

Electron beam generation and structure of defects in carbon and boron nitride nanotubes

Alberto Zobelli

Laboratoire de Physique des Solides, Université Paris-Sud
Institut für Physikalische Chemie und Elektrochemie, Technische Universität Dresden,

October 3rd 2007

Outline

- 1 Irradiating nanotubes
- 2 Simulation techniques
- 3 Defects in h-BN and BN nanotubes
- 4 Electron knock-on cross sections
- 5 Nanotube engineering using a STEM
- 6 Conclusions and perspectives

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Nanotube irradiation

- Carbon nanotubes have unique electronic and mechanical properties.
- Synthesized nanotubes are far from being homogenous.
- Various post-growth modification methods have been suggested to functionalise the as-synthesized nanotubes.
- Defects in nanotubes can strongly affect their chemical or physical characteristics.
- Nanotube irradiation could be deliberately used to generate defects and thus to functionalise the tubes.
- Irradiation is also an unavoidable secondary effect occurring when highly energetic particles are used to investigate structural and spectroscopic properties of the tubes.

Nanotube irradiation

Irradiation experiments on nanotubes have been performed using many different energetic particles:

- Protons

V. Basiuk *et al.* Nano Lett. **2**, 789 (2002)

B. Khare *et al.* Nano Lett. **3**, 643 (2003)]

- Ions

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- γ rays

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LETTERS

Tuning the conductance of single-walled carbon nanotubes by ion irradiation in the Anderson localization regime

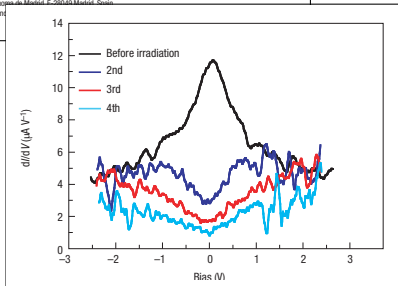
C. GÓMEZ-NAVARRO¹, P. J. DE PABLO¹, J. GÓMEZ-HERRERO^{1*}, B. BIEL², F. J. GARCIA-VIDAL², A. RUBIO³ AND F. FLORES²

¹Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

²Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

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*e-mail: julio.gomez@uam.es



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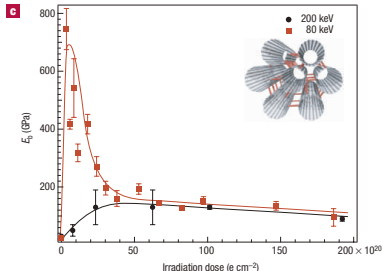
F. Beneu *et al.* PRB **59**, 5945 (1999)

ARTICLES

Reinforcement of single-walled carbon nanotube bundles by intertube bridging

A. KIS¹, G. CSÁNYI², J.-P. SALVETAT³, THIEN-NGA LEE¹, E. COUTEAU¹, A. J. KULIK¹, W. BENOIT¹, J. BRUGGER⁴ AND L. FORRÓ¹

¹Institute of Physics of Complex Matter, Ecole Polytechnique
²Cambridge Laboratory, University of Cambridge, Cambridge
³Centre de Recherche sur la Matière Condensée (CRMD), CNRS
⁴Institute of Microelectronics and Microsystems, EPFL, CH-1700
 Lausanne, Switzerland
 *e-mail: laszlo.forro@epfl.ch



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Advantages of electron irradiation

Compared to other irradiation techniques, electrons are easier to handle:

- Electron beam energies can be easily tuned.
- Electron beams can be focused into probes from the subnanometer to the micrometer scale.
- Electron sources are available into SEM and TEM in an energy range between few hundred of eV up to 1 MeV.

Irradiation in transmission electron microscopy

Whereas transmission electron microscopy is largely used in the study of nanotubes, at normal acceleration voltage nanotubes are strongly affected by the beam electrons.

Irradiation in a transmission electron microscopy

Two irradiation modes can be used

- **Homogeneous irradiation**

it allows the imaging of single vacancy formation during irradiation (parallel electron beams, TEM).

A. Hashimoto et al., *Nature* **430**, 870 (2004)

K. Suenaga et al. *Nature Nanotech.* **2**,358 (2007)

- **Localised irradiation**

it allows a high spatial control of the defect generation (focused electron beams, STEM).

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Direct evidence for atomic defects in graphene layers

Ayako Hashimoto¹, Kazu Suenaga¹, Alexandre Gloter^{1,2}, Koki Urita^{1,3} & Sumio Iijima¹

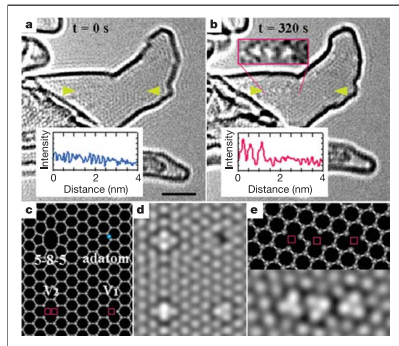
¹Research Center for Advanced Carbon Materials, National Institute for Advanced Industrial Science and Technology (AIST), Tsukuba, 305-8565, Japan

²Laboratoire de Physique des Solides, CNRS UMR 8502, Université Paris-Sud, Orsay, 91405, France

³Graduate School of Science and Technology, Chiba University, Chiba, 263-8522 Japan

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Atomic-scale defects in graphene layers alter the physical and



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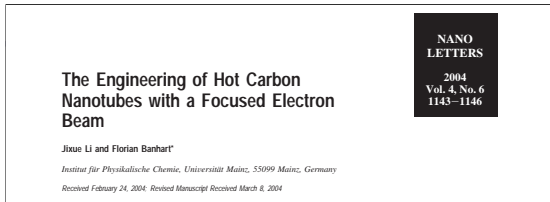
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Irradiation in a transmission electron microscopy

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ation during irradiation

- **Localised irradiation**

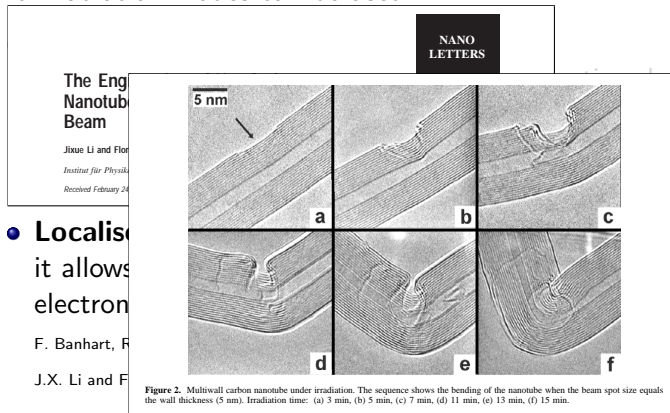
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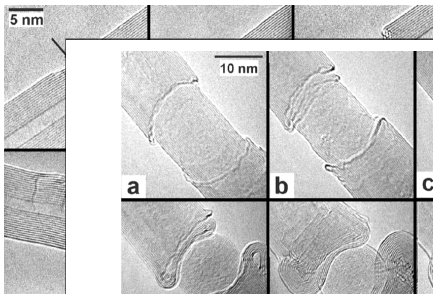
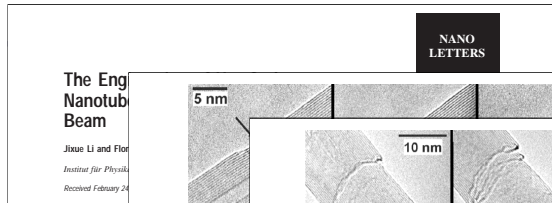


Figure 2. Multiwall carbon nanotube with the wall thickness (5 nm).

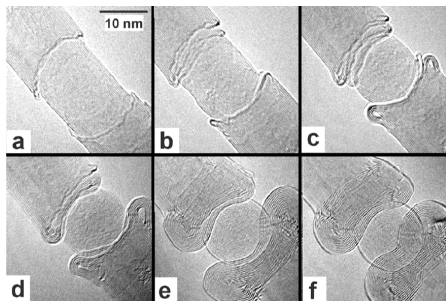


Figure 3. Irradiation of a tube with a beam spot size slightly larger than the diameter of the tube leads to the removal of the outer layer and to successive curling of the inner shells until a spherically closed onion-like structure connects the two halves of the tube. Irradiation time: (a) 2 min, (b) 4 min, (c) 6 min, (d) 8 min, (e) 15 min, (f) 22 min.

- Localisation of the electron beam allows the study of the structure of the nanotube.

F. Banhart, F. Banhart, F. Banhart
J.X. Li and F. Banhart

Purposes

- Defect production in single walled BN nanotubes.
- Thermal stability of defects in h-BN and BN nanotubes.
- Appearance under irradiation of extended defects.
- Knock-on cross sections in nanotubes.
- A better control of the irradiation conditions for single walled nanotubes.

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 - DFTB
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Modelling defective nanostructures

- Realistic models of defective systems on nanostructures involve large numbers of atoms (200-1000 atoms).
- Extended molecular dynamics (MD) simulations can describe defect generation and temperature evolution.
- Fast computational techniques are needed, as is the ability to describe structures far from the equilibrium configuration.

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Methods

- Density functional theory (DFT) using pseudopotentials and localised basis sets.
- Density functional tight binding (DFTB).

Density functional tight binding

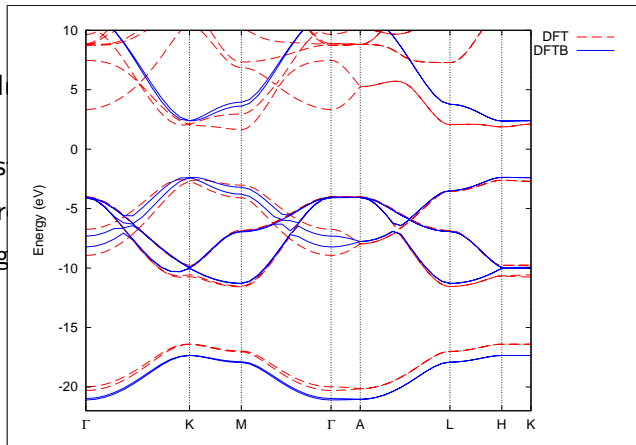
- Quantum method.
- A second-order expansion of the Kohn-Sham total energy in Density-Functional Theory (DFT) with respect to charge density fluctuations.
- All interaction integrals from DFT \Rightarrow high chemical transferability.
- Similar accuracy to ab initio DFT with the efficiency of semiempirical methods.

Density functional tight binding

- Finite (cluster, molecules) and infinite (solids, liquids, surfaces) models.
- Large systems (~ 10000 atoms).
- Rough processes, involving bond breaking and bond formation.
- Very long MD trajectories (a few ps).

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 - Homogeneous irradiation of single walled BN nanotubes
 - NEB
 - Vacancy migration
 - Preferential sites for vacancy creation
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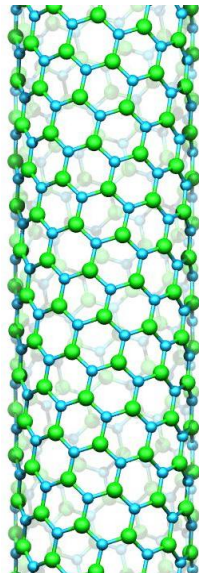
Single walled boron nitride nanotubes

- Structurally, boron nitride (BN) nanotubes are equivalent to carbon nanotubes.
- Unlike carbon nanotubes, BN nanotubes are large gap semiconductors whatever their chirality.

Boron



Nitrogen



Irradiation in transmission electron microscopy

Two irradiation modes can be used

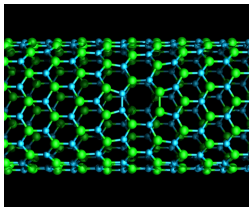
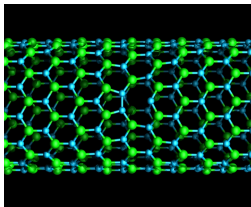
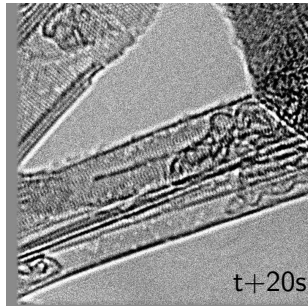
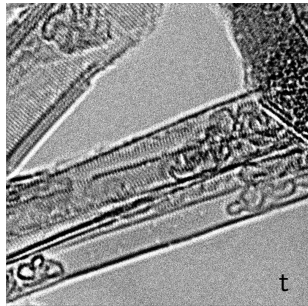
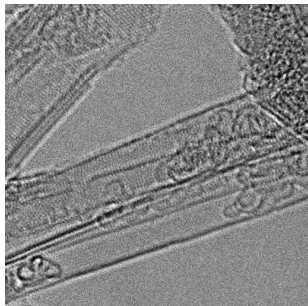
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it allows the imaging of single vacancies formation during irradiation (parallel electron beams, TEM).

- **Localised irradiation**

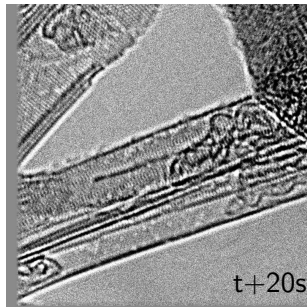
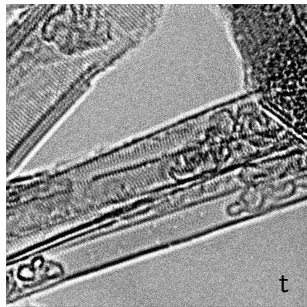
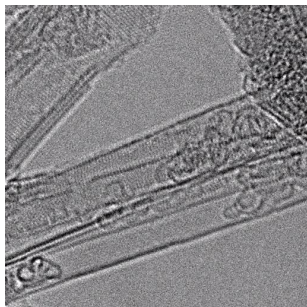
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Point defects



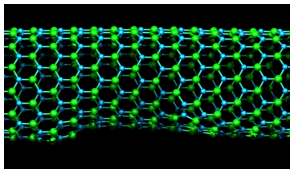
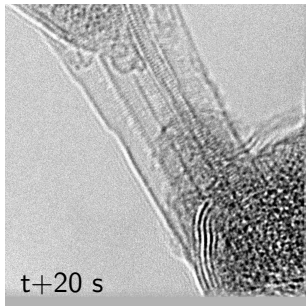
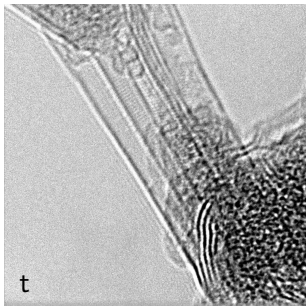
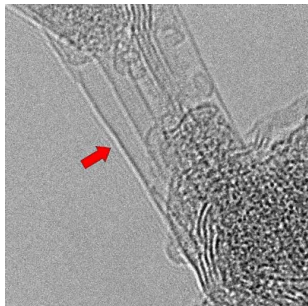
As for carbon tubes under irradiation, bright spots appear in the high resolution images that can be interpreted as limited defective structures.

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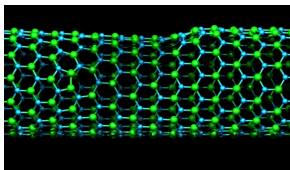
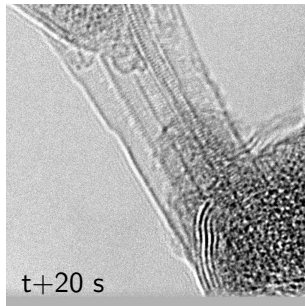
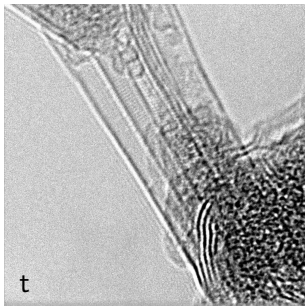
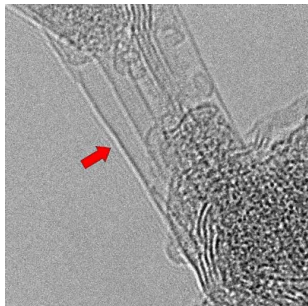
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Vacancy lines



A vacancy line could explain the pictures above.

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How can we pass from single vacancies to a vacancy line?

Defects production is mainly due to direct knock-on processes between the relativistic electrons of the beam and the atoms.

This explains the creation of single vacancies but how to obtain vacancy lines?

Several ways have to be considered:

- Thermal vacancy migration and nucleation.
- Preferential sites for vacancy creation.

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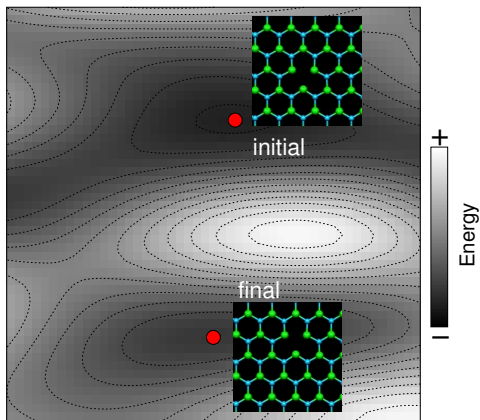
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Nudged elastic band method

The activation migration energy is the maximum of the minimum-energy path connecting the initial and final state.

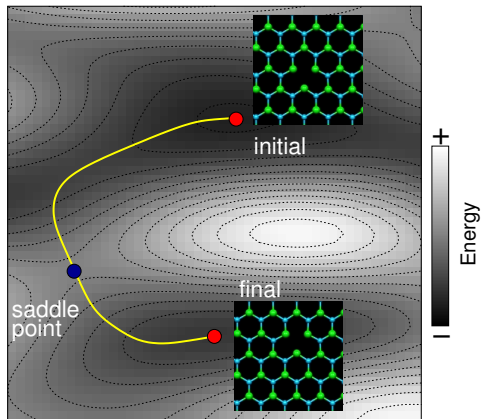


Configuration space (dimension $3N$)

- "Automatic" way of exploring the configuration space through a chain of states method: several images connected together via springs.
- Energies are derived from DFT based calculations.

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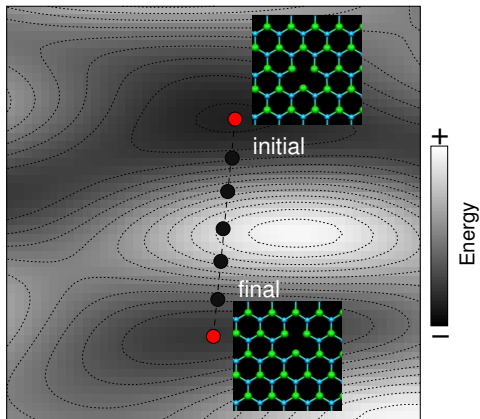


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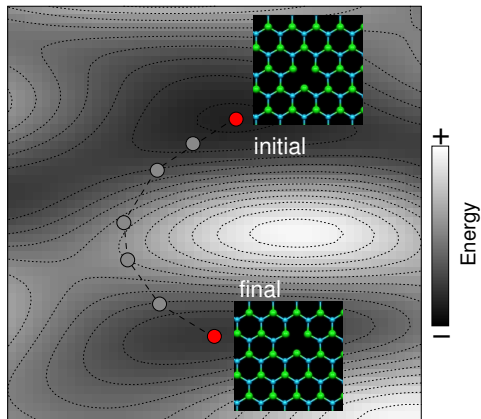


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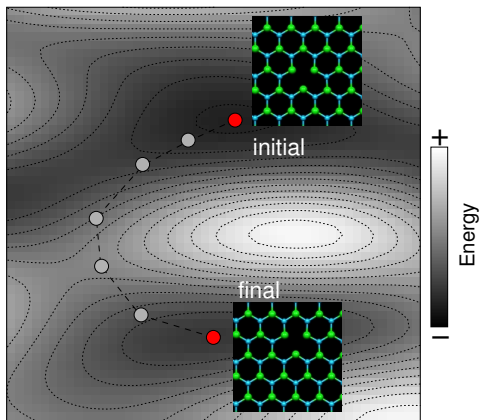


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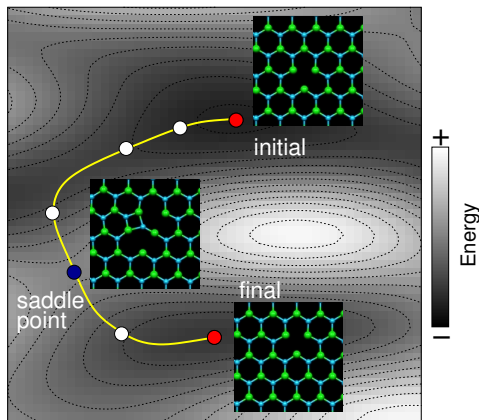


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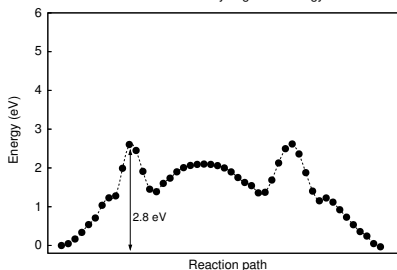
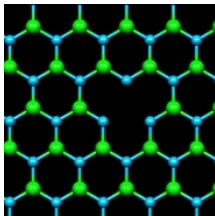
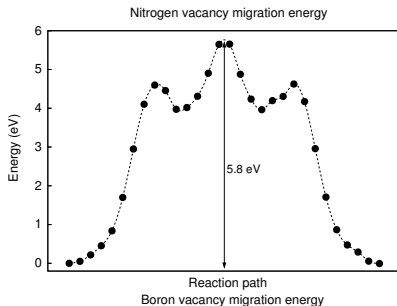
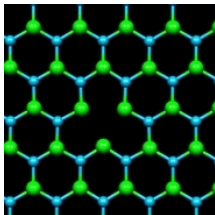
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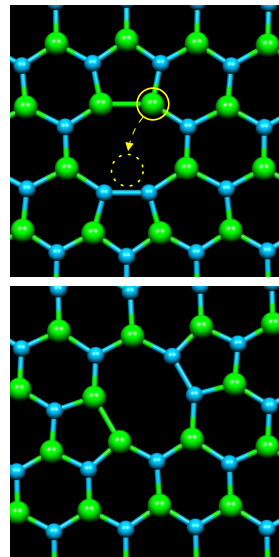
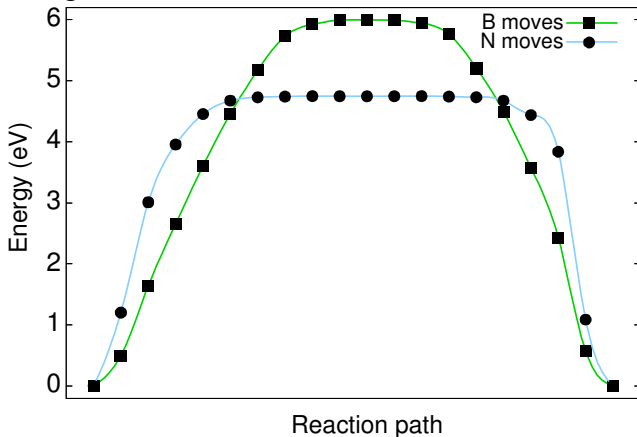
Vacancy migration activation energies: monovacancies



The paths pass through metastable configurations with reconstructions for dangling bonds.

Vacancy migration activation energies: divacancies

Two possible ways: moving a boron or moving a nitrogen atom.



Gibbs free energy, activation barriers

Since a defective crystal is a grand canonical ensemble, the correct thermodynamical function to consider is the Gibbs free energy:

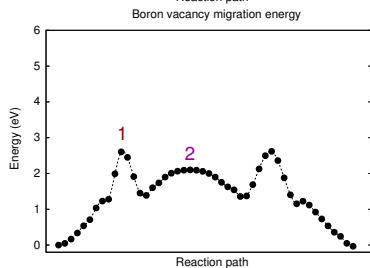
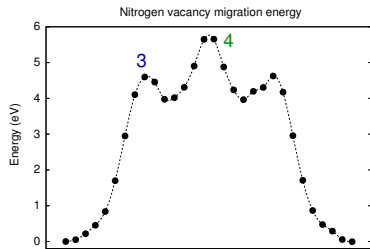
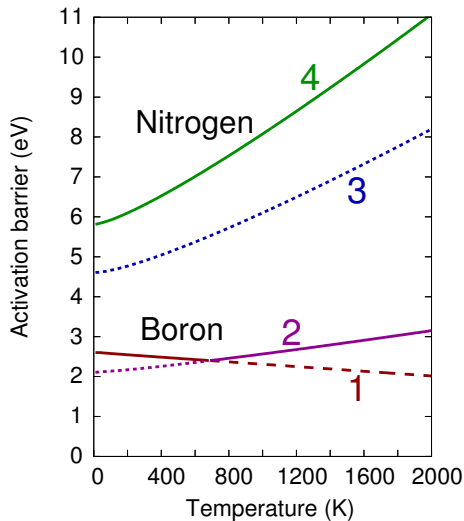
$$G = E + U_{vib} - TS_{vib} + pV - \sum_i \mu_i N_i$$

We calculate the vibrational energy and entropy considering a Boltzmann distribution of harmonic oscillators:

$$U_{vib} = \sum_{i=1}^{3N} \left\{ \frac{\hbar\omega_i}{\exp(\hbar\omega_i/k_B T) - 1} + \frac{1}{2}\hbar\omega_i \right\}$$

$$S_{vib} = k_B \sum_{i=1}^{3N} \left\{ \frac{\hbar\omega_i}{k_B T} \left[\exp\left(\frac{\hbar\omega_i}{k_B T}\right) - 1 \right]^{-1} - \ln \left[1 - \exp\left(\frac{-\hbar\omega_i}{k_B T}\right) \right] \right\}$$

Temperature dependence of the activation barriers

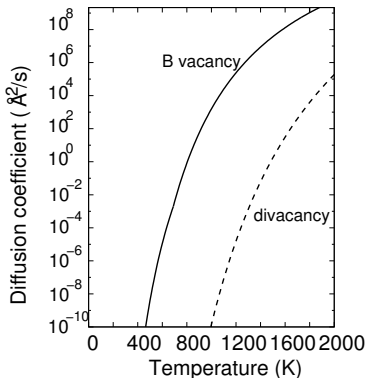


Diffusion coefficient

Considering the Arrhenius formula:

$$D = D_0 e^{-\frac{\Delta G(T)}{k_B T}}$$

- **Below 700K:** vacancies are immobile
- **700K-1200K:** just B vacancies are mobile and N vacancies tend to trap them to form divacancies
- **Above 1200K:** divacancies become mobile
- **N vacancies** are always immobile up to the melting point

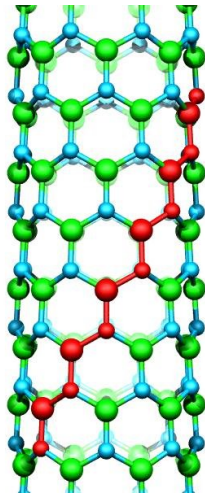


Vacancy migration in a TEM

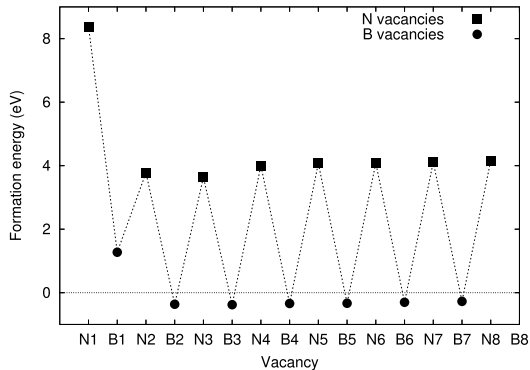
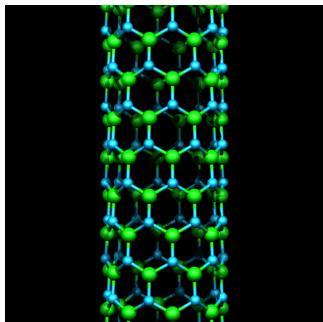
- Migration can not explain TEM experimental observations at room temperature.
- Electron irradiation heating effect in nanotubes is limited and thus electron beam assisted vacancy migration should also be excluded.

Preferential sites for vacancy creation

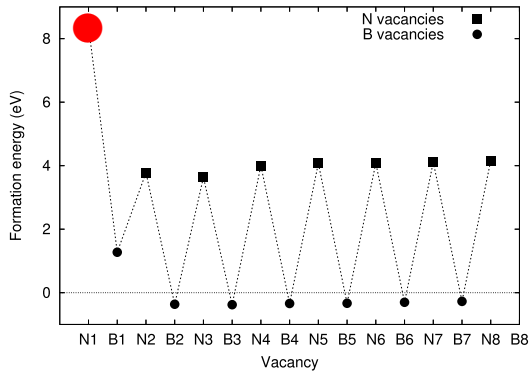
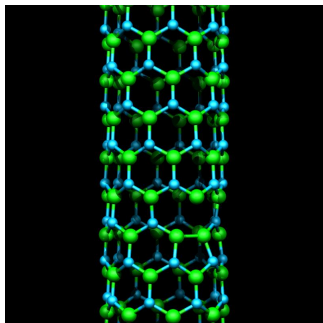
The energetically most favorable way to remove the atoms is along a sinusoidal line rolling around the tube.



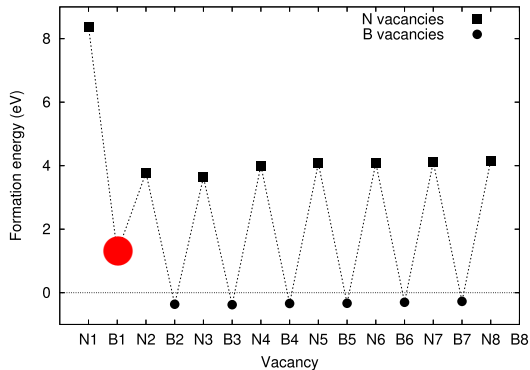
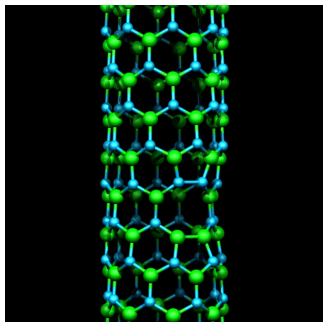
Vacancy lines formation energies



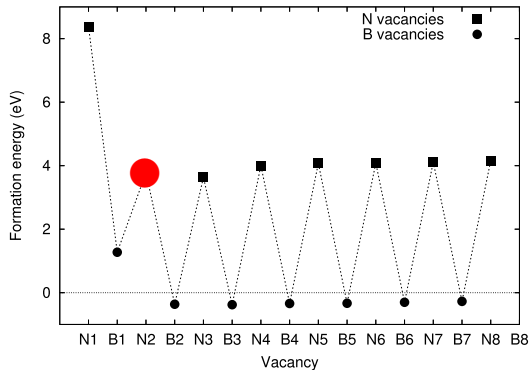
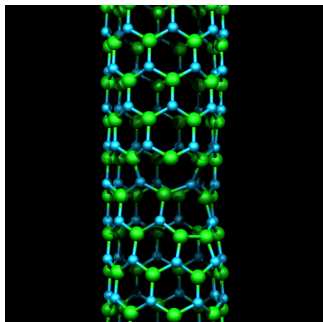
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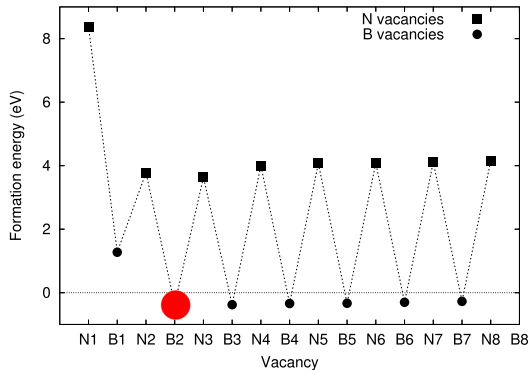
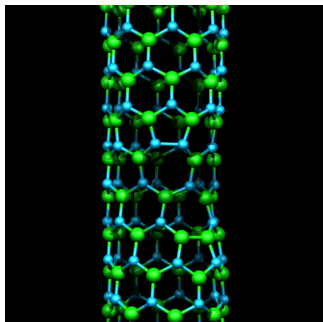
Vacancy lines formation energies



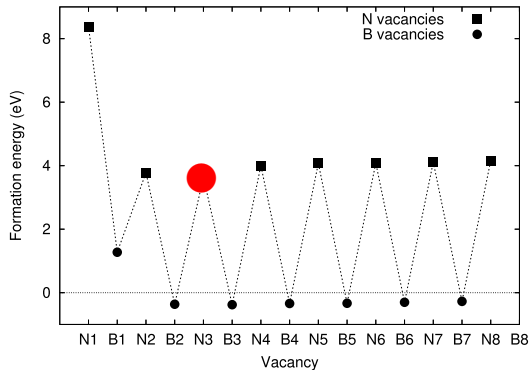
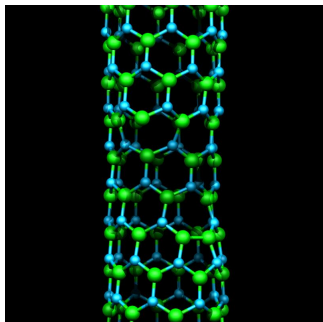
Vacancy lines formation energies



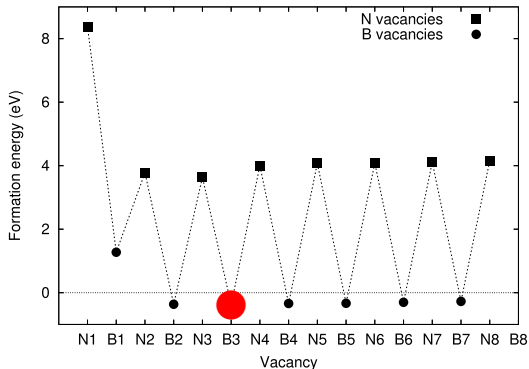
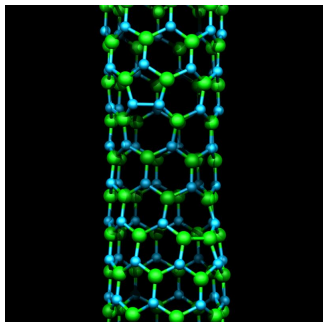
Vacancy lines formation energies



Vacancy lines formation energies

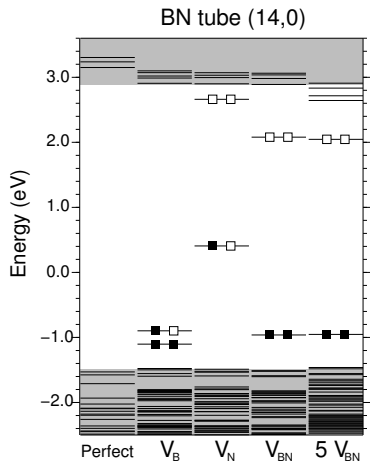


Vacancy lines formation energies



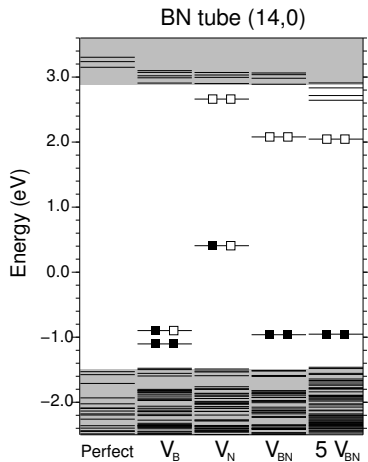
- Single vacancies should not be the most common form of defects: probably vacancies appear in neighbouring pairs.
- Strong driving force for linear vacancy clustering.

Electronic levels of defective structures



- Energy of a shallow donor associated with a boron vacancy is a fraction of an eV.
- This channel for doping the BN structure is strongly reduced by a neighbouring nitrogen vacancy.
- Neutral divacancies and more extended dislocation lines introduce levels in the band gap, but remove half-filled energy states.

Electronic levels of defective structures

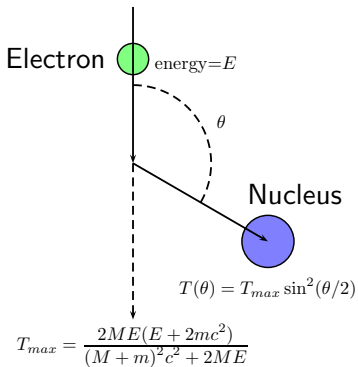


Although in principle we have an extremely complex system (multiple nanotubes with a range of diameters and chiralities, and a mixture of point and line defects), these essentially reduce to a single simple, uniform electronic system.

Outline

- 1 Irradiating nanotubes
- 2 Simulation techniques
- 3 Defects in h-BN and BN nanotubes
- 4 Electron knock-on cross sections**
 - The Mott theory
 - Emission energy threshold
 - Nanotube knock-on cross sections
- 5 Nanotube engineering using a STEM
- 6 Conclusions and perspectives

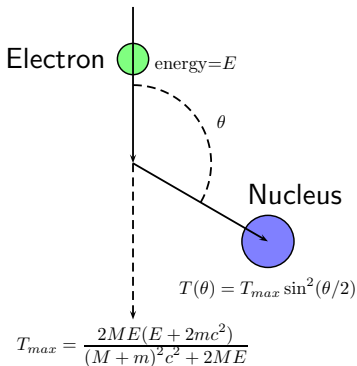
Electron Knock-on cross section



The cross section for Coulomb scattering between a relativistic electron and a nucleus can be written as a modified classical Rutherford scattering cross section σ_R :

$$\sigma(\theta) = \sigma_R \left[1 - \beta^2 \sin^2 \theta/2 + \pi \frac{Ze^2}{\hbar c} \beta \sin \theta/2 (1 - \sin \theta/2) \right]$$

Electron Knock-on cross section

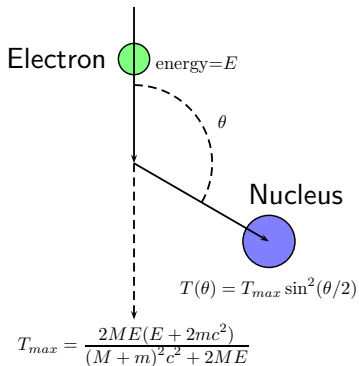


Differential cross section as function of the transferred energy:

$$\sigma(T) = \left(\frac{Ze^2}{4\pi\epsilon_0 2m_0 c^2} \frac{T_{max}}{T} \right)^2 \frac{1 - \beta^2}{\beta^4} \left[1 - \beta^2 \frac{T}{T_{max}} + \pi \frac{Ze^2}{\hbar c} \beta \left(\sqrt{\frac{T}{T_{max}}} - \frac{T}{T_{max}} \right) \right]$$

The total cross section is obtained by integrating this expression between the displacement energy threshold and the maximum energy transferred.

Electron Knock-on cross section



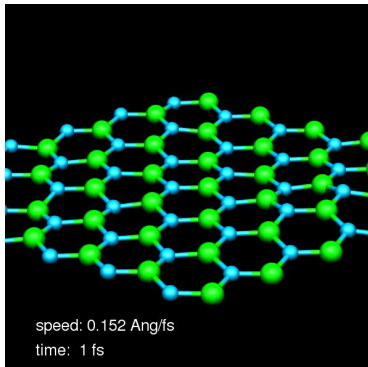
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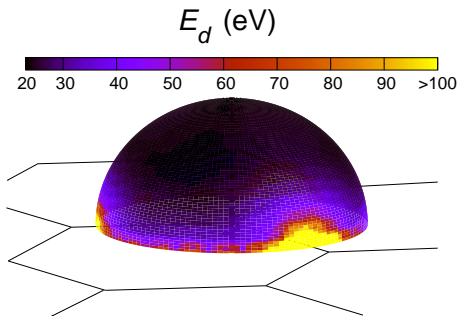
The emission energy threshold anisotropy has to be taken into account.

Molecular dynamics simulations of the emission process



- Emission energy threshold can be obtained by extended DFTB based molecular dynamics simulations varying the initial speed of the atom we want to emit.
- By varying the direction of emission we can map the emission energy threshold anisotropy.

Emission energy threshold anisotropy map

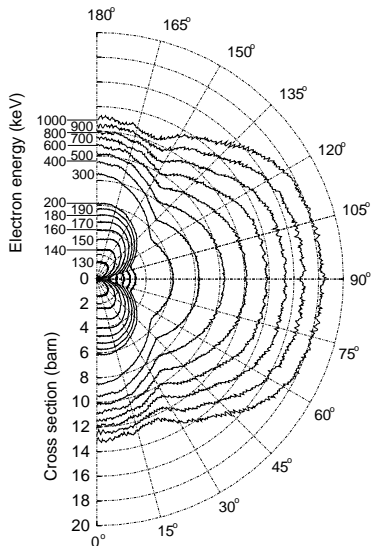


- The minimum value of the emission energy threshold is 23 eV, for emission orthogonal to the plane.
- For initial momenta imparted within the plane there is a strong dependence on the emission direction.

- If the tube diameter is large enough the structure can locally be considered as equivalent to a single graphene sheet.

Carbon nanotubes knock-on cross sections

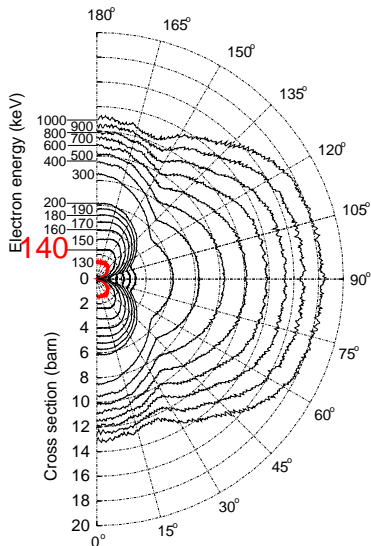
We can plot the knock-on cross section as a function of the incident electron energy and the position of the atom within the tube circumference.



Carbon nanotubes knock-on cross sections

"LOW" ELECTRON ENERGIES

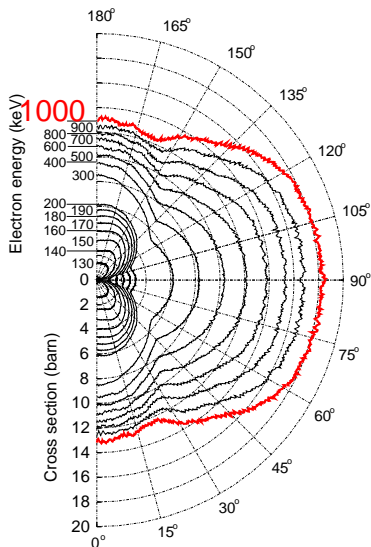
- The cross section decreases with increasing angle between the beam incidence direction and the normal to the tube.
- A forbidden emission region appears corresponding to the side walls of the tube.



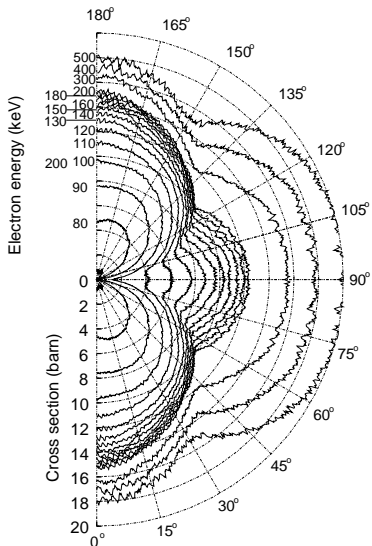
Carbon nanotubes knock-on cross sections

"HIGH" ELECTRON ENERGIES

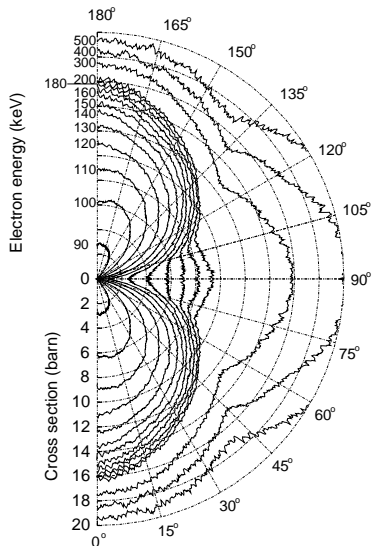
- Knock-on cross section increase significantly.
- For high energies, emission is largely homogeneous around the tube circumference.



BN nanotubes knock-on cross sections

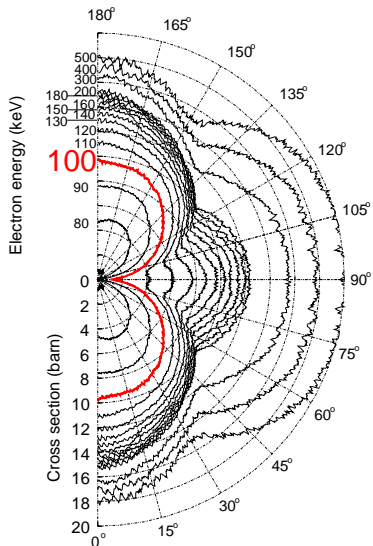


B atom emission

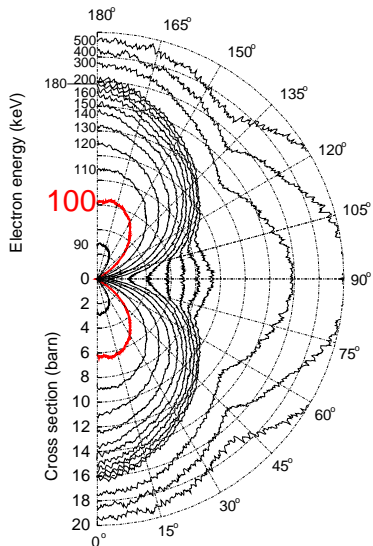


N atom emission

BN nanotubes knock-on cross sections

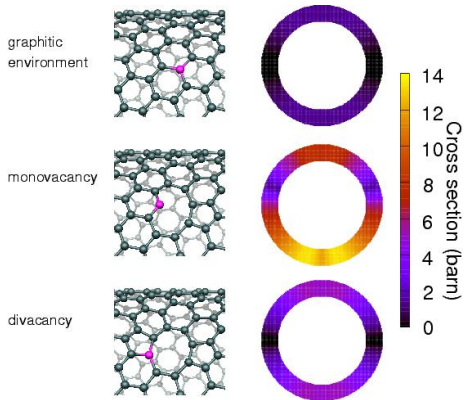


B atom emission



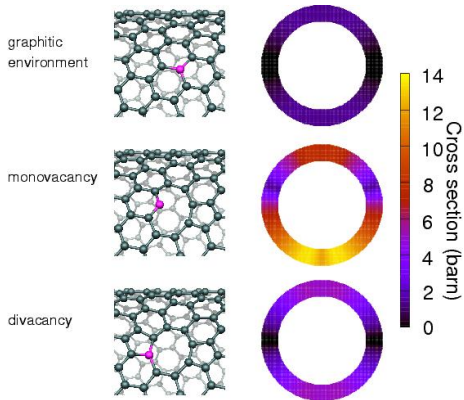
N atom emission

Defective carbon nanotubes knock-on cross sections



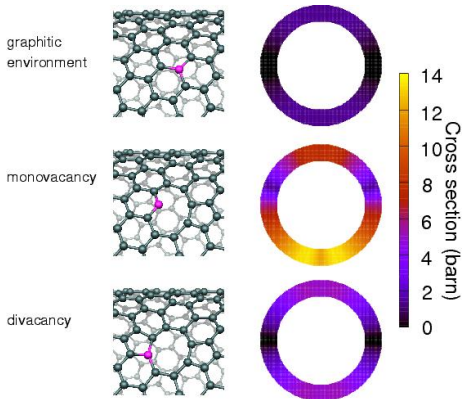
- The cross section for emitting one atom close to a pre-existent vacancy is one order of magnitude higher than for an atom in a perfect graphitic environment.
- For an atom close to a di-vacancy it is nearly four times higher.

Defective carbon nanotubes knock-on cross sections



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Defective carbon nanotubes knock-on cross sections



- The cross section for emitting one atom close to a pre-existent vacancy is one order of magnitude higher than for an atom in a perfect graphitic environment.
- For an atom close to a di-vacancy it is nearly four times higher.

- Higher knock on cross sections close to defective sites explain the dynamics for the formation of vacancy lines.

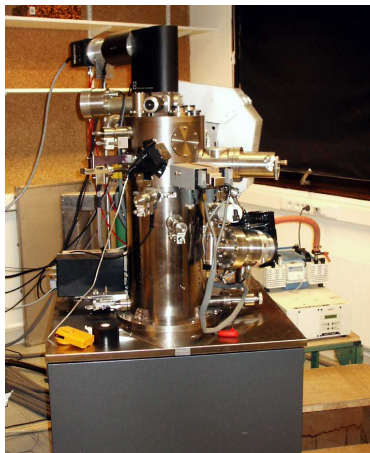
Outline

- 1 Irradiating nanotubes
- 2 Simulation techniques
- 3 Defects in h-BN and BN nanotubes
- 4 Electron knock-on cross sections
- 5 Nanotube engineering using a STEM
 - STEM
 - Carbon nanotube irradiation
 - Irradiating BN nanotubes
 - Number of emitted atoms
 - Non destructive electron microscopy

Can we obtain an high spatial control of the irradiation ?

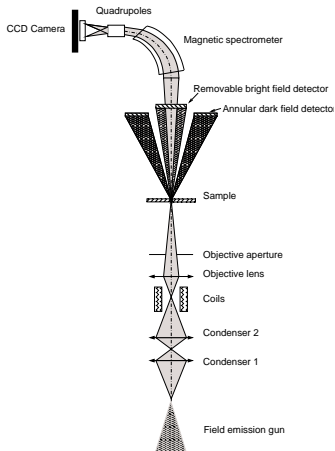
- Structure and formation mechanism of extended defects.
- Defect stability at room temperature.
- Knock-on cross sections for single walled nanotubes.
- A STEM dedicated microscope can reach nanometrer precision on the localization of the electron probe.

VG-STEM microscope



- Tungsten cold FEG operated between 60 keV and 100 keV
- Spatial resolution: 0.5 nm (probe size)

VG-STEM microscope



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Irradiation in a transmission electron microscopy

Two irradiation modes can be used

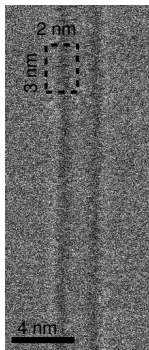
- **Homogeneous irradiation**

it allows the imaging of single vacancies formation during irradiation (parallel electron beams, TEM).

- **Localised irradiation**

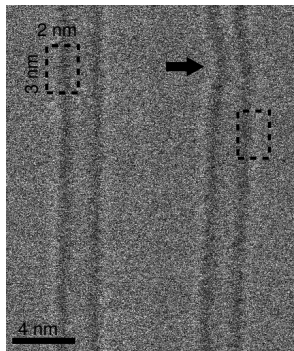
it allows a high spatial control of the defect generation (focused electron beams, STEM).

Nanotube engineering using a STEM

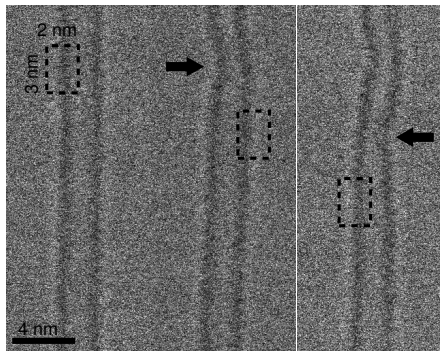


- Single walled carbon nanotubes
- Electron energy 100 KeV
- Current 100 pA
- Irradiation time 30 s between pictures
- Scanning area $2 \times 3 \text{ nm}^2$

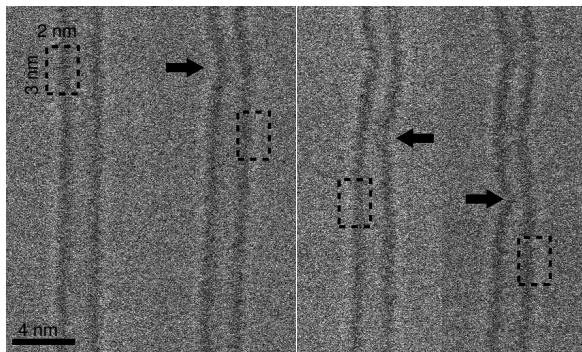
Nanotube engineering using a STEM



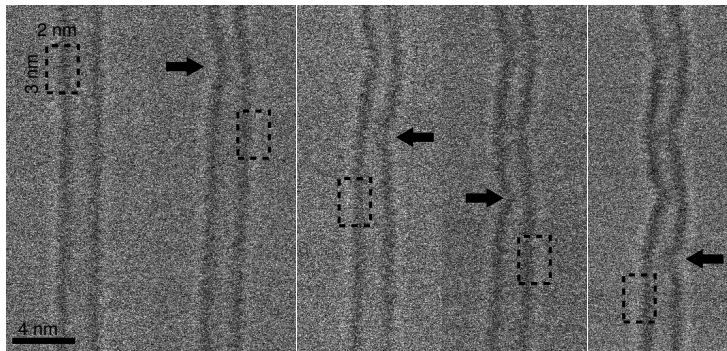
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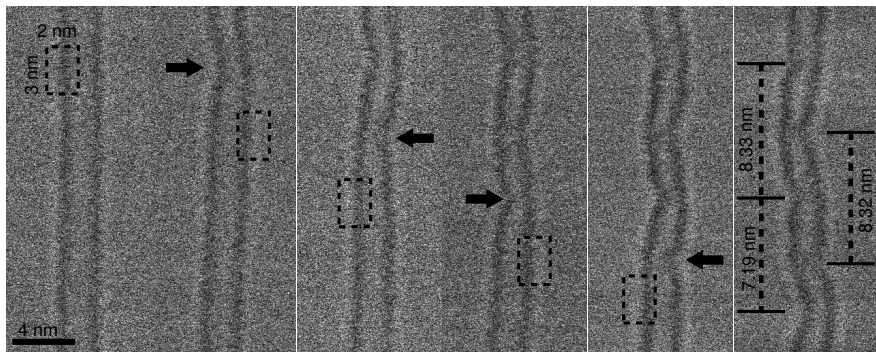
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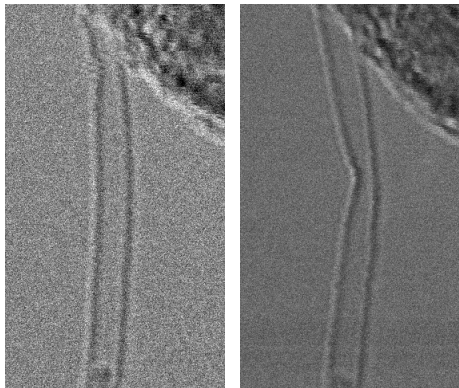


Nanotube engineering using a STEM



- Nanometric spatial control of defect generation.
- Local modification of the tube chirality.

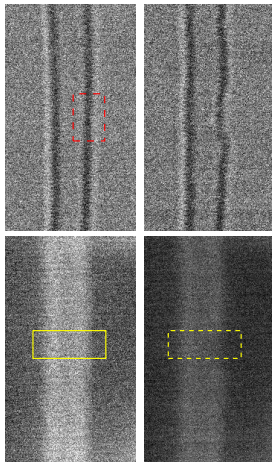
Irradiating BN nanotubes



- Single walled BN nanotubes.
- Electron energy 80 KeV.

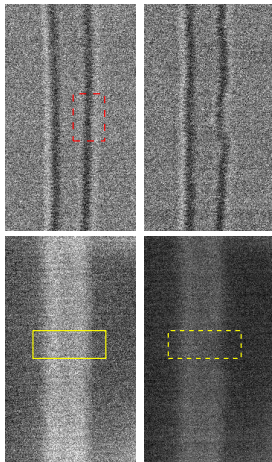
Dark field images: emitted atom quantification

2 nm



Dark field images: emitted atom quantification

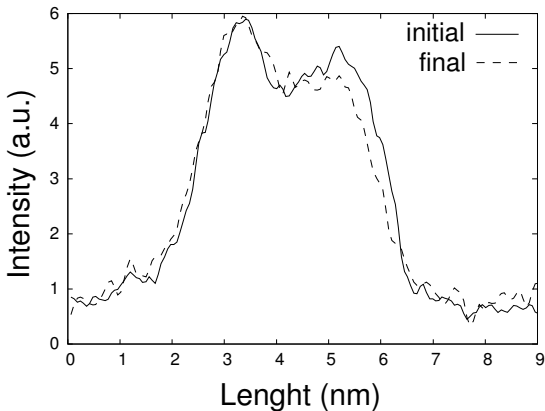
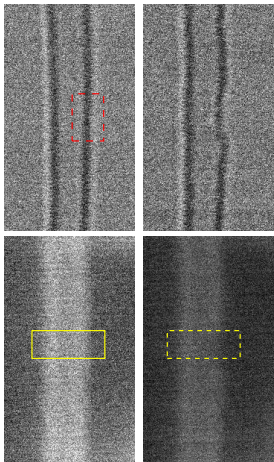
2 nm



- The diameter shrinks from 2 nm to 1.8 nm.

Dark field images: emitted atom quantification

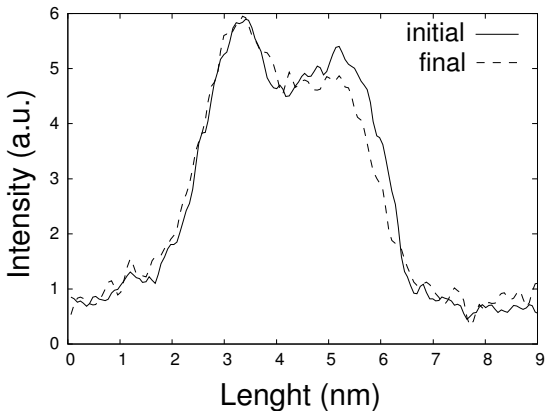
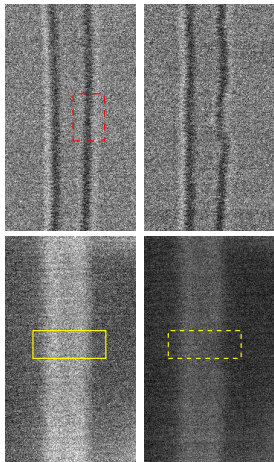
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Dark field images: emitted atom quantification

2 nm

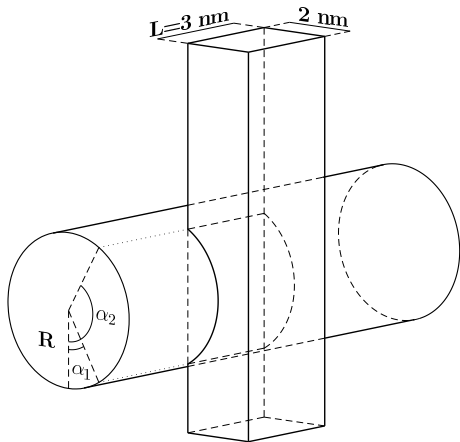


- The diameter shrinks from 2 nm to 1.8 nm.
- The profile integral is proportional to the number of atoms.
- 4% of the atoms have been emitted corresponding to ~ 40 atoms.

Calculating the number of emitted atoms

Emitted atoms in the tube section
between the angles α_1 and α_2

$$N = jRLt \int_{\alpha_1}^{\alpha_2} \sigma(\alpha) \rho |\cos(\alpha)| d\alpha$$



Calculating the number of emitted atoms

Experimental parameters:

$$j = 150 \cdot 10^{28} \text{ e}^- / (\text{s} \cdot \text{m}^2)$$

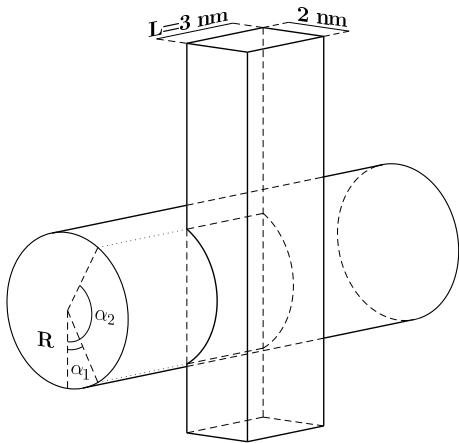
$$\rho = 9.68 \text{ Atom/nm}^2$$

$$R = 1 \text{ nm}$$

$$L = 3 \text{ nm}$$

$$t = 60 \text{ s}$$

$$\alpha_1 = 60^\circ \text{ and } \alpha_2 = 120^\circ$$



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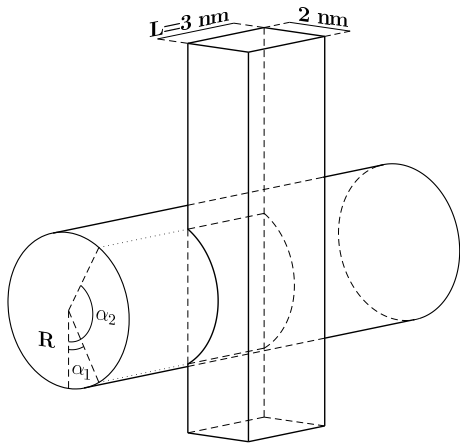
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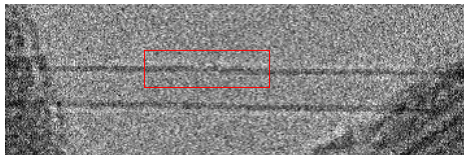
$$\alpha_1 = 60^\circ \text{ and } \alpha_2 = 120^\circ$$



Under these experimental conditions a total number of ~ 3 primary vacancies are generated.

These primary vacancies act as seeds for the creation of dislocation lines.
Totally a few tens of atoms are removed.

Non destructive electron microscopy



Initial



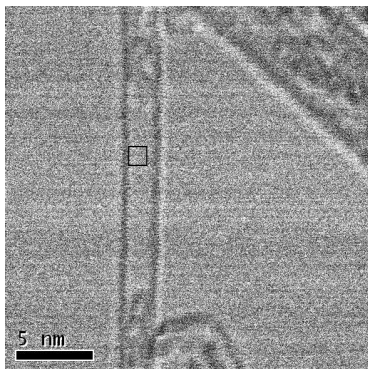
After
5'

- Single walled carbon nanotubes
- Electron energy 80KeV
- Current 100pA

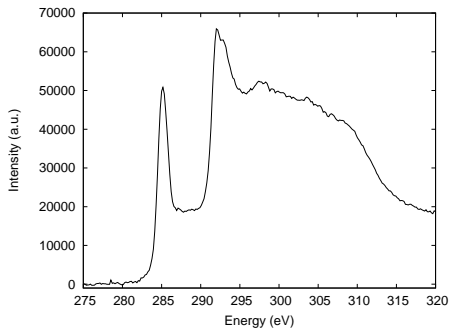


After
15'

Non destructive EELS analysis



Carbon K edge



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- Electron microscopy is a powerful technique for imaging single and more extended defects on BN nanotubes.
- Vacancies in h-BN and BN nanotubes are thermally stable up to elevated temperature.
- Vacancy lines are generated due to preferential sites for vacancy creation. Divacancies seem to be the most common defect in BN tubes.
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- EEL spectroscopy of defective structures.
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WAITING FOR THE SUPER-STEM...

SUPER-STEM



- Spherical aberrations corrector.
- Probe size lower than 1 Å.
- Operating energies between 40 and 100 keV.

