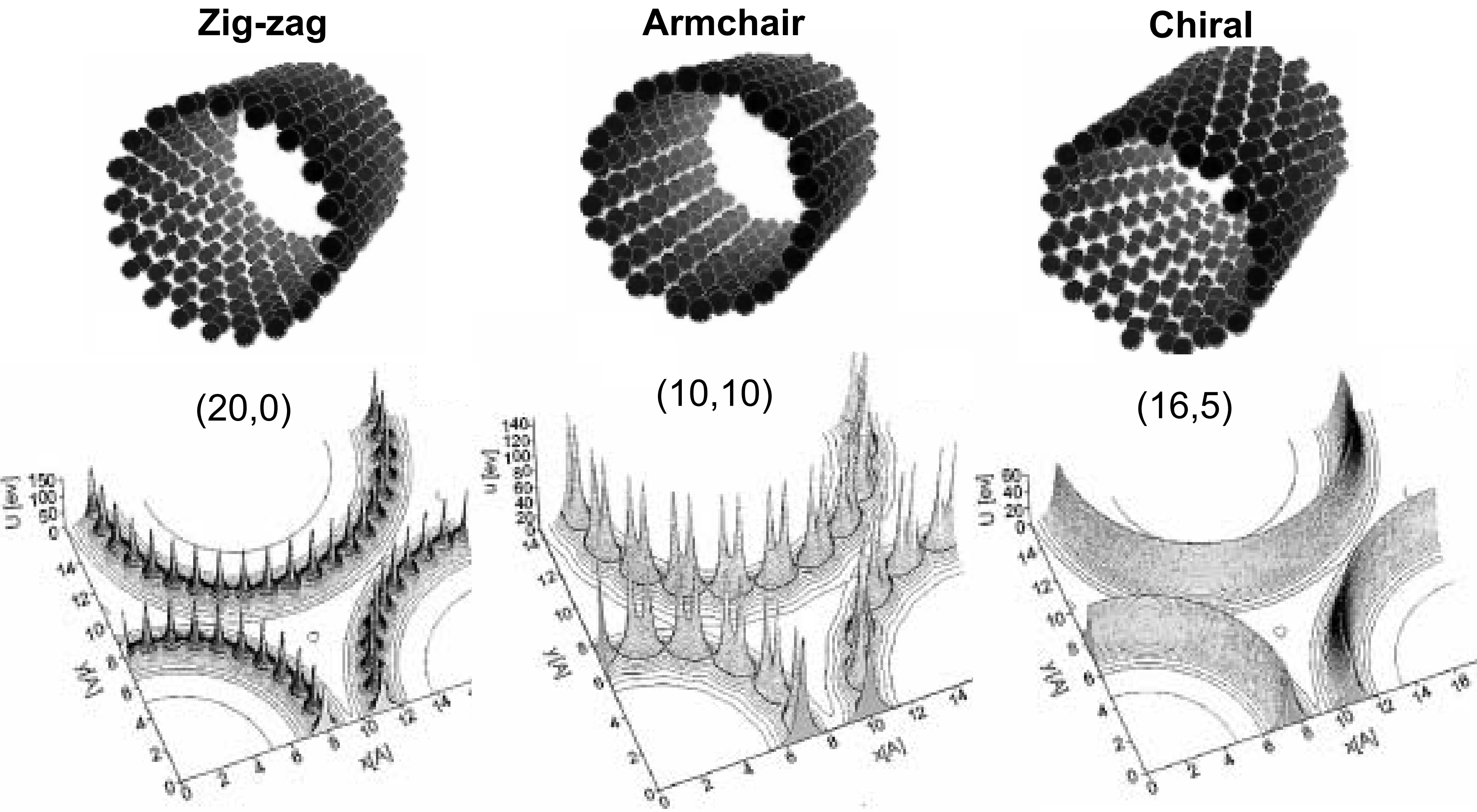


Continuum approximations for the repulsive atomic potential in SWNTs

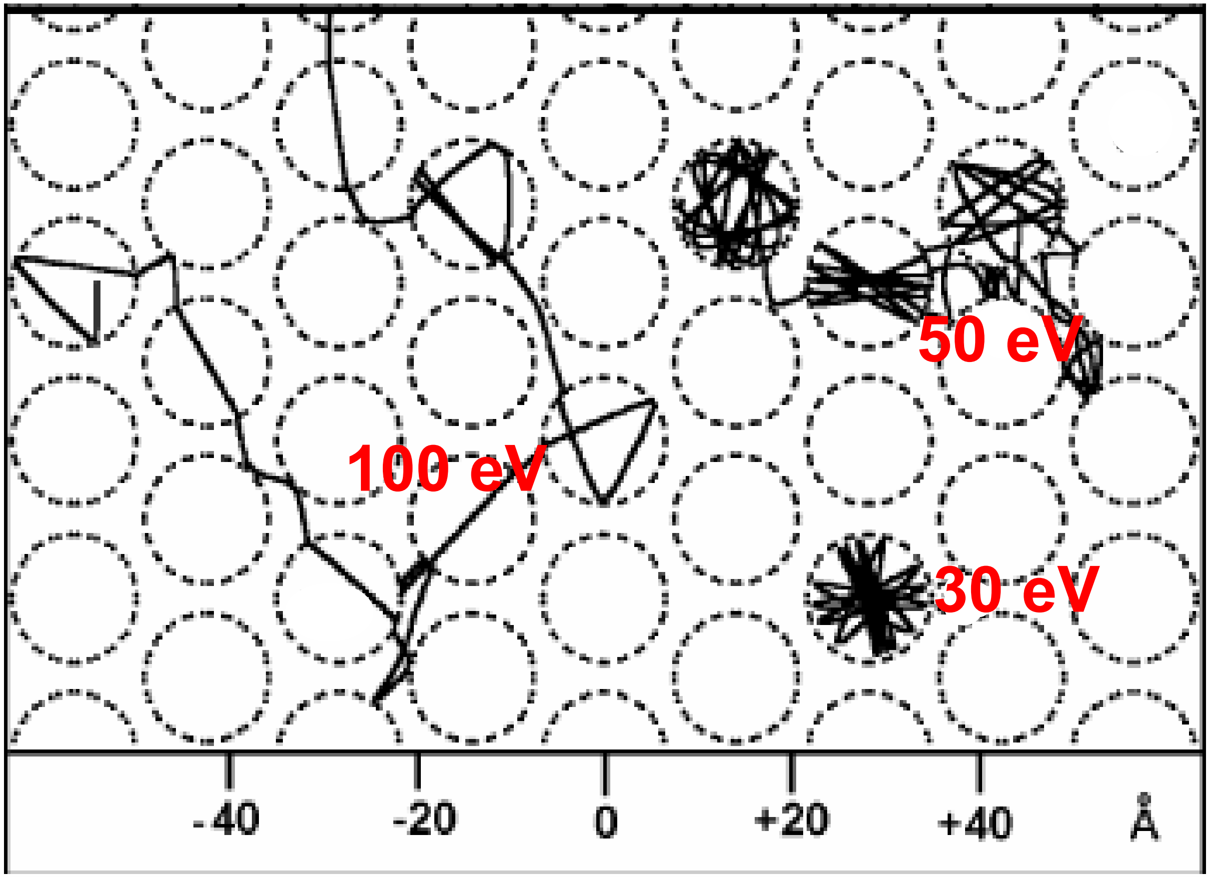
X. Artru *et al.*, *Phys. Reports* 412 (2005) 89



Ion channelling through rope of straight SWNTs(10,10)

A.A. Greenenko and N.F. Shulga, *Nucl. Instr. Meth.* B 205 (2003) 767

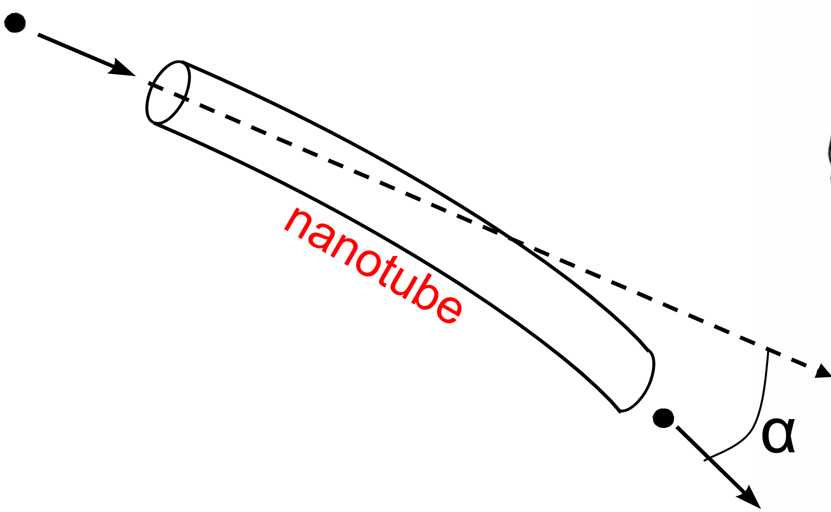
Ion trajectories with beam momentum 10 GeV/c
and perpendicular energies 30, 50, and 100 eV



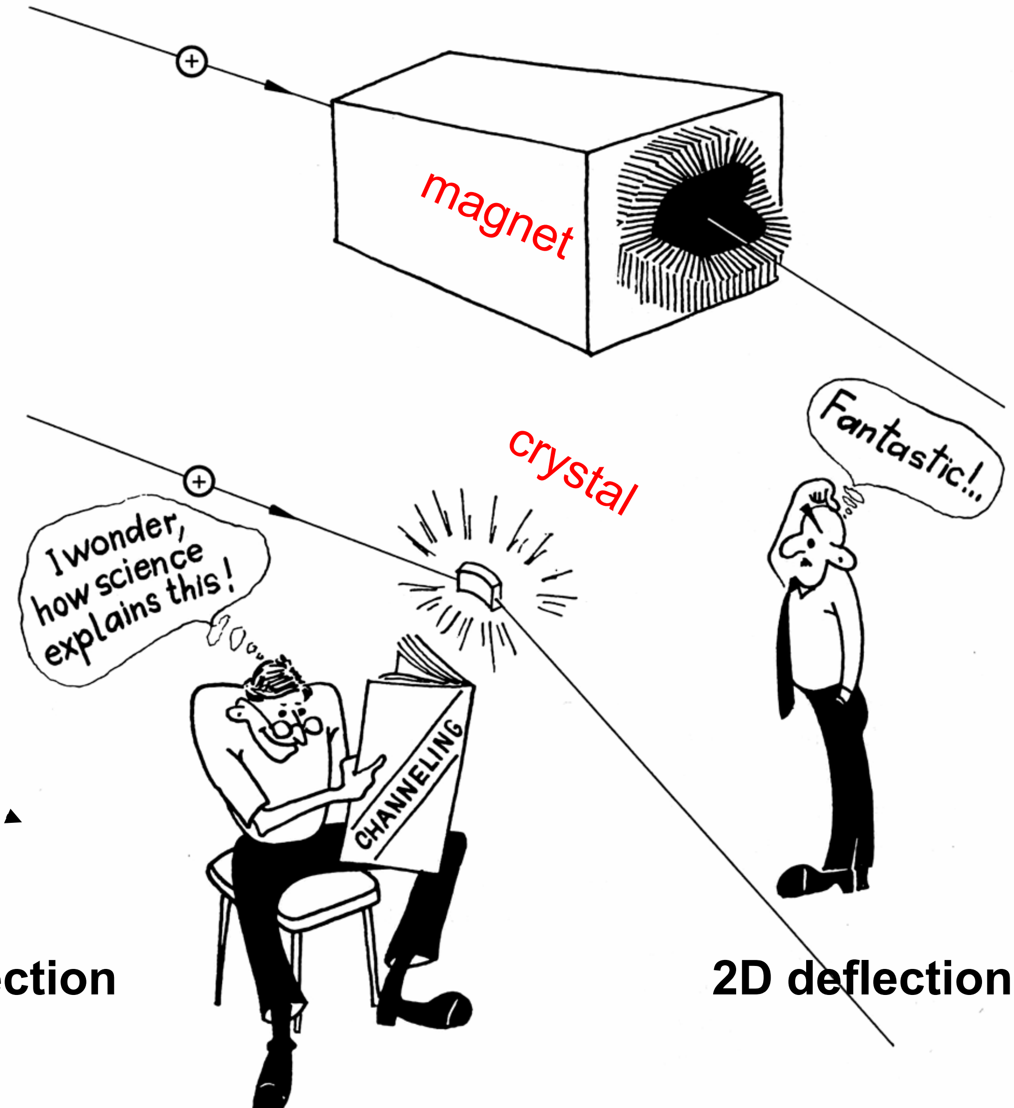
Beam deflection at particle accelerators by bent crystal

V.M. Biryukov *et al., Crystal Channeling and Its Applications at High-energy Accelerators* (1997)

How effective are bent nanotubes compared to bent crystals ?



3D deflection



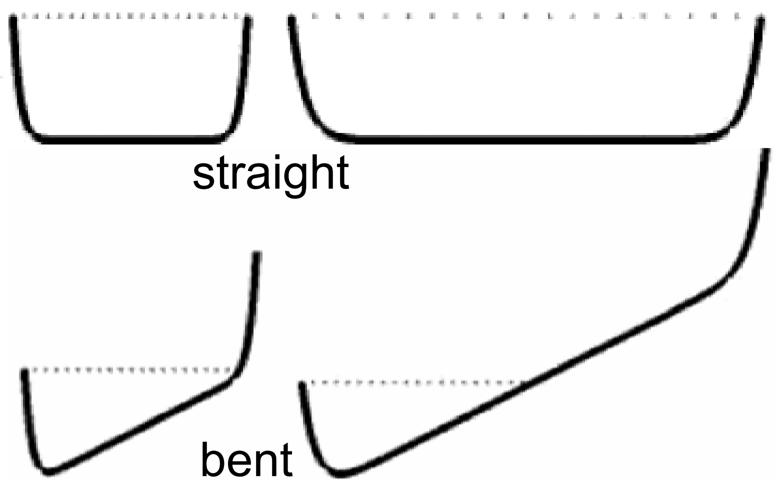
2D deflection

Optimal nanotube diameter for GeV proton beam steering in bent chiral SWNTs

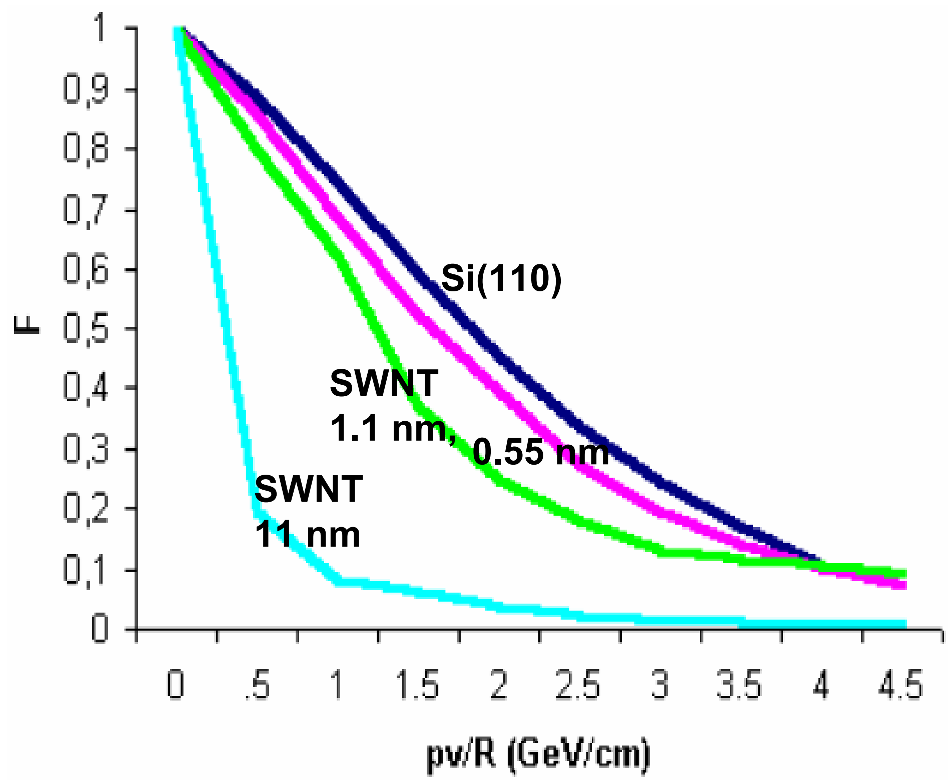
V.M. Biryukov and S. Bellucci, *Phys. Lett.* B 542 (2002) 111

Effective potentials inside narrow and wide SWNTs

$$U_{eff}(x) = U(x) + \frac{pv}{R}x$$



Fractions of channelled protons vs nanotube curvature ***pv*** / ***R*** for: Si(110) crystal channel and three SWNTs with different diameters



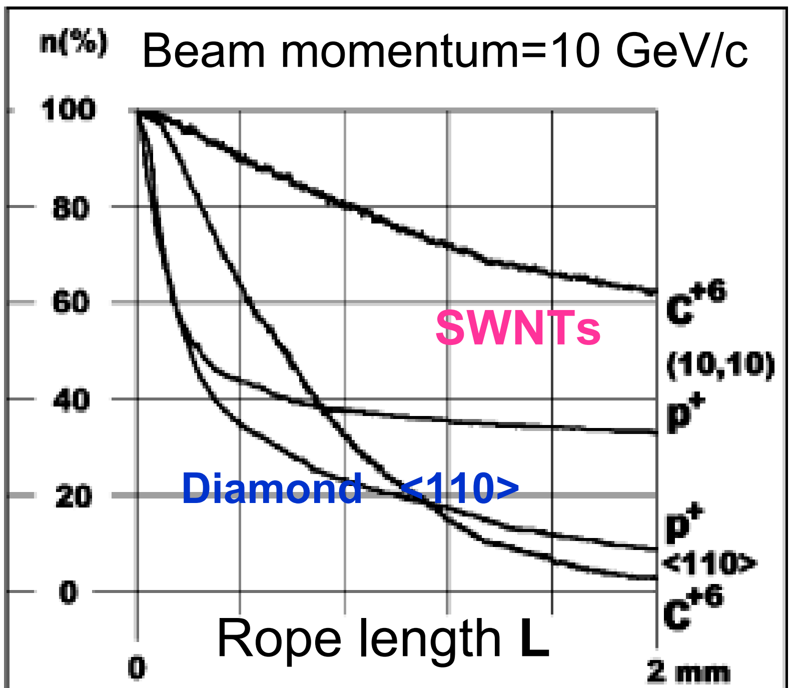
Conclusion: wide SWNTs are not more effective for beam steering

De-channelling of ion beam due to:

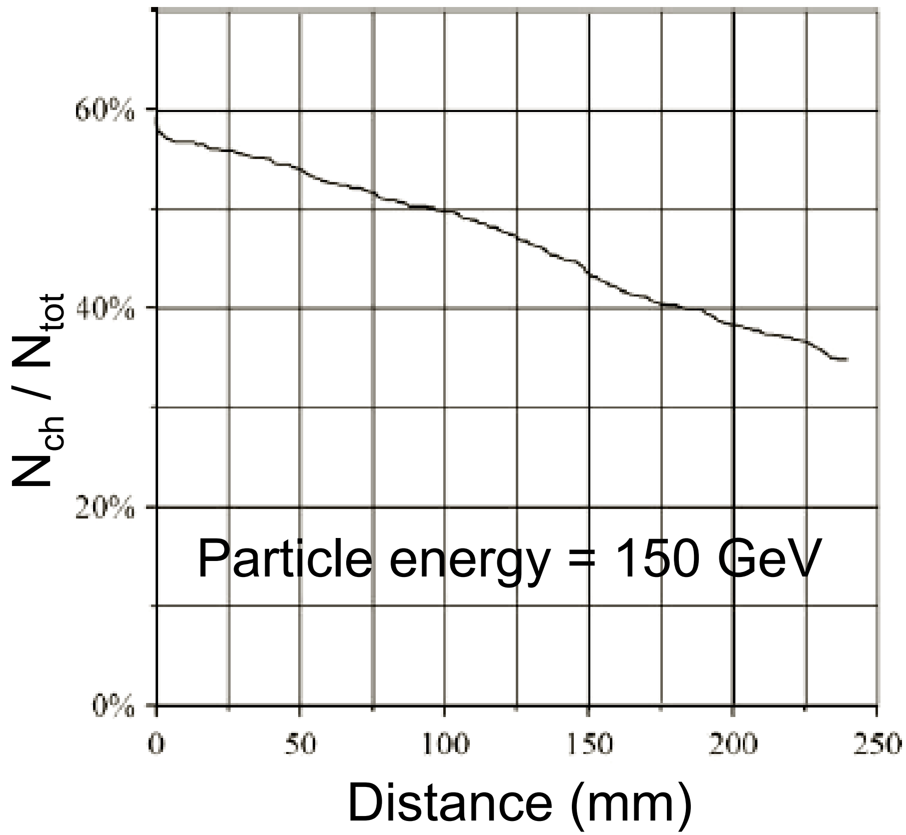
Bending of a rope of SWNTs(10,10)	Incoherent scattering in a SWNT(11,9)

A.A. Greenenko and N.F. Shulga, *Nucl. Instr. Meth.* B 205 (2003) 767

N.K. Zhevago and V.I. Glebov, *Phys. Lett.* A 310 (2003) 301



Curvature radius R = 20 cm
Bending angle α < 10 mrad



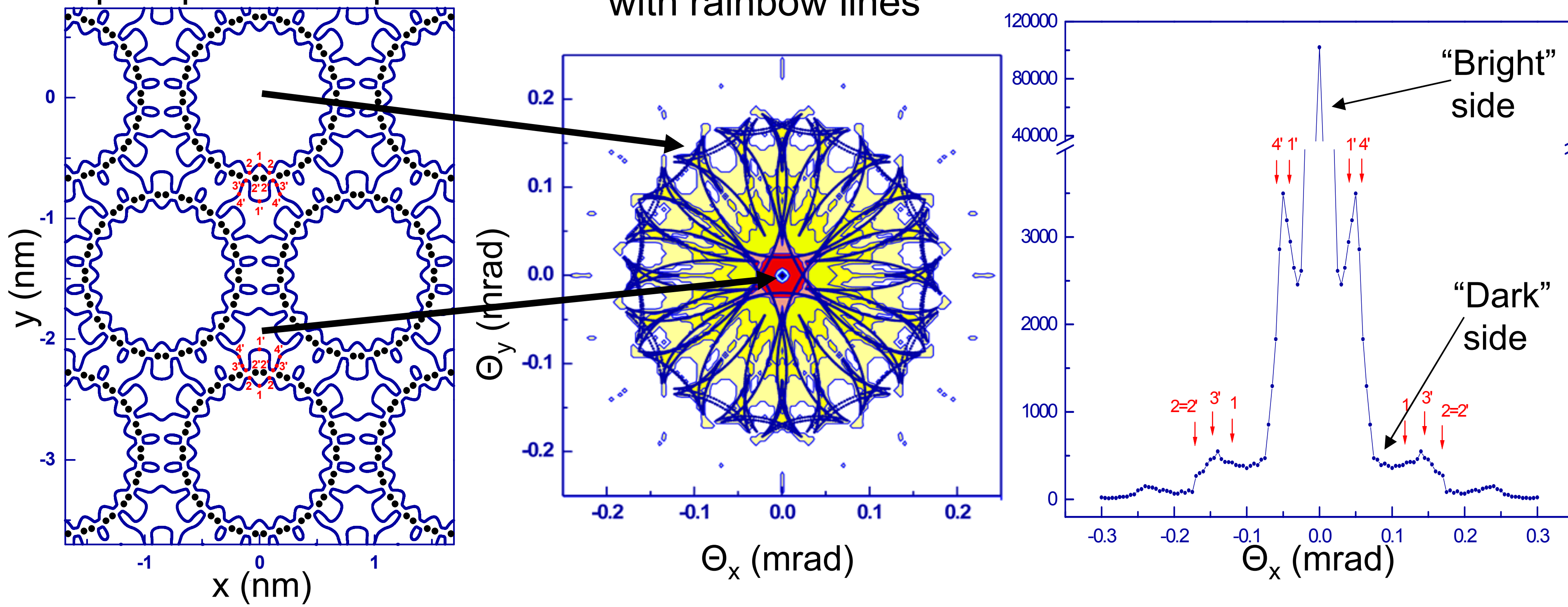
Rainbow effect after 1GeV proton channelling through a short rope of SWNTs(10,10)

S. Petrovic *et al.*, *Eur. Phys. J.* B 44 (2005) 41

Rainbow lines in the impact parameter plane

Angular distribution with rainbow lines

Yield of protons along Θ_x line

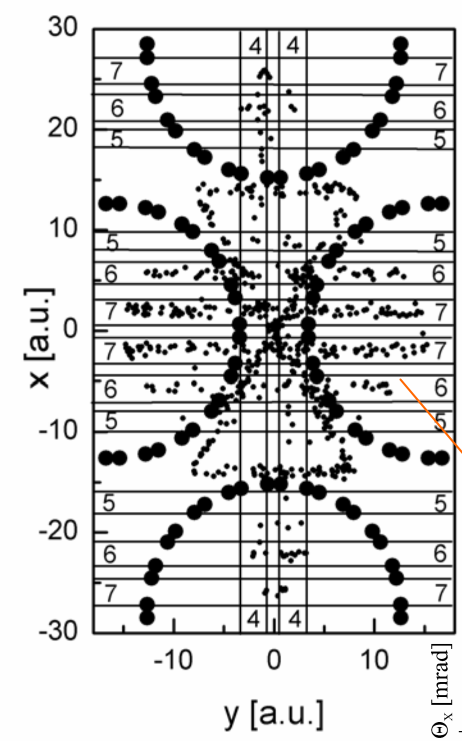


Rope length 1 μm

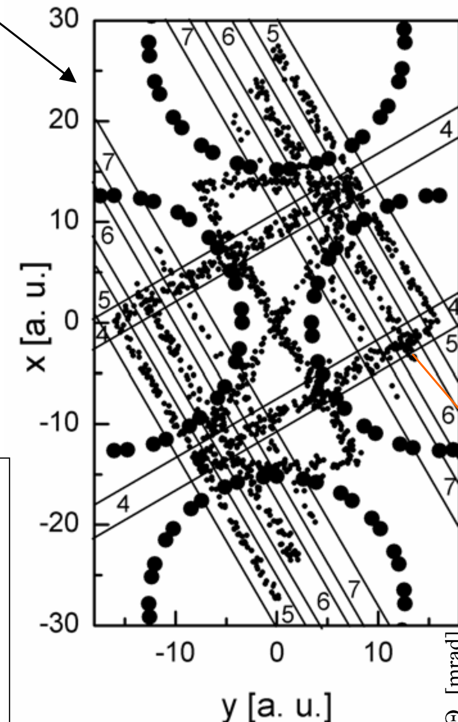
Star effect in channeling of divergent 1GeV proton beam through long ropes of SWNTs(10,10)

D. Borka *et al., Nucl. Instr. Meth* A 354 (2006) 457

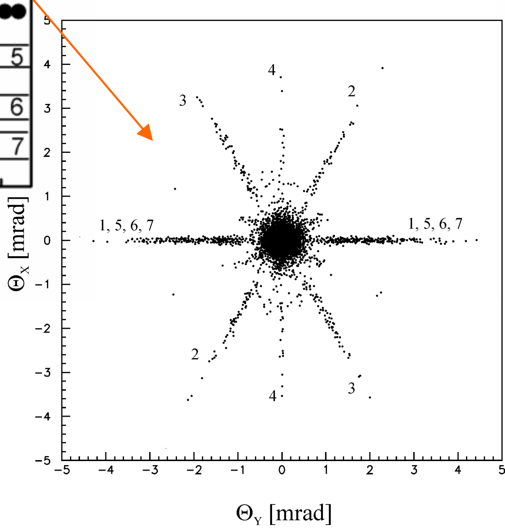
Proton impact parameters

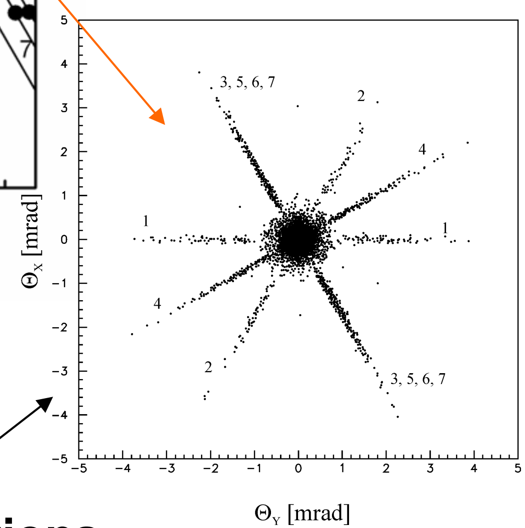


Relative orientation of nanotubes = π/60



Rope length 10 μm





Angular distributions

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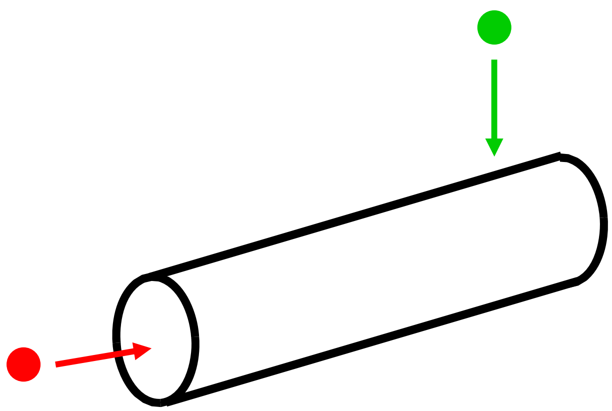
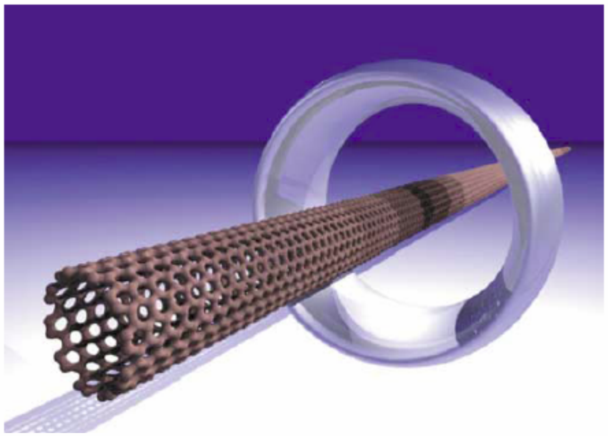
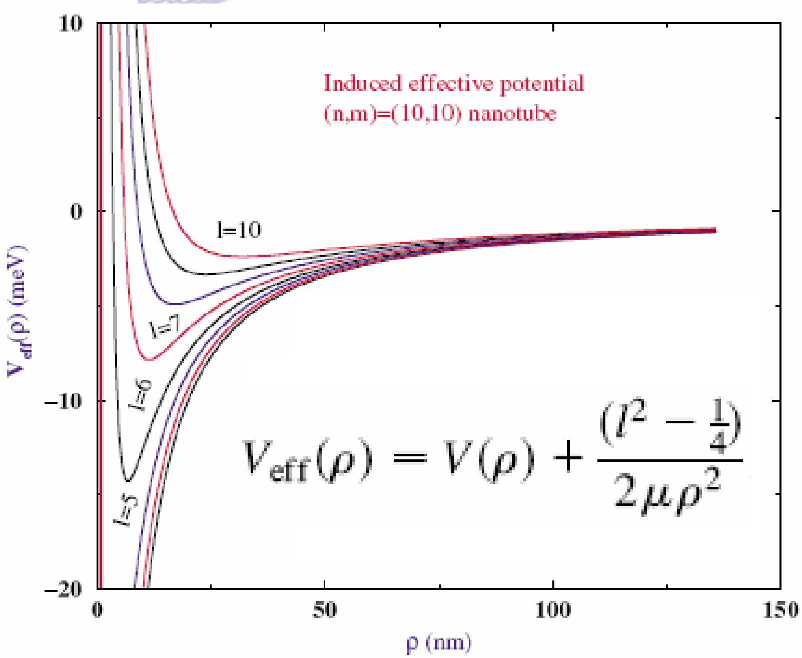


Electron image states around carbon nanotubes

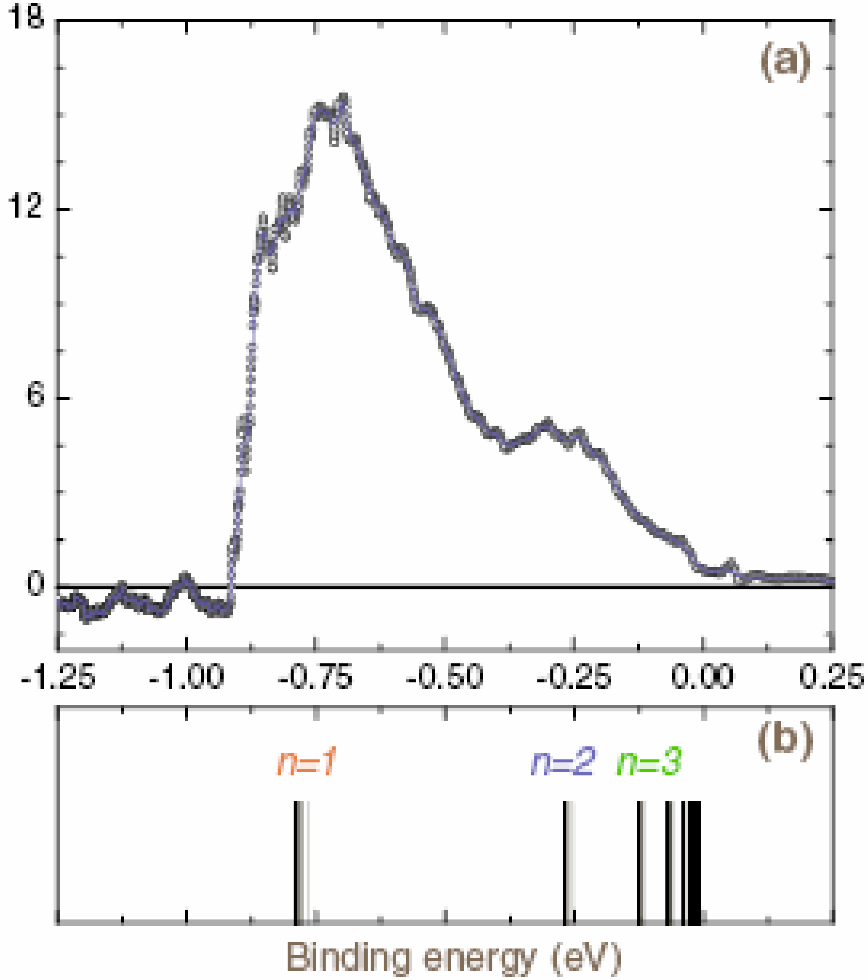
Theoretical prediction: B.E. Granger *et al.*, *Phys. Rev. Lett.* 89 (2002) 135506

Experimental confirmation: M. Zamkov *et al.*, *Phys. Rev. Lett.* 93 (2004) 156803





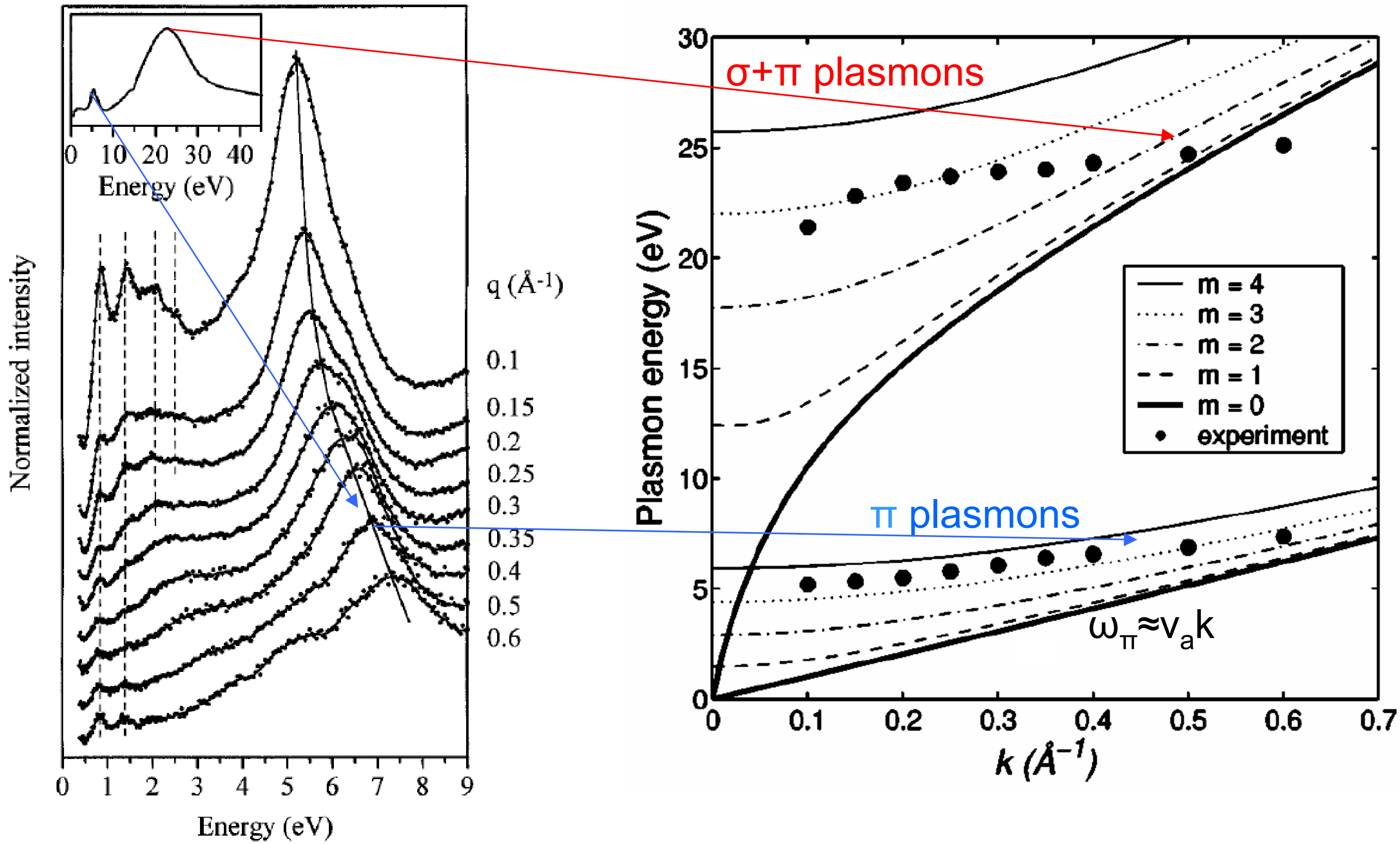
Photoelectron signal from image state



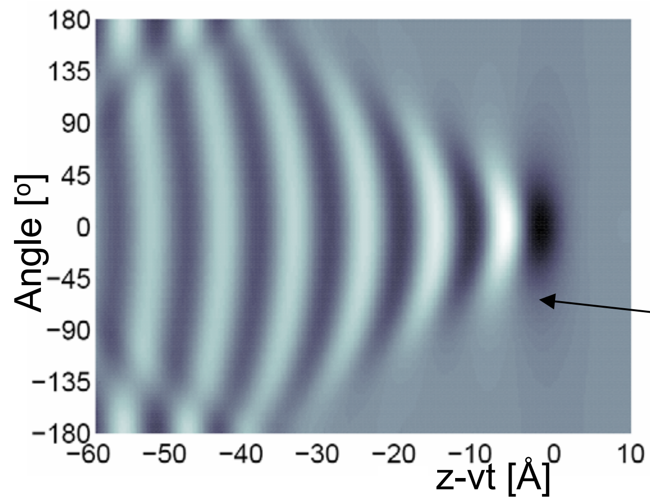
Plasmon spectra: σ and π electrons on SWNT

EELS experiment: T. Pichler *et al.*, *Phys. Rev. Lett.* 80 (1998) 4729

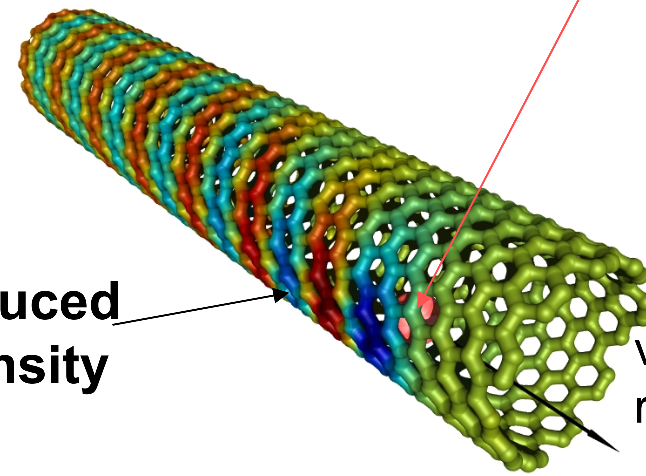
2D hydrodynamic model: Mowbray *et al.*, *Phys. Rev.* B 70 (2004) 195418



Dynamic polarization of electrons on SWNT by proton



Wake in induced electron density



v = 3 a.u.
$r_0 = a / 2$

Stopping power

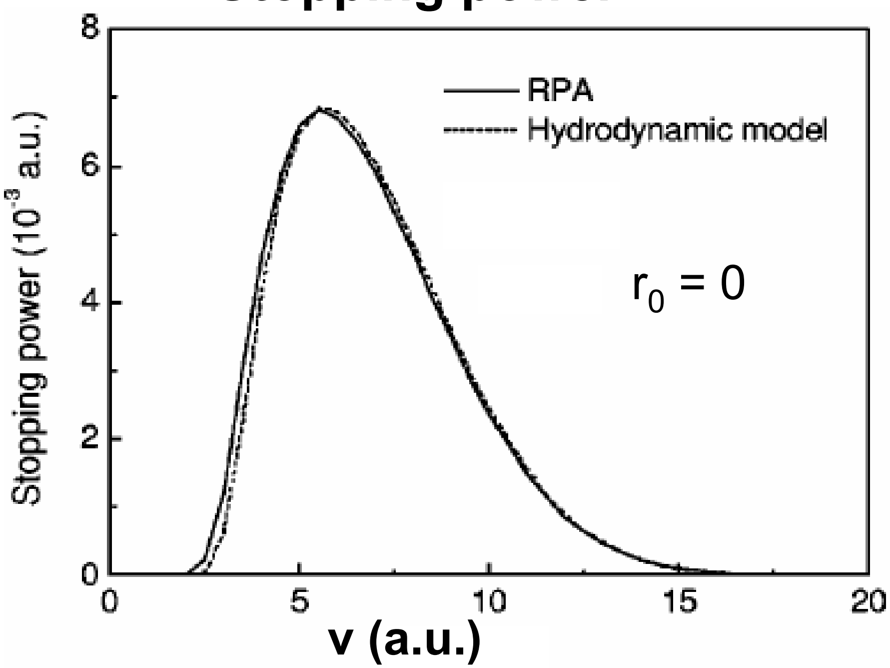


Image potential

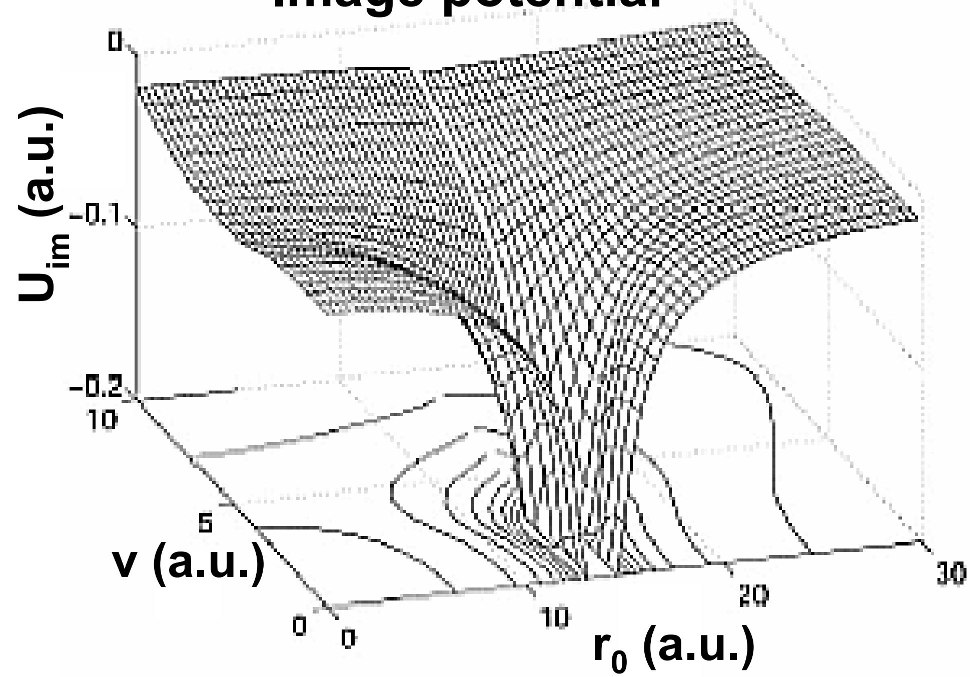
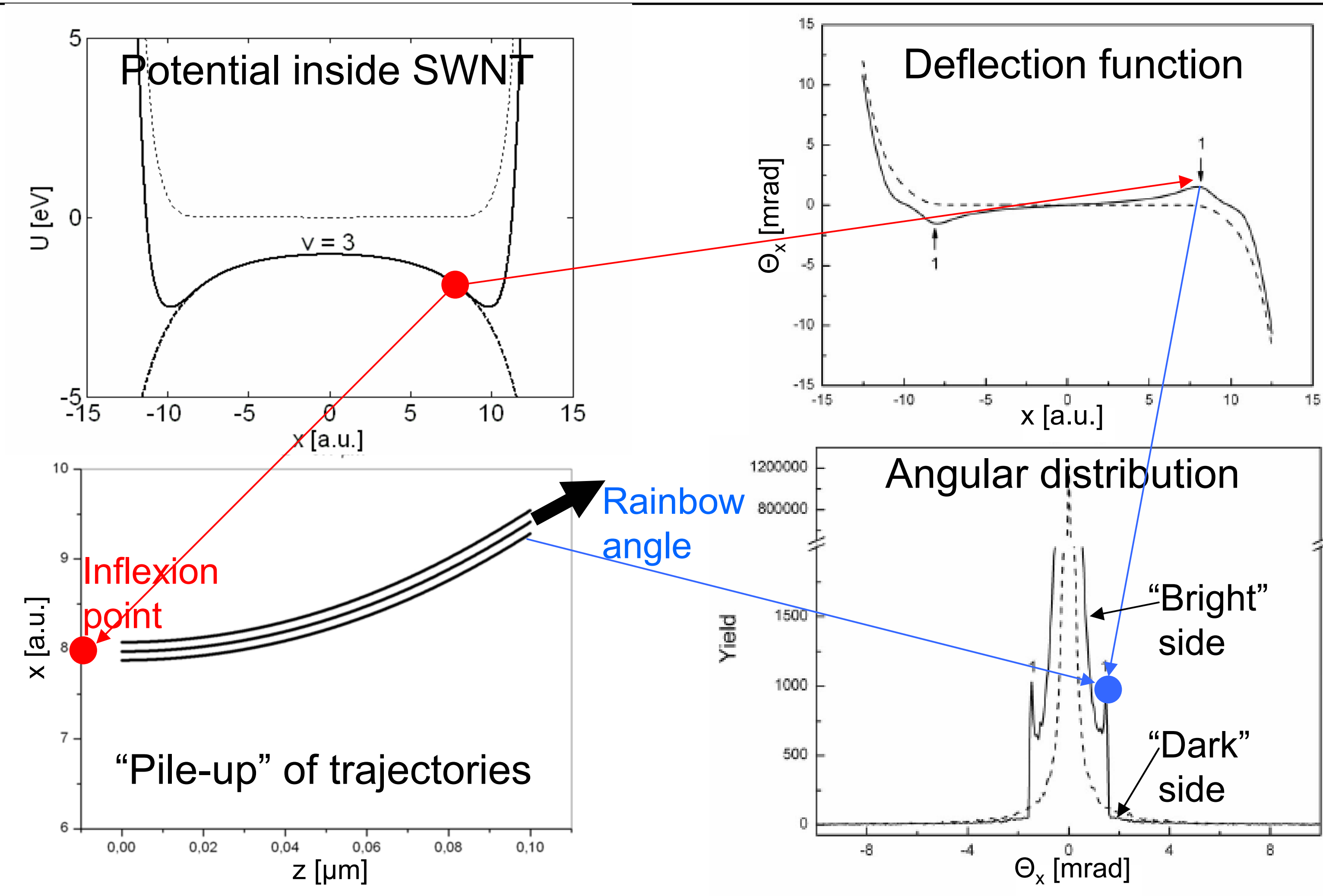


Image-induced **rainbow effect** for proton channelling in short SWNT(11,9)

D. Borka *et al.*, *Phys. Rev.* A 73 (2006) 62902

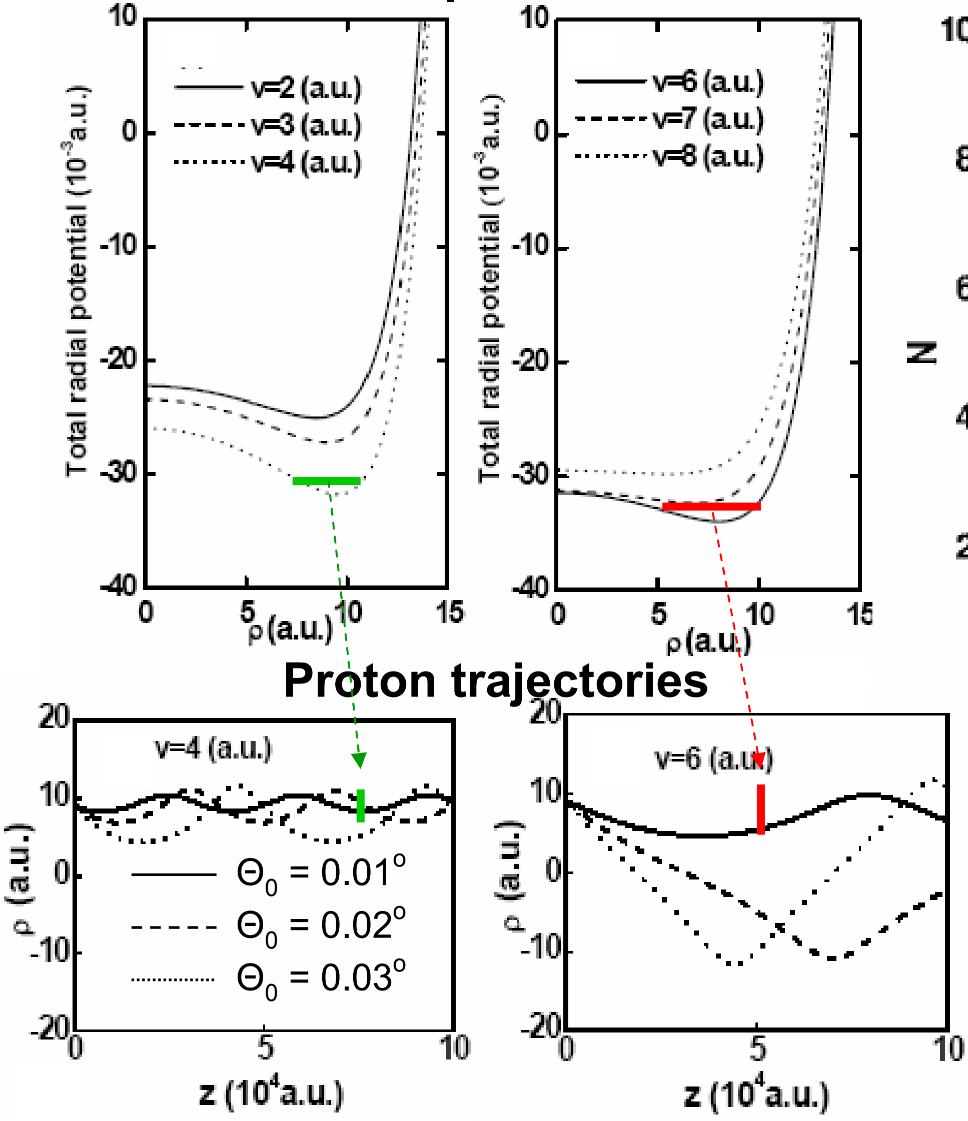


Nanotube length = 0.1 μm, proton speed = 3 a.u.

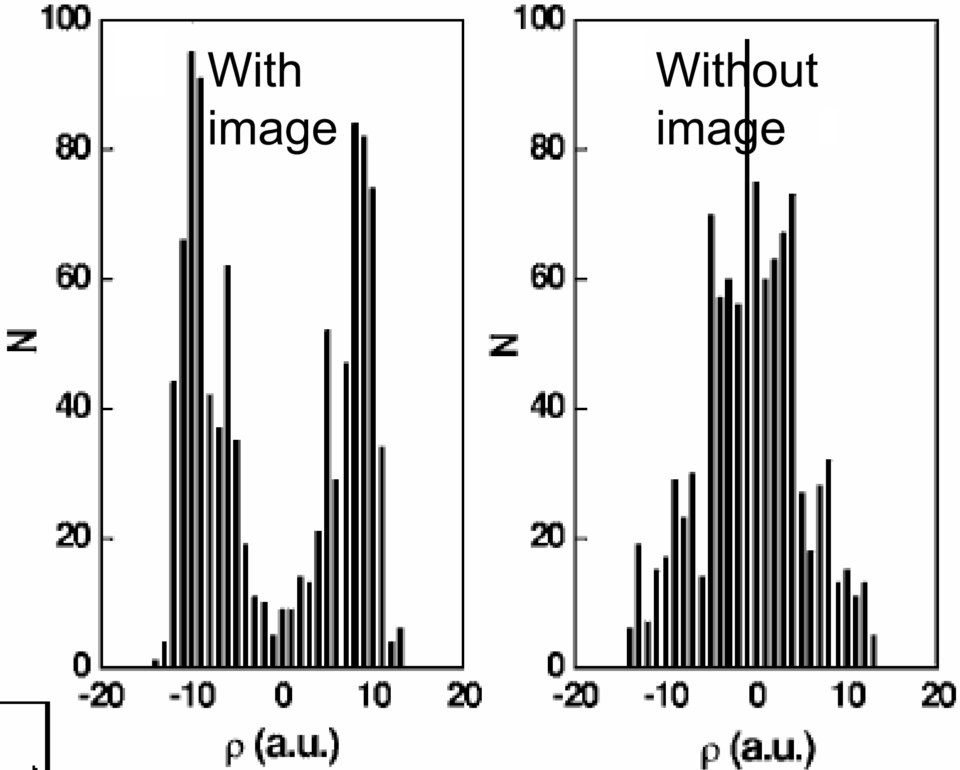
Image-induced **hollow beam** in long chiral SWNT

D.P. Zhou *et al.*, *Phys. Rev.* A 72 (2005) 23202

Total potential



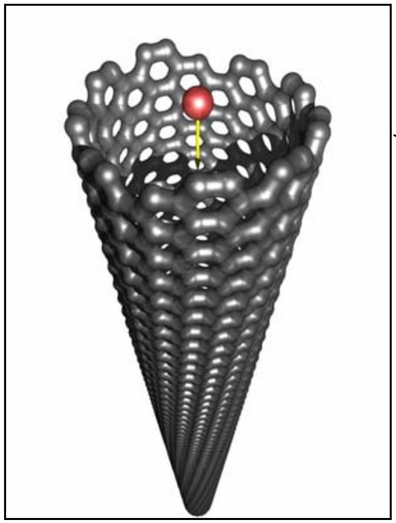
Radial distributions of proton flux

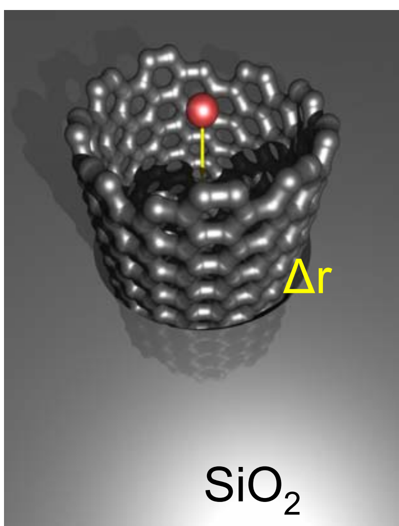


Nanotube length = 5.3 μm,
proton speed = 4 a.u.,
incident angle = 0°

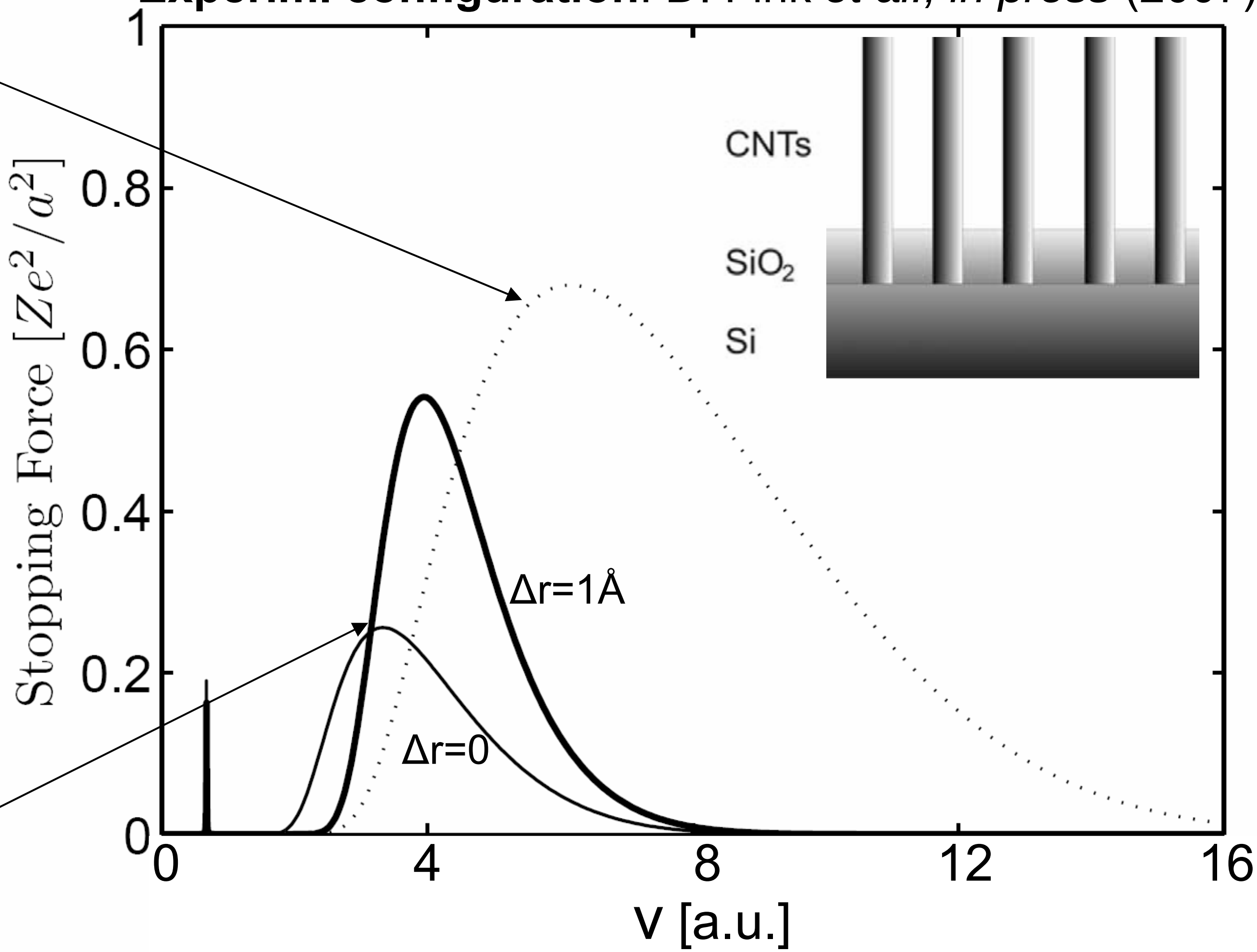
Effects of dielectric media on proton stopping: SWNT grown in SiO_2 channel

D.J. Mowbray *et al., Phys. Rev.* B 74 (2006) 195435





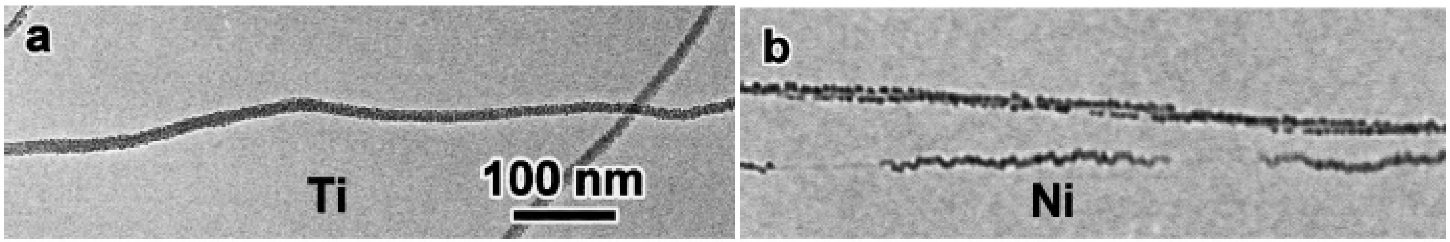
Experim. configuration: D. Fink *et al., in press* (2007)

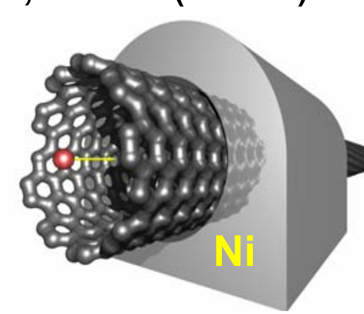


Dynamic polarization of SWNT coated by metal

D.J. Mowbray *et al.*, *Phys. Rev.* B 74 (2006) 195435

Experim. configuration: TEM images of a=5 nm SWNT: Zhang *et al.*, *CPL* (2000)





Stopping power

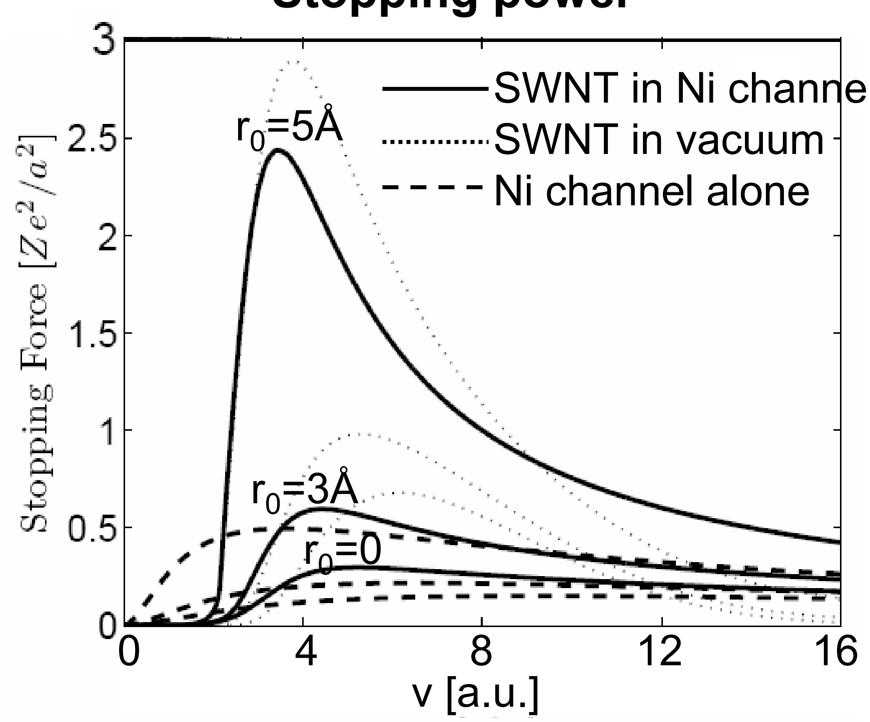
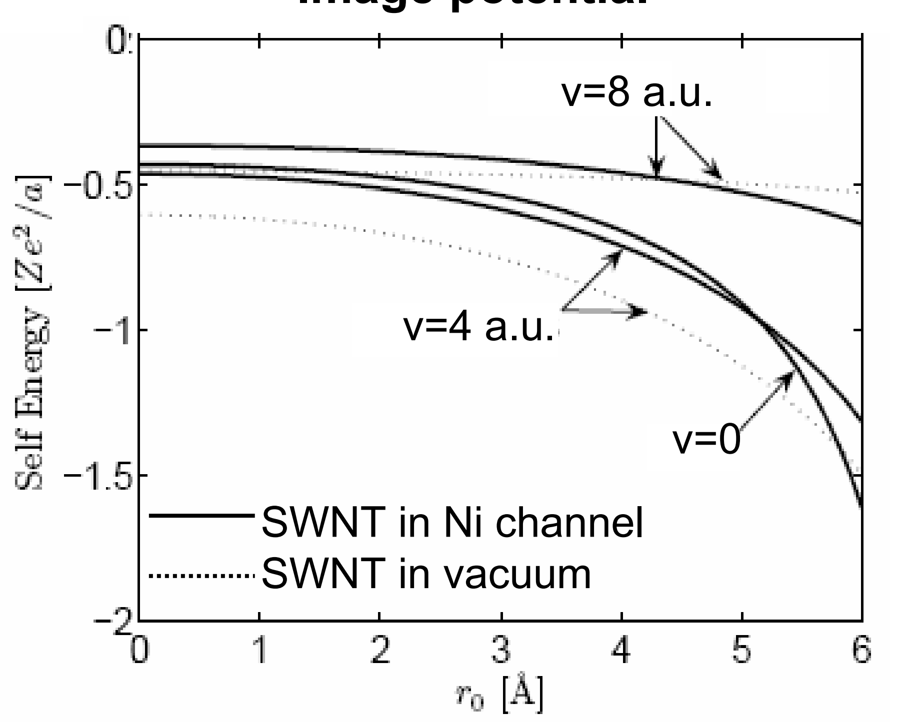


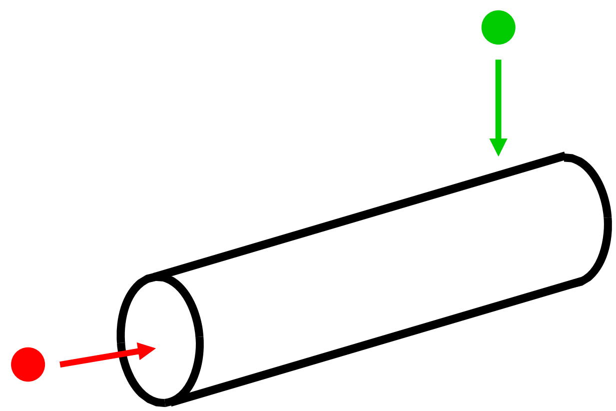
Image potential



Outline

- ❑ Properties and applications of carbon nanotubes
- ❑ Irradiation of carbon nanotubes by ion beams
  - Some experiments
  - MD simulations
- ❑ Ion channelling through carbon nanotubes
  - High energies
  - Medium energies
  - Low energies

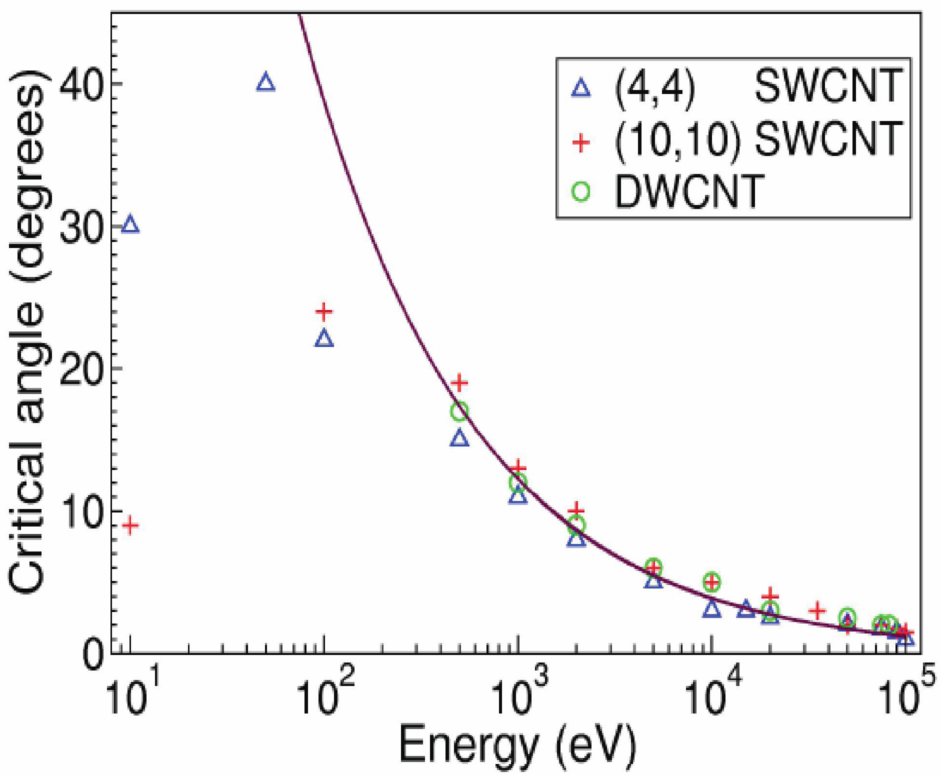
  } Theory & simulation
  - Experimental facts
- ❑ Outlook

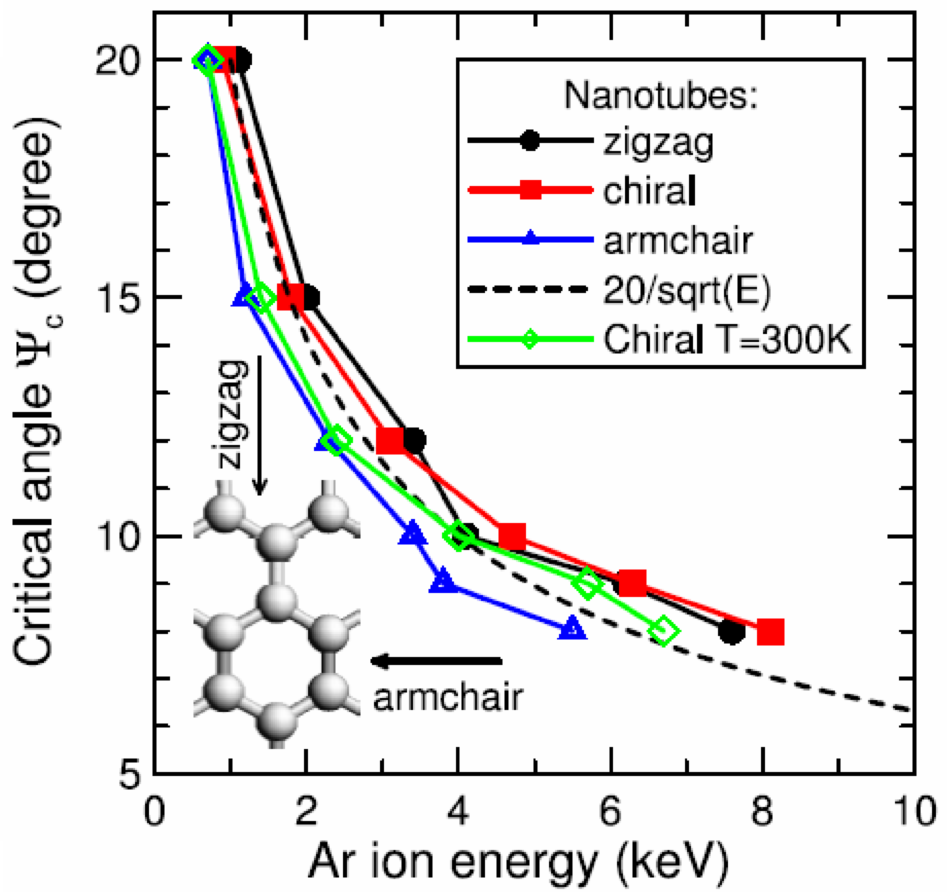


MD simulations: critical angle for channeling similar to continuum theory $\approx 1/\sqrt{E}$

C^+ ions: C.S. Moura and L. Amaral, *J. Phys. Chem.* B 109 (2005) 13515

Ar^+ ions: A.V. Krasheninnikov and K. Nordlund, *P.R.* B 71 (2005) 245408

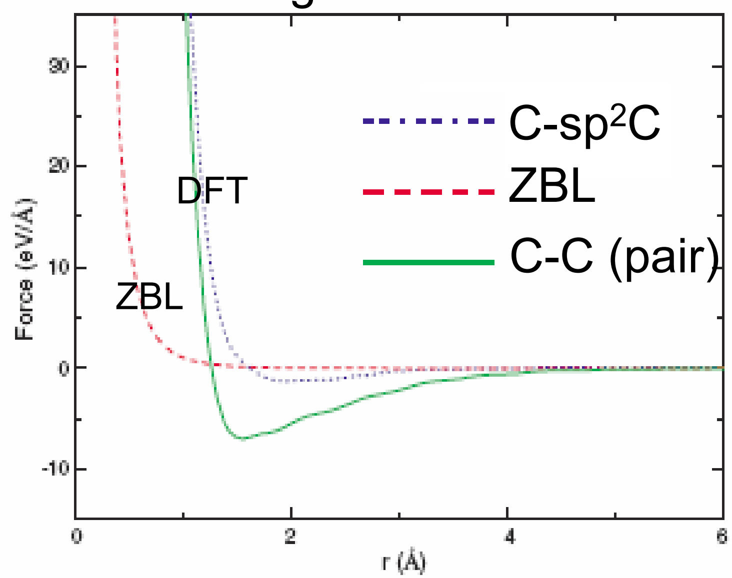


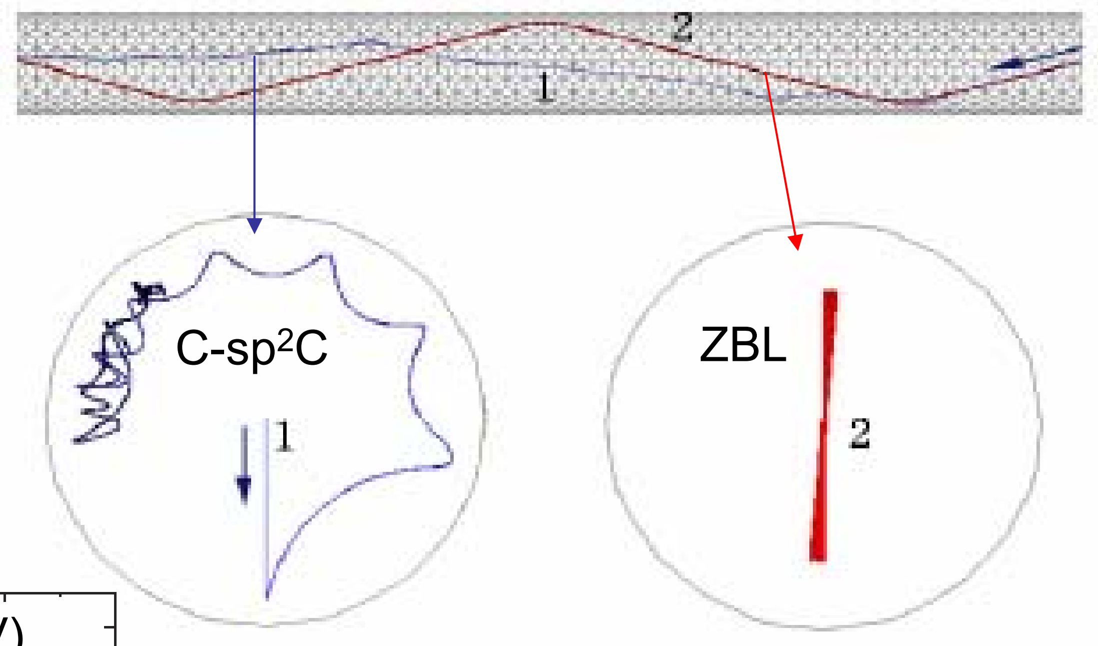


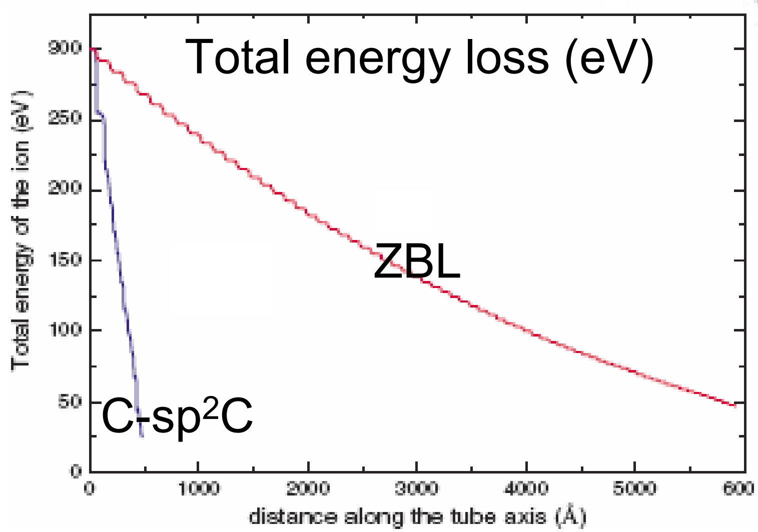
MD sim. of channelling of ~100eV C^+ ions in SWNT

W. Zhang *et al.*, *Nanotechnology* 16 (2005) 2681

Scattering force: DFT & ZBL







Electronic energy loss modeled by:

- modified Firsov
- Brandt-Kitagawa

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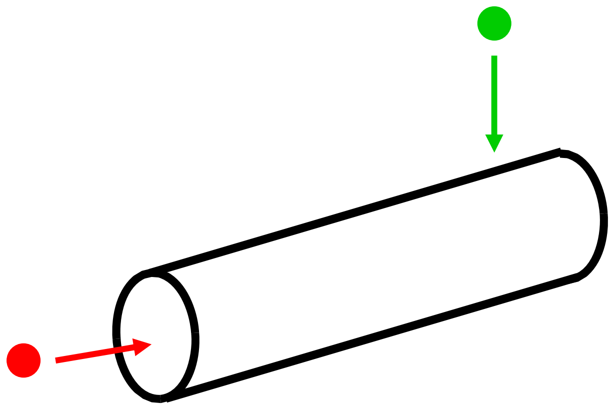
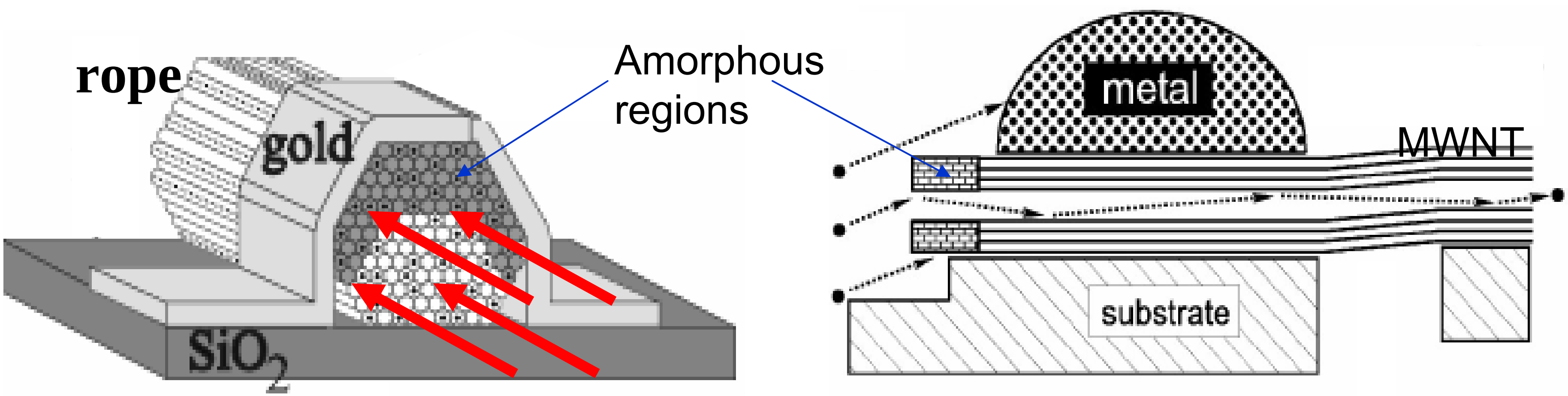


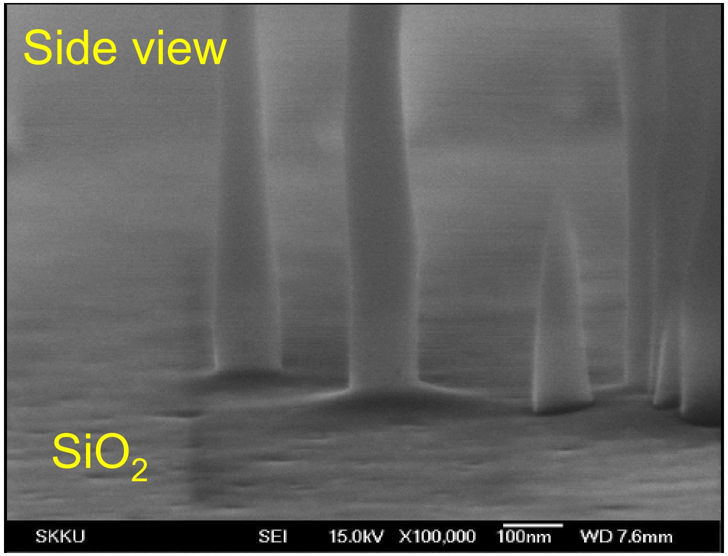
Main problem: damage to open nanotube ends

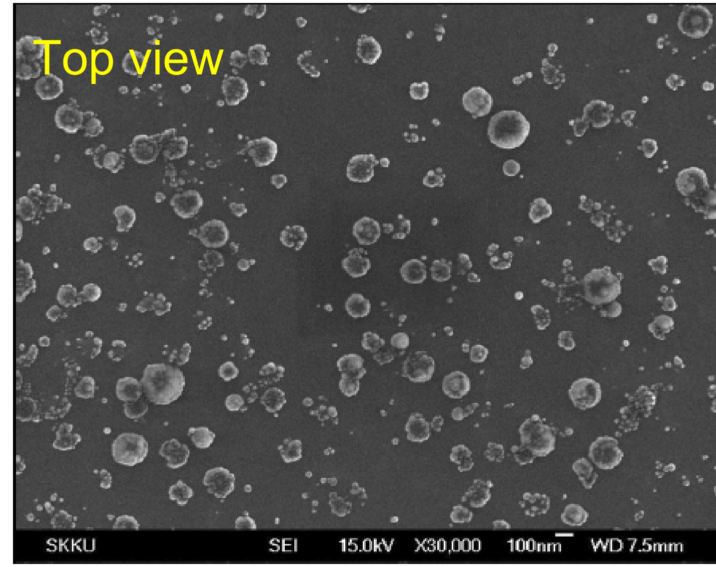
- ❑ Amorphization of open nanotube ends at **low** ion energies
  (A.V. Krasheninnikov and K. Nordlund., *Phys. Rev.* B 71 (2005) 245408).

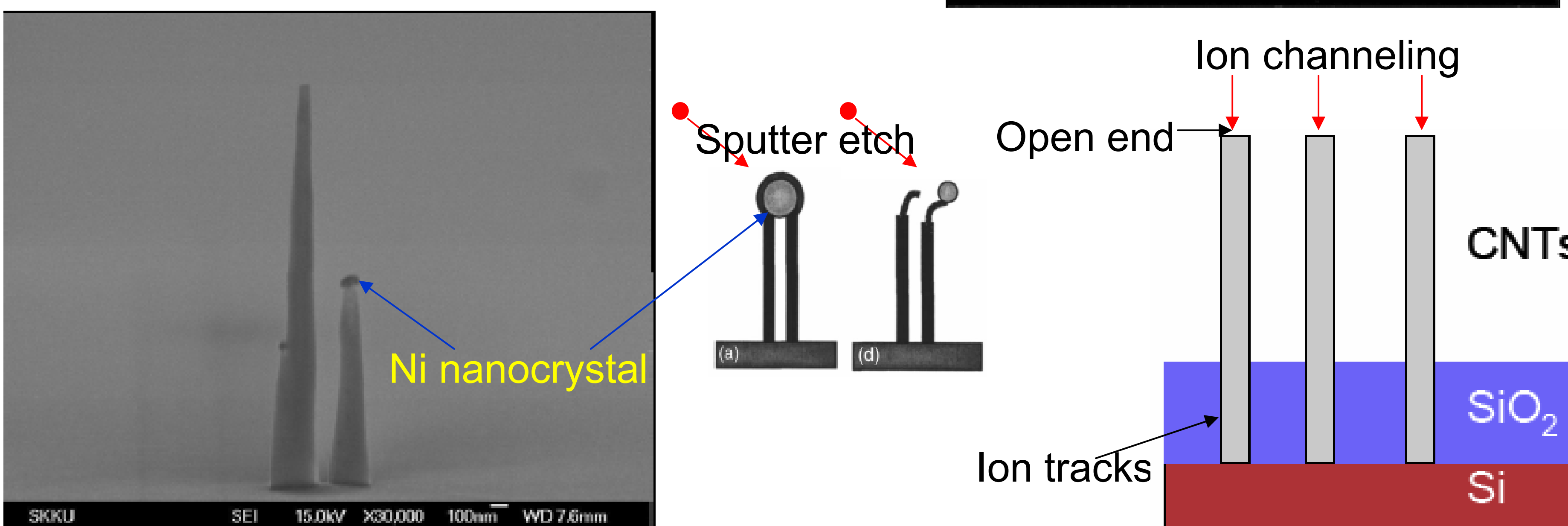


- ❑ At **high** ion energies: amorphization is delayed
  (experiment:100 MeV Au^+ ions: A. Misra *et al., Diamond & Rel. Mater*. (2006)).
- ❑ Electronic damage still uncertain in channeling (however,
  CNTs are ballistic conductors: *S.* Bellucci, *NIMB* (2005)) .

Possible experimental solution using CNTs grown in etched ion tracks in SiO_2 (D. Fink *et al., in press*)





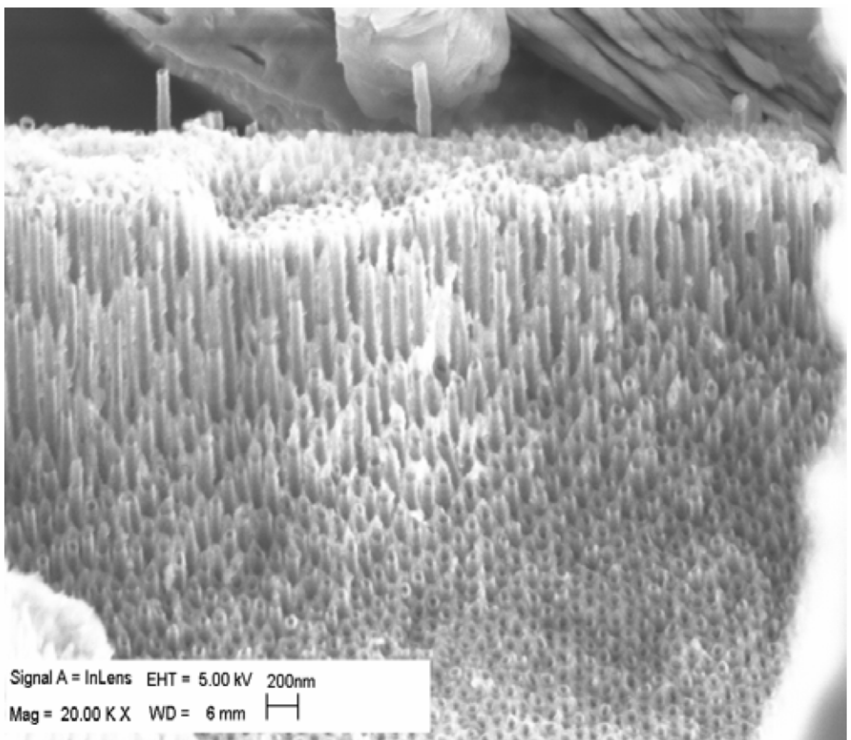


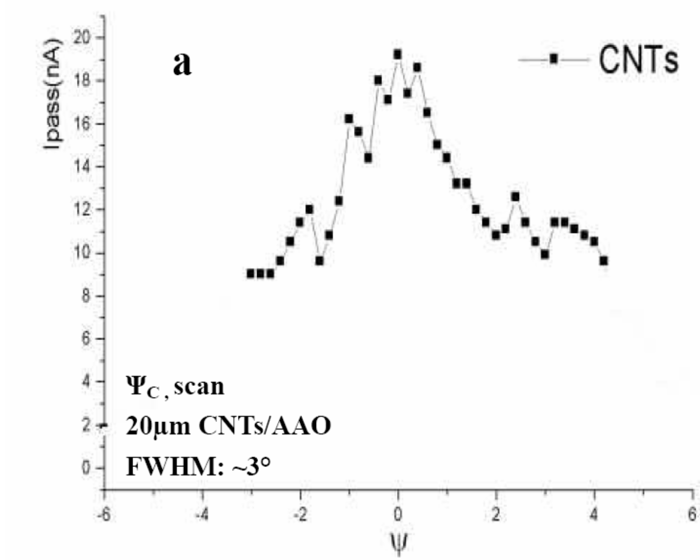
Actual experimental realization of channelling of 2 MeV He^+ ions in MWNTs grown in Anodic Aluminium Oxide

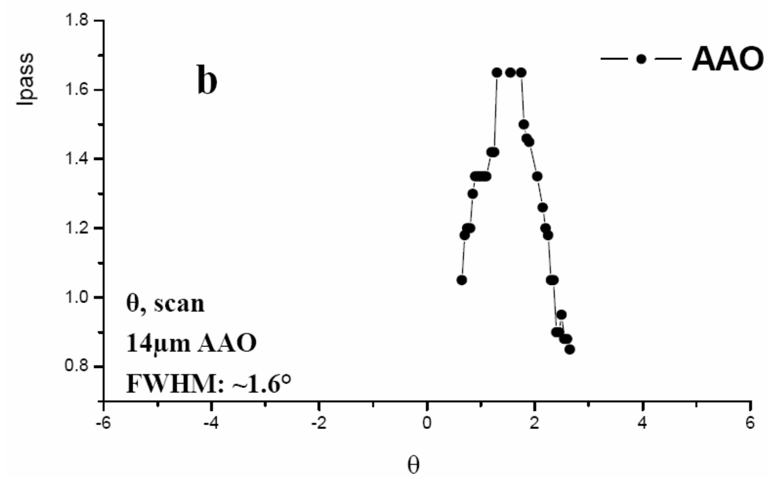
Z. Zhu *et al.*, *Proc. SPIE* 5974 (2005)

Current intensity distributions vs. incidence angles

Side view of AAO membrane







Outlook

- Ion beam irradiation is versatile tool for making local, controllable changes in structural, mechanical, chemical, and electrical properties of carbon nanotubes for variety of applications
- MD simulations successfully predict and interpret irradiation effects, mostly at low ion energies, but need improvements at higher energies
- Simulations of ion channelling through carbon nanotubes predict great advantages in comparison with single crystals & offer new applications
- Theoretical modeling of ion interactions with nanotubes needs improvements at all energies (ab-initio potentials, dynamic response, energy loss, ion charge states, …)
- Preliminary experimental realization of ion channelling already achieved, all major technical issues seem manageable
- Exciting new developments expected in near future for ion-beam interactions with carbon nanotubes