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

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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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6. Conclusions and perspectives
Carbon nanotubes have unique electronic and mechanical properties. Synthesized nanotubes are far from being homogeneous. 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**

- **Ions**

- **γ rays**

- **Electrons**
Nanotube irradiation

Irradiation experiments allow us to control the electrical transport properties of any nanotube.

- **Protons**
  
  
  

- **Ions**
  

- **γ rays**
  
  H. Hulman *et al.* J. Appl. Phys. 98, 243311 (2005),
  

- **Electrons**
  
  Kis *et al* Nature Mat. 3, 153 (2004),
  
  F. Beneu *et al.* PRB 59, 5945 (1999)
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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 subnanometrer to the micrometre 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).
  
  

- **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 Gloter¹,², Koki Urita¹,³ & Sumio Iijima³

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Atomic-scale defects in graphene layers alter the physical and...
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Two irradiation modes can be used:

- **Localised irradiation** it allows a high spatial control of the defect generation (focused electron beams, TEM).

- **Parallel irradiation** it allows the focusing of nanometer- or even Ångstrom-sized electron beam spots onto the specimen. Electron irradiation at high temperature offers therefore a high potential for manipulation of single-wall or multiwall nanotubes (SWNT, MWNT), we can change the structure locally, i.e., on the nanometer or even Ångstrom scale, cutting them by an STM tip, or just on individual shells, we could create devices that are bending, or breaking, or just on individual shells, we could create devices that are cutting them by an STM tip, or just on individual shells, we could create devices that are cutting them by an STM tip. At high temperatures offers therefore a high potential for changing the structure only along a short section of the tube.

**Figure 1.** Multiwall carbon nanotube under irradiation. The sequence shows the bending of the nanotube when the beam spot size equals approximately 2 nm). The outermost layer is locally removed from different suppliers were used (e.g., “bucky paper” from extreme carbon film (i.e., shape transformations or bending of the nanotube with a focused electron beam. When the edge of the wall thickness (5 nm). Irradiation time: (a) 3 min, (b) 5 min, (c) 7 min, (d) 11 min, (e) 13 min, (f) 15 min.}

**Figure 2.** Multiwall carbon nanotube under irradiation. The sequence shows the bending of the nanotube when the beam spot size equals the wall thickness (5 nm). Irradiation time: (a) 3 min, (b) 5 min, (c) 7 min, (d) 11 min, (e) 13 min, (f) 15 min.
Two irradiation modes can be used:

- **Localised irradiation:** it allows for the handling of tools for altering the structure of nanotubes.
- **Homogeneous irradiation:** it allows a high spatial control of the defect generation (focused electron beams, STEM).

Irradiation in a transmission electron microscopy

Figure 2. Multiwall carbon nanotubes with a diameter of approximately 600 nm in diameter and beam current densities up to 10^4 A/cm^2, depending on the beam diameter (the beam current density at 20 nm in diameter is shown in Figure 4).

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.
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.
Outline

1. Irradiating nanotubes

2. Simulation techniques
   • DFTB

3. Defects in h-BN and BN nanotubes

4. Electron knock-on cross sections

5. Nanotube engineering using a STEM

6. Conclusions and perspectives
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 ($\sim 10000$ atoms).
- Rough processes, involving bond breaking and bond formation.
- Very long MD trajectories (a few ps).

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1. Irradiating nanotubes

2. Simulation techniques

3. Defects in h-BN and BN nanotubes
   - Homogeneous irradiation of single walled BN nanotubes
   - NEB
   - Vacancy migration
   - Preferential sites for vacancy creation

4. Electron knock-on cross sections

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6. Conclusions and perspectives
Structurally, boron nitride (BN) nanotubes are equivalent to carbon nanotubes. Unlike carbon nanotubes, BN nanotubes are large gap semiconductors whatever their chirality.
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).
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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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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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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Figure: Configuration space (dimension 3N)

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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:

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

\[ S_{vib} = k_B \sum_{i=1}^{3N} \left\{ \frac{\hbar \omega_i}{k_B T} \left[ \exp \left( \frac{\hbar \omega_i}{k_B T} \right) - 1 \right]^{-1} - \ln \left[ 1 - \exp \left( -\frac{\hbar \omega_i}{k_B T} \right) \right] \right\} \]
Temperature dependence of the activation barriers

- Nitrogen vacancy migration energy
- Boron vacancy migration energy

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.
The energetically most favorable way to remove the atoms is along a sinusoidal line rolling around the tube.
Defects in h-BN and BN nanotubes

Preferential sites for vacancy creation

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.

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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.
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4. Electron knock-on cross sections
   - The Mott theory
   - Emission energy threshold
   - Nanotube knock-on cross sections
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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 $\sigma_R$:

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

where $\beta = \frac{E}{M c}$, and $E$ is the electron energy, $M$ is the mass of the nucleus, $m$ is the electron mass, $c$ is the speed of light, $Z$ is the atomic number of the nucleus, and $e$ is the elementary charge.

Electron knock-on cross sections

W. McKinsley and H. Feshbach, Phys. Rev. 74, 1759 (1948)
Electron Knock-on cross section

Differential cross section as function of the transferred energy:

\[
\sigma(T) = \left( \frac{Ze^2}{4\pi\varepsilon_0 m_0 c^2} \frac{T_{\text{max}}}{T} \right)^2 \frac{1 - \beta^2}{\beta^4} \left[ 1 - \beta^2 \frac{T}{T_{\text{max}}} \right] + \pi \frac{Ze^2}{\hbar c} \beta \left( \sqrt{\frac{T}{T_{\text{max}}}} - \frac{T}{T_{\text{max}}} \right)
\]

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.

Electron knock-on cross sections

The Mott theory

Electron Knock-on cross section

Electron

energy\(=E\)

Nucleus

\(T(\theta) = T_{\text{max}} \sin^2(\theta/2)\)

\(T_{\text{max}} = \frac{2 ME(E + 2mc^2)}{(M + m)^2 c^2 + 2 ME}\)
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.

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

Electron knock-on cross sections

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

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   • 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 nanometer 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)
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Irradiation in a transmission electron microscopy

Two irradiation modes can be used

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- **Localised irradiation**
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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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Carbon nanotube irradiation

Nanometric spatial control of defect generation.
Local modification of the tube chirality.
Nanotube engineering using a STEM

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Irradiating BN nanotubes

- Single walled BN nanotubes.
- Electron energy 80 KeV.
Dark field images: emitted atom quantification

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 $\sim 40$ atoms.
Dark field images: emitted atom quantification

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4% of the atoms have been emitted corresponding to $\sim 40$ atoms.
Calculating the number of emitted atoms

Emitted atoms in the tube section between the angles $\alpha_1$ and $\alpha_2$

\[ N = jRLt \int_{\alpha_1}^{\alpha_2} \sigma(\alpha) \rho |\cos(\alpha)| \, d\alpha \]
Calculating the number of emitted atoms

Experimental parameters:

\[ j = 150 \cdot 10^{28} \text{ e}^{-}/(\text{s} \cdot \text{m}^2) \]
\[ \rho = 9.68 \text{ Atom}/\text{nm}^2 \]
\[ R = 1 \text{ nm} \]
\[ L = 3 \text{ nm} \]
\[ t = 60 \text{ s} \]
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Under these experimental conditions a total number of \( \sim 3 \) 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

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

Initial

After 5'

After 15'
Non destructive EELS analysis

Carbon K edge

Intensity (a.u.) vs Energy (eV)
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Conclusions

- 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.
- Irradiated BN nanotubes have a homogeneous electronic structure with additional empty levels in the band gap.
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Conclusions

- The map of the anisotropy emission energy threshold has been calculated for different graphitic systems.
- Total knock-on cross sections have been derived as a function of the electron beam energy and the atom position within the tube circumference.
- Electron irradiation experiments demonstrate the possibility of engineering single walled nanotubes with nanometric precision.
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Perspectives

- Atomic DF images of defective structures.
- EEL spectroscopy of defective structures.
- *In situ* conductivity measurements on the generated defective structures.
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*WAITING FOR THE SUPER-STEM...*
SUPER-STEM

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