Chapter 1

Irradiation-induced phenomena in carbon nanotubes


Arkady V. Krasheninnikov\textsuperscript{1,2}

\textsuperscript{1}Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, 02015, Finland
\textsuperscript{2}Accelerator Laboratory, University of Helsinki, P.O.Box 43, 00014, Finland

tel. +358-9-19150010
fax +358-9-19150042
e-mail: akrashen@acclab.helsinki.fi
Contents

1 Irradiation-induced phenomena in carbon nanotubes 1
  1.1 Introduction .................................................. 4
  1.2 Interaction of energetic particles with solid targets ....... 6
    1.2.1 Ion irradiation: stopping of energetic ions in solids .... 6
    1.2.2 Electron irradiation: energy transfer from energetic electrons to the target atoms ......................... 7
  1.3 Experimental methods and theoretical tools to study irradiation-induced and native defects in carbon nanotubes ........ 8
    1.3.1 Experimental identification of point defects in nanotubes 8
    1.3.2 Computational tools for studying defect properties and defect production in carbon nanotubes .................... 9
  1.4 Irradiation-induced and native defects in carbon nanotubes ... 10
    1.4.1 Simulations of defect production in carbon nanotubes under irradiation ........................................... 10
    1.4.2 Vacancies in carbon nanotubes ............................. 13
    1.4.3 Carbon adatoms as interstitials in single-walled carbon nanotubes .................................................... 16
    1.4.4 Carbon atom displacement energy ........................... 17
    1.4.5 Stone-Wales defects ........................................ 18
    1.4.6 Irradiation-induced defects in multi-walled nanotubes and nanotube bundles ........................................... 19
    1.4.7 Annealing of irradiation-induced defects .................... 19
    1.4.8 Relationship between point defects in nanotubes and those in graphite ................................................. 21
  1.5 Electron irradiation of carbon nanotubes ...................... 21
    1.5.1 Electron irradiation of free-standing single-walled carbon nanotubes .................................................. 21
    1.5.2 Irradiation-induced links between single-walled carbon nanotubes in bundles ......................................... 22
    1.5.3 Electron irradiation of multi-walled carbon nanotubes ... 23
    1.5.4 Welding and coalescence of carbon nanotubes under electron irradiation ................................................. 25
    1.5.5 Engineering carbon nanotube structures with a focused electron beam .................................................. 27
  1.6 Ion irradiation of carbon nanotubes ............................ 28
    1.6.1 Experiments on heavy ion irradiation of carbon nanotubes 29
    1.6.2 Light ions: Proton irradiation of carbon nanotubes ....... 33
    1.6.3 Welding of nanotubes by ion beams .......................... 34
1.1 Introduction

Carbon nanotubes [1, 2] have unique electronic and mechanical properties [3] which can be used in many applications [3, 4] such as nanometer-scale electronic devices and reinforcement agents in composites. However, the as-grown nanotube material not always has the desired functionality. For example, nanotube samples are frequently produced as a mixture of nanotubes with different chiralities, and thus with different electronic structures: depending on how the nanotube was rolled up from the graphene sheet, it can be either metal or semiconductor, while nanotubes of a particular type are frequently required for the application.

Various post-growth modification methods have been suggested for tailoring the properties of the as-synthesized nanotubes [3]. Among them, modification of nanotubes properties by beams of energetic particles–ions [5–27], electrons [28–48] and even high-energy photons [49,50] has received much attention. Irradiation is widely used nowadays in the semiconductor materials science [51] for altering the properties of materials in a controllable manner by introducing, for example, dopant atoms [52, 53], patterning substrates (in particular for spatially selective growth of carbon nanotubes [54]) or creating defects which may improve on the operation of the device, as in GaAs nanostructures [55]. Thus it was tempting to try using irradiation for nanotube-based materials processing.

The experiments indeed showed that this approach is effective. This is an important and, from the viewpoint of the fundamental aspects of irradiation effects in solids, very interesting result, as nanotubes substantially differ from bulk carbon systems (graphite and diamond), not to mention metals or semiconductors. Beams of energetic particles may have either destructive or beneficial effect on the target properties, with the former being usually much stronger (recall that the research of irradiation effects in solids started due to the necessity to understand the material radiation resistance for nuclear technology). Thus, it was not clear a priori if irradiation could indeed have beneficial effects on nano-structured carbon systems.

Moreover, as irradiation allows one to produce defects in a controllable manner and monitor how the defects change the properties of nanotubes, experiments on irradiated nanotubes should also shed light on the role of native defects in these systems. Despite the prevailing conception of carbon nanotubes
1.1. INTRODUCTION

continues to be one of perfectly crystalline wires, recent experiments [56] on pristine single-walled nanotubes demonstrated that even high-quality nanotubes contain one defect per 4 micrometers on average. Although this defect density compares favorably to high-quality, silicon single-crystals, the presence of a single defect can have tremendous effects on mechanical and electronic properties of quasi-one-dimensional systems such as nanotubes.

Thus, a great body of work has been done to study the properties of defects in nanotubes and irradiation effects in the nanotube materials. An additional motivation for this was incomplete understanding of the behavior of graphite under intense irradiation. Although defects in graphite—a fission reactor material—have been studied since the 1950s, still there is no comprehensive microscopic picture of defect annealing and agglomeration in this material. Many early results [57] (for example, migration energies of point defects) turned out to be misinterpreted, as recent experimental [28, 29] and theoretical [58–61] studies showed. Due to their somewhat simpler structure (e.g., only one graphene layer in single-walled nanotubes), one can hope that irradiated nanotubes can help to better understand the nature of defects in graphite.

Recently, substantial progress in understanding the irradiation effects and properties of defects in carbon nano-materials was achieved. This was possible in part due to improvements on the resolution of the transmission electron microscopy and progress in computer atomistic simulations of the defects. The advantage of the transmission electron microscope (TEM) is that it makes it possible to create defects in situ and monitor their evolution in real time with atomic resolution at various temperatures. On the theoretical side, the advent of high-performance computers stimulated the development of computational tools for realistic simulations [62] of pristine and defected nano-structured carbon systems.

In this Chapter, we give a summary of the experimental/theoretical data on irradiation effects and related phenomena in carbon nanotubes. Since ion irradiation of nanotubes has received much less attention than electron irradiation (for the latter see, e.g., review articles [38, 63]), we pay particular attention to ion bombardment. We discuss the most promising applications of electron and ion irradiation of nanotube-based materials and outline the matters which still lack complete understanding while being important for further progress in this field. We do not describe in detail experimental techniques to produce and analyze the defects, nor we address computational methods used in theoretical studies. We also assume that the Reader is familiar with the atomic structure of nanotubes and the nomenclature (chiral indices) used to describe the nanotube structure in terms of the unit vectors of graphene [3].

The Chapter is organized as follow: In Section 1.2 we briefly review the interaction of energetic particles—electrons and ions—with carbon targets. A short overview of experimental techniques used to identify the defects in nanotubes and computational tools for simulating defect properties will be given in Section 1.3. In Section 1.4 we dwell on the most typical defects which appear in nanotubes under irradiation, as well as on native defects. Effects of electron irradiation on carbon nanotubes and electron-beam-assisted nano-engineering are discussed in Section 1.5, while Section 1.6 deals with ion irradiation of nanotubes. Throughout the Chapter, equal amount of attention will be given to experimental and simulation results. Finally, the influence of defects on the properties of nanotubes will be summarized.
1.2 Interaction of energetic particles with solid targets

As full understanding of irradiation effects in solids is not possible without the proper description of the target atom and energetic ion/electron collisions, a huge body of work has been done to develop a comprehensive theory of ion and electron stopping in solid targets [53, 64–67]. In this Section we briefly review the fundamentals of the interactions between the target atoms and energetic particles used nowadays for modifying the properties of materials. As we focus on nanotubes, we will illustrate the most important moments by the example of C targets.

1.2.1 Ion irradiation: stopping of energetic ions in solids

When an energetic ion\(^1\) penetrates a solid, it collides with the nuclei and the electrons of the target. For the ion energies typically used in materials science (lower/much lower than several hundred MeV), the slowing down of the ion can be separated into two different channels\(^2\): electronic and nuclear stopping.

The nuclear stopping originates from elastic collisions between the ion and the nuclei of atoms in the target, so that ion kinetic energy is partly transmitted to a target atom as a whole resulting in its translatory motion. The energy loss is determined by screened Coulomb interactions. A common feature for all ions is that the nuclear stopping is important only for relatively slow and heavy ions, see Fig. 1.1. When the target recoil atom acquires kinetic energy enough to leave its position in the atomic network, various atomic-scale defects may appear in the target. Most energy lost by the ion in a series of collisions (collision cascades) is eventually converted to heat due to defect recombination and annealing, but some of the defects may remain in the systems.

The electronic stopping is governed by inelastic collisions between the moving ion and the electrons in the target, which can be either bound or free. Many different physical processes contribute to the electronic stopping: ionization of the target atoms, generation of phonons due to the electron-phonon coupling, collective electronic excitations, e.g., plasmons, etc. Electronic stopping dominates at high ion energies, Fig. 1.1. Note also that for hydrogen (protons), electronic stopping always prevails.

Due to electronic excitations, the electronic structure of the target strongly affects the outcome of the ion impact. In metals the electronic excitations are delocalized due to the presence of conduction electrons. This makes the excitations less important, so that radiation damage comes mostly from knock-on atom displacements. In insulators (e.g., diamond [68]), excitations may result in local bond breaking, giving rise to the so-called “tracks”-amorphous regions which appear along the trajectory of the ion. As nanotubes are excellent heat and charge conductors [3], the radiation-induced changes in carbon nanotubes are dominated by knock-on atom displacements [38]. This appears to be true

\(^1\)Although the ion can be quickly neutralized by capturing electrons from the target, in what follows, the incoming particle is always referred to as “ion” to differentiate between the projectile and recoil atoms

\(^2\)For higher energies the contributions from nuclear reactions and relativistic corrections must be taken into account
1.2. INTERACTION OF ENERGETIC PARTICLES WITH SOLID TARGETS

For both metallic and semiconducting tubes, as the gap in the latter is quite small, around 1 eV.

It should be pointed out that applications of the conventional theory of ion stopping to nanosystems is somewhat questionable, as the theory is based on averaging over many collisions of the projectile with the target atoms, which is obviously incorrect for nano-objects. Besides this, the conventional separation of the ion energy loss into two components ignores the possible correlation between hard nuclear collisions and inelastic losses due to electronic excitations, which may be particular important for nano-objects. The inadequacy of the conventional approach to ion-nanosystem interactions has been demonstrated for fullerenes [69] and very thin targets [65]. Nevertheless, although some experimental observations still lack the explanation (See. Section 1.6.2), overall the conventional approach can be applied to nanotubes.

1.2.2 Electron irradiation: energy transfer from energetic electrons to the target atoms

The physics of collisions of energetic electrons with atoms in carbon nanostructured materials was recently reviewed by Banhart [38, 63]. Thus we keep the discussion of this subject to the minimum. The most important (from the viewpoint of defect production) channel of energy transfer from electrons to the target atoms are the ballistic collisions of the electrons with the nuclei. The collision time is very short as compared to the characteristic time of the atomic motion, the recoil atom essentially instantaneously acquires some kinetic energy, and the transferred energy $T$ can be expressed as

$$T = T_{\text{max}} \cos^2 \theta,$$

where $\theta$ is the angle between the initial direction of the electron motion and the direction of the scattered atom motion. The maximum energy is transferred in
a head-on collision (\( \theta = 0 \)), so the carbon recoil atom can acquire kinetic energy

\[
T_{\text{max}} = \frac{2E(E + 2m_e c^2)}{m_e c^2}
\]

(1.2)

where \( E \) is the electron energy, \( m_e \) and \( m_c \) are the masses of electron and C atom (nucleus), respectively, and \( c \) is the speed of light.

For low electron energies, or when \( \theta \) is not small (this corresponds to big impact parameters), the initial kinetic energy of the recoil atom is too small to create a defect, so the electron impact gives rise to atom vibrations, as the kinetic energy of the recoil is shared with other atoms. However, for the typical electron densities used in TEM during irradiation experiments (\( 10^2 \) – \( 10^3 \) A/cm\(^2\); note that the typical beam densities for imaging in TEM are much less, about \( 1 \) A/cm\(^2\)), heating effects are normally negligible (for carbon nanotubes): the transferred energy is dissipated into the environment before the new electron hits the atom neighborhood.

If after the electron impact the recoil C atom gets energy enough to leave its position in the atomic network (or, in other words, the recoil energy is higher than the displacement threshold energy \( T_d \approx 15 \) eV, see Section 1.4.4) atomic defects may appear.

The probability of scattering event is determined by the displacement cross-section \( \sigma \) [38,70]. This quantity is of high importance, as it provides information on how frequently, for a certain electron beam current density, the atoms are displaced. The cross-section depends on many parameters [38,70], in particular it is inversely proportional to \( T_d \). The production of defects in nanotubes under electron irradiation will be further discussed in Sections 1.4.1 and 1.4.4.

1.3 Experimental methods and theoretical tools to study irradiation-induced and native defects in carbon nanotubes

In this Section we briefly outline the experimental techniques used to analyze irradiation-induced and native defects in carbon systems. We also give a short summary of computational methods successfully employed for calculations of defect properties and defect production under irradiation.

1.3.1 Experimental identification of point defects in nanotubes

Native and irradiation-induced defects in carbon nanotubes can be detected by various experimental techniques.

The defects can directly be observed by scanning tunneling microscopy (STM) [18,71] and transmission electron microscopy (TEM) [28,29,38]. Even point defects can be imaged with the both methods. Scanning electron microscopy (SEM) makes it possible to detect irradiation-induced changes in the morphology of nanotubes (e.g., welding due to irradiation [8]), but this technique does not provide enough resolution to detect point defects.

One of most widely used techniques for defect identification in nanotubes is Raman scattering [9,12–14]: The ratio of the intensity of the so-called “D-band”
at around 1300 cm$^{-1}$ to the intensity of “G-band” at 1590 cm$^{-1}$ increases when defects are present, and satellite structures appear [12].

The signatures of defects can be detected with X-ray photo electron spectroscopy (XPS) [14–17] by monitoring changes in the C1s peak shape, which is very sensitive to the type of carbon bonding, and with the electron spin resonance (ESR) method [72].

Electronic transport measurements for individual nanotubes [5,11] and macroscopic nanotube samples [24,44] can provide useful, although indirect, information on irradiation-induced defects. A special technique based on selective electrochemical deposition and on probing the local electronic resistance of nanotubes was recently developed for identifying defects in carbon nanotubes [56].

At the same time, some of the standard techniques used for identification of defects in semiconductors [73] cannot be applied to nanotubes because of their nanometer scale and unusual structure. For example, positron annihilation can hardly be used due to the abundance of open space in the nanotube samples, so that positron-electron annihilation will more likely occur there rather than at irradiation-induced vacancies.

### 1.3.2 Computational tools for studying defect properties and defect production in carbon nanotubes

The standard program to evaluate the amount of damage produced by irradiation in a solid target is TRIM [74]. The code is based on the binary-collision approximation approach and uses statistical algorithms to calculate how the moving ion loses its energy in the target. Overall, the code gives reasonable numbers for various materials, including nano-structured carbon. However, TRIM can hardly be used for quantitative estimates of the radiation damage and defect distribution in nanotubes, as it treats the irradiated sample as an amorphous structure with a homogeneous mass density, which is obviously not relevant to highly anisotropic covalent systems like nanotubes. Besides this, only binary collisions between the ion and the sample atoms are taken into consideration, while many-atom effects should be important, especially during the thermalization of the system. Note also that the as-grown carbon nanotubes normally come as a network of tangled individual tubes [3] combined with amorphous carbon and catalytic particles (if catalyst was used during the growth). The average density of the material is usually much less than that of graphite, and fluctuations in the density are large, which complicates the use of TRIM.

Atomistic molecular dynamics (MD) simulations which involve numerical solution of the Newton equations of motion to determine the time evolution of a system of interacting particles [64,75] have provided lots of insight into the damage production in nanotubes under impacts of energetic ions and electrons and facilitated the interpretation of the experimental results. The interaction between the target atoms and the ion can be described at different levels of theory: empirical potential (EP), tight-binding (TB) and density functional theory (DFT) force models are normally used.

DFT-based and other first-principle ab initio methods [76] have a high accuracy but are computationally very expensive (simulations are normally limited to systems composed of a few hundred atoms and picosecond time scales), which makes the use of such methods in practice impossible for tackling some
irradiation-related problems, e.g., formation of defects under irradiation or direct dynamical simulations of defect diffusion. However, the DFT methods have successfully been used for calculating properties of defects.

Computationally cheaper TB [77] and EP [78–80] methods can be applied to considerably larger systems ($\sim 10^3$ and $10^6$ atoms respectively). The main difference between these two methods is that the EP energy is described by an analytical function of atom coordinates usually fitted to experimental data, whereas in the tight-binding method the energy is calculated by solving the Schrödinger equation for electrons in the field of atom cores, although the exact many-body Hamiltonian operator is replaced with a parameterized Hamiltonian matrix. The basis set usually is atomic-like so that it has the same symmetry properties as the atomic orbitals.

The drawback of the empirical approach is its low accuracy and transferability (the ability to describe systems different from those used for fitting the parameters). At the same time, although first-principles methods generally provide the best overall accuracy, the tight-binding approach is a reasonable compromise between the computational efficiency and the reliability of the model used.

In the following discussion, many examples of applications of the above methods to simulations of irradiation effects in nanotubes will be given.

1.4 Irradiation-induced and native defects in carbon nanotubes

Defects in nanotubes can appear either at the growth stage, or later on, during the post-growth treatment. Lots of damage is created during ion and electron irradiation. Similar to defects in bulk materials, the defects in nanotubes can conventionally be divided into point (atomic scale) defects such as interstitial-vacancy pairs and defects of higher dimensions: for example, the local change in the chirality can be interpreted as a dislocation [28].

Despite the similarities in the defect structure classification, the damage production in nanotubes is somewhat different from that observed in most other solids. Due to the open structure of the nanotubes, even recoils which have received energy only slightly above the threshold energy can be displaced quite far, which is in contrast to many other types of materials (e.g., in densely-packed metals a stable interstitial-vacancy pair is normally formed by a replacement collision sequence). There are many other peculiarities in defect production, as detailed below.

1.4.1 Simulations of defect production in carbon nanotubes under irradiation

Computer simulations [15, 41, 61, 81–112] of electron and ion irradiation of nanotubes proved to be a very useful tool for understanding the defect production mechanisms, relative abundance of particular types of defects and defect atomic structures. The simulations showed that if the energy of the impinging particle (electron or ion) is high enough, the collision of the particle with a carbon atom in a SWNT will result in displacement of the atom, i.e., formation of a vacancy
1.4. IRRADIATION-INDUCED AND NATIVE DEFECTS IN CARBON NANOTUBES

Figure 1.2: Molecular models of carbon nanotubes with point defects. (a) Short fragment of a single-walled nanotube with a vacancy (V) and a double-coordinated carbon atom (A) adsorbed onto the outer surface of the tube. These defects correspond to a Frenkel pair in nanotube samples. (b) Carbon adatoms in different configurations on a zigzag nanotube. (c) Stone-Wales topological defect associated with the rotation of a C-C bond. Thin lines correspond to the atomic network of the pristine tube.

(single- or multi- vacancies, see Figs. 1.2 and 1.6) and a number of primary recoil atoms which leave the tube. Energetic recoils can displace other atoms from the SWNT. The displaced C atoms frequently adsorb onto the tube walls, Fig. 1.2(a,b). These adsorbed atoms (adatoms) play the role of interstitials [81, 82] in nanotube samples. Notice that due to the quasi-one-dimensional morphology, all displaced atoms can be sputtered from the SWNT, so that no interstitial can exist in the system. Due to voids in the SWNT sample, the interstitial-vacancy (Frenkel pair) separation can be large preventing instant recombination even at modest energies of incident particles.

As for ion irradiation of isolated nanotubes, impacts of 50-3000 eV Ar ions onto SWNTs was modeled in [81, 82] by the EP MD method. The SWNTs were assumed to be suspended by their ends (such nanotubes can experimentally be manufactured [113]). It was found that single vacancies were the most prolific defects in nanotubes which appeared after ion impacts. Carbon adatoms on both external and internal sides of the nanotube walls were also common. Besides this, other complex defects like SW defects and amorphous regions were observed.

In order to quantitatively characterize the damage in the SWNT at different energies of incident Ar ions, the number of C atoms with a coordination other than three (recall that all carbon atoms in the intact nanotube are three-coordinated) is shown in Fig. 1.3 as a function of ion energy. When the energy of the incident ion is higher than the defect creation threshold energy (about 50 eV for Ar [81]), the number of defects increases with the energy up to roughly 600 eV, then it remains practically constant. The reason for such behavior is that at low energies the damage production grows with ion energy, since there is simply more energy available for it. At higher ion energies, although defect production in the SWNT drops as the nuclear collision cross section for de-
Figure 1.3: Average coordination defect numbers for irradiated single-walled nanotubes as functions of incident Ar ion energy. Full circles/squares stand for the number of C atoms with a coordination other than three for suspended/supported nanotubes. Open circles/squares are the corresponding coordination defect numbers after 100 ps annealing at 1500 K.

When a nanotube deposited on a substrate is irradiated, in addition to the damage created by the ion and primary recoils, the nanotube can be damaged by atoms sputtered from the substrate, which gives rise to an increase in the defect number. Annealing of defects decreased their amount by 20-50%, and the residual damage after annealing was practically independent of the substrate type.

Other aspects of damage production in SWNTs and MWNTs under ion
irradiation, as well as irradiation of more complicated nanotube-based systems were theoretically studied in Refs. [15, 90, 93, 94, 109–112].

As for electron irradiation, the impacts of energetic electrons onto nanotubes can be modeled [34, 41, 101, 109, 114] by assigning some kinetic energy to a carbon atom in the nanotube network (recall that the impact time is extremely short, well below femtosecond range [38], see also Section 1.2.2) and then by using the MD method to simulate the subsequent atom motion to understand if the impact results in the formation of a defect. The orientation of the initial velocity vector can be chosen either randomly if the main goal is to simulate the response of the system to a prolonged irradiation or in the direction [34] which will more likely result into the formation of a defect, if the defect formation energy is the quantity of interest.

![Figure 1.4: Average coordination defect numbers (the total damage) in single-walled nanotubes as functions of incident ion energy for various noble gas ions.](image)


### 1.4.2 Vacancies in carbon nanotubes

Unlike metals [115] where the structure of a vacancy is essentially a missing atom in the lattice, carbon nanotubes exhibit a strong reconstruction of the atomic network near the vacancy, which, as discussed below, results in many interesting effects, e.g. pressure build-up inside irradiated nanotubes [37, 116].

DFT and DFT-based TB calculations [61, 117–119] showed that single vacancies in nanotubes reconstruct by saturating two dangling bonds and forming a pentagon, see Fig. 1.6. In graphite, single vacancies reconstruct as well due to the Jahn-Teller distortion [59, 60, 89]. However, in nanotubes the reconstruction
Figure 1.5: Cross-section for the defect production in nanotubes as a function of incident ion energy for various ions. Reprinted from Ref. [93] A. V. Krasheninnikov and K. Nordlund, Irradiation effects in carbon nanotubes, Nucl. Instr. and Meth. in Phys. Res. B 216, 355 (2004), Copyright (2004), with permission from Elsevier.

Figure 1.6: Reconstructions of single and di-vacancies in a (6,6) armchair carbon nanotube. (a) The original non-reconstructed configuration which is unstable with respect to the Jahn-Teller distortion. (b) The lowest energy configuration. (c) A metastable configuration: the “pentagon bond” is parallel to the tube axis. (d) The atomic network with a non-reconstructed di-vacancy. (e) The lowest energy configuration for a di-vacancy.
1.4. IRRADIATION-INDUCED AND NATIVE DEFECTS IN CARBON NANOTUBES

is much stronger due to the curvature and inherent nano-size of the system: it is easier for the tube to contract locally to “heal” the hole and thus saturate energetically unfavorable dangling bonds. The curvature gives rise to a shorter bond in the pentagon (as compared to the bond in graphite) and a considerable drop in the vacancy formation energy $E_{sv}$, Fig. 1.7 ($E_{sv} \sim 7.5$ eV in graphite [59, 120]).

As curvature breaks the trigonal symmetry of the graphene sheet, the configuration when the new bond in the pentagon is parallel (or nearly parallel) to the tube axis is higher in energy as compared to the case when the bond is perpendicular to the axis, cf. Figs. 1.6 (b) and (c). Similar phenomena occur in nanotubes with other chiralities, and the energetics is affected by the orientation of the new bond.

Di-vacancies in nanotubes also reconstruct, see Fig. 1.6(d,e). One can expect the di-vacancy formation energy $E_{dv}$ in nanotubes to be smaller than the formation energy of two single vacancies, as there are no dangling bonds in the system. The di-vacancy formation energy $E_{dv} = 8.7$ eV in graphite [59] is indeed lower than twice $E_{sv} = 7.7$ eV. $E_{dv}$ was calculated [61] for armchair and zigzag nanotubes as a function of nanotube diameters (see Fig. 1.7). Similar to single vacancies, $E_{dv}$ decreases when the diameter becomes smaller, which can be understood in terms of the easier reconstructions of the nanotube atomic network. The diameter locally decreases, so no dangling bond or strongly strained bonds (typical for the case of graphite) are present. However, the most surprising is that for nanotubes is smaller than the formation energy of one single vacancy. Such behavior is inherently related to the nano size and the unique atomic structure of SWNTs, and is fundamentally different from most mono-atomic solids [121], including graphite [59]. Extrapolating the data presented in Fig. 1.7, one can assume that this is the case for nanotubes with diameters under 30Å or even larger. It is important that, unlike di-vacancies, single vacancies

Figure 1.7: Formation energies of single and double vacancies in armchair and zigzag nanotubes as functions of nanotube diameter as calculated by the tight binding and DFT methods [61].

As curvature breaks the trigonal symmetry of the graphene sheet, the configuration when the new bond in the pentagon is parallel (or nearly parallel) to the tube axis is higher in energy as compared to the case when the bond is perpendicular to the axis, cf. Figs. 1.6 (b) and (c). Similar phenomena occur in nanotubes with other chiralities, and the energetics is affected by the orientation of the new bond.

Di-vacancies in nanotubes also reconstruct, see Fig. 1.6(d,e). One can expect the di-vacancy formation energy $E_{dv}$ in nanotubes to be smaller than the formation energy of two single vacancies, as there are no dangling bonds in the system. The di-vacancy formation energy $E_{dv} = 8.7$ eV in graphite [59] is indeed lower than twice $E_{sv} = 7.7$ eV. $E_{dv}$ was calculated [61] for armchair and zigzag nanotubes as a function of nanotube diameters (see Fig. 1.7). Similar to single vacancies, $E_{dv}$ decreases when the diameter becomes smaller, which can be understood in terms of the easier reconstructions of the nanotube atomic network. The diameter locally decreases, so no dangling bond or strongly strained bonds (typical for the case of graphite) are present. However, the most surprising is that for nanotubes is smaller than the formation energy of one single vacancy. Such behavior is inherently related to the nano size and the unique atomic structure of SWNTs, and is fundamentally different from most mono-atomic solids [121], including graphite [59]. Extrapolating the data presented in Fig. 1.7, one can assume that this is the case for nanotubes with diameters under 30Å or even larger. It is important that, unlike di-vacancies, single vacancies

Figure 1.7: Formation energies of single and double vacancies in armchair and zigzag nanotubes as functions of nanotube diameter as calculated by the tight binding and DFT methods [61].

As curvature breaks the trigonal symmetry of the graphene sheet, the configuration when the new bond in the pentagon is parallel (or nearly parallel) to the tube axis is higher in energy as compared to the case when the bond is perpendicular to the axis, cf. Figs. 1.6 (b) and (c). Similar phenomena occur in nanotubes with other chiralities, and the energetics is affected by the orientation of the new bond.

Di-vacancies in nanotubes also reconstruct, see Fig. 1.6(d,e). One can expect the di-vacancy formation energy $E_{dv}$ in nanotubes to be smaller than the formation energy of two single vacancies, as there are no dangling bonds in the system. The di-vacancy formation energy $E_{dv} = 8.7$ eV in graphite [59] is indeed lower than twice $E_{sv} = 7.7$ eV. $E_{dv}$ was calculated [61] for armchair and zigzag nanotubes as a function of nanotube diameters (see Fig. 1.7). Similar to single vacancies, $E_{dv}$ decreases when the diameter becomes smaller, which can be understood in terms of the easier reconstructions of the nanotube atomic network. The diameter locally decreases, so no dangling bond or strongly strained bonds (typical for the case of graphite) are present. However, the most surprising is that for nanotubes is smaller than the formation energy of one single vacancy. Such behavior is inherently related to the nano size and the unique atomic structure of SWNTs, and is fundamentally different from most mono-atomic solids [121], including graphite [59]. Extrapolating the data presented in Fig. 1.7, one can assume that this is the case for nanotubes with diameters under 30Å or even larger. It is important that, unlike di-vacancies, single vacancies
always have a dangling bond, so that a perfect reconstruction around a single vacancy is not possible.

Saturation of dangling bonds and the local contraction of the nanotube also takes place for multi-vacancies [122]. Further reconstructions can occur by changing locally the atomic network, as in graphite [123]. Thus carbon nanotubes can be referred to as self-healing materials under irradiation. An additional piece of evidence for self-healing of irradiation-induced defects in nanotubes was recently obtained in experiments on controlled telescopic motion of MWNTs in a TEM [124].

1.4.3 Carbon adatoms as interstitials in single-walled carbon nanotubes

The adsorption of carbon adatoms onto nanotubes [91] and graphite [87] was recently studied by DFT-based methods. It was found that the adatom on the outer surface of the SWNT occupies the bridge position above the C-C bond. Similar to vacancies, due to the SWNT curvature the adatom adsorption onto sites above C-C bonds being parallel and perpendicular to the nanotube axis results in different adsorption energies and local atom arrangements, see Fig. 1.2(b). Adatoms inside the SWNT are displaced from the bridge position due to curvature-enhanced interactions with the neighbor atoms.

![Figure 1.8: Adsorption energies of carbon adatoms on armchair SWNTs as functions of tube diameter as calculated with a tight-binding method. The numbers stand for the tube chirality indices.](image-url)

In Fig. 1.8 the adatom adsorption energies are shown as functions of nanotube diameters for armchair SWNTs. For adatoms on the outer surface the absolute value of $E_a$ decreases with an increase in the SWNT diameter. This seems to be a general tendency: similar behavior of Al, H [125] and N [126] adatoms on SWNTs has been reported. The adsorption energy is always lower...
for configurations when the adatom is above the C-C bond oriented perpen-
dicular to the SWNT axis than for the "parallel" configuration. This can be
understood from simple carbon bonding considerations: in the "perpendicular"
case it is easier for the adatom to pull the two adjacent nanotube atoms apart
(notice that the bond is actually broken, thus avoiding the energetically unfa-
vorable four-coordinated atom configurations. Similar results were obtained for
zigzag nanotubes [91,92].

1.4.4 Carbon atom displacement energy

The dependence of vacancy formation energy on the tube diameter implies that
the carbon atom displacement energy $T_d$ in carbon nanotubes may also depend
on the nanotube diameter, that is on the curvature of the atomic network, and
nanotube chirality. Early experimental and theoretical studies [33,34] revealed
a strongly anisotropic threshold for atomic displacement, but did not report
any dependence on the chirality. It was shown that in an isolated SWNT with
a diameter over 1 nm, a lower energy (roughly half the value) is required to
displace a carbon atom into the direction perpendicular to the tube surface
($T_d \sim 15 - 17$ eV), than into the tangential direction (30-50 eV). This value
(perpendicular direction) was very close to the corresponding value for graphite
(15-20 eV) [38].

Later calculations [41,101] showed that for small nanotubes with diameters
less than 1 nm, $T_d$ indeed depends on the tube diameter and chirality. Fig. 1.9
shows $T_d$ as a function of tube diameter for armchair nanotubes. The energy was
calculated by a DFTB-based TB model dynamically (diamonds) and statically
(triangles). In the dynamical approach some kinetic energy was assigned to
a carbon atom in the nanotube network, then the MD method was used to
simulate the behavior of the system. $T_d$ was determined as the minimum kinetic
energy of the atom to escape from the system. In the static simulation setup,
$T_d$ was calculated as

$$T_d = E(N + 1) + E(N - 1) - 2E(N),$$

where $E(N + 1)$ is the total energy of the system with a carbon adatom, $E(N - 1)$
the energy of the system with a vacancy, $E(N)$ stands for the energy of
the perfect system composed of $N$ atoms. Physically, this expression gives
the energy of a spatially separated vacancy-interstitial pair, which is obviously
related to the formation energies of single vacancies and adsorption energy of
carbon adatoms.

The static approach gives the lower bound on $T_d$, while the dynamical ap-
proach likely overestimates the value [101]. Independent of the absolute value
of $T_d$ (the true value should be somewhere in between the two bounds), both
simulation setups showed that $T_d$ is less for nanotubes with smaller diameters,
which can be related to the curvature-induced strain in the nanotube atomic
network.

By setting $T_d = E_{max}$ in equation 1.2, one can estimate the minimum in-
cident, or threshold, electron energy for damage production in nanotubes un-
der electron irradiation. For graphite and nanotubes with large diameters the
threshold energy is around 80 keV, which agrees well with the experimental
value [33] of 86 keV.
Knowing $T_d$ one can also estimate the threshold energy $E_{th}$ for impinging ion through a simple head-on binary collision approximation formula:

$$T_d = \frac{4m_cm_I}{(m_c + m_I)^2} E_{th} \quad (1.4)$$

where $m_I$ is the energy of the ion, $m_c$ is the mass of a carbon atom. This would be a lower bound on the energy, as a part of the energy is always transferred to the atoms neighboring the recoil atom.

### 1.4.5 Stone-Wales defects

Along with vacancies and interstitials (one atom is missing or one extra atom in the system), defects of another type may exist in nanotubes: the pentagon/heptagon Stone-Wales (SW) defects [127] associated with a rotation of a bond in the nanotube atomic network, Fig. 1.2(c). Note that the number of atoms is the same as in the pristine network, and that all atoms are three-coordinated, so we have an example of the topological disorder.

SW defects can appear in nanotubes after impacts of energetic ions [82] and electrons [41, 101]. These defects are also thought to be responsible for the release of excessive strain under axial mechanical load of nanotubes [128–130]. The formation energy of SW defects proved to be dependent on the tube diameter and chirality [131,132], analogously to other point defects. Overall, MD simulations showed that the concentration of SW defects after impact of energetic ions [81,82,88,90] and electrons [101] is much smaller than those for adatoms and interstitials.
1.4.6 Irradiation-induced defects in multi-walled nanotubes and nanotube bundles

In addition to the simple point defects, a number of more complex defects can be formed in MWNTs and bundles of single-walled nanotubes. An important example of these defects are inter-shell covalent bonds (formed e.g. by two dangling bonds at the vacancies in the adjacent shells) in MWNTs, see Fig.1.10(a). Likewise, defect-mediated covalent bonds between adjacent SWNTs in the bundle can appear, Fig.1.10(b). The bonds can be due to vacancies or the so-called Wigner defects [133], a metastable atom configuration formed by a vacancy and a nearby interstitial. The behavior of these complex irradiation-induced defects is governed in part by annealing and diffusion of original defects—vacancies and interstitials. As shown below, these defects heavily affect the mechanical properties of the nanotubes.

High irradiating doses eventually amorphize the tubes, Fig.1.10(c).

![Figure 1.10](image-url)

Figure 1.10: Irradiation induced links between nanotubes. (a) A covalent bond between two nearby vacancies in the adjacent shells of a MWNT. (b) Covalent bonds between SWNTs in a nanotube bundle. (c) The atomic network of a MWNT before and after 300-eV Ar ion irradiation with a dose of $2 \times 10^{16}$ cm$^{-2}$ as simulated with empirical potential molecular dynamics.

1.4.7 Annealing of irradiation-induced defects

Experiments on electron [38] and ion [134] irradiation of both SWNTs and MWNTs indicate that much of irradiation-induced damage in nanotubes can be annealed in situ at temperatures higher than 300°C. Fig. 1.11 shows a TEM image of a multi-walled nanotube after electron irradiation at room temperature (a) and at 700°C (b). It is evident that the number of defects is much higher for the former tube. Thus radiation damage in nanotubes can be avoided at relatively high temperatures. Note that in most common FCC metals, close Frenkel pairs annihilate at or even below room temperature, [135].

Two mechanisms govern the defect annealing [82]. The first mechanism is vacancy healing through dangling bond saturation and by forming non-hexagonal
rings as described in Section 1.4.2.

The second mechanism of annealing is the migration of carbon interstitials and vacancies, followed by Frenkel pair recombination. The interstitial can migrate over the surface of SWNTs (isolated or bundled-up). Early calculations [136,137] indicated that the adatom migration energy $E_{m}^{(a)}$ is very low, but more rigorous recent results [87,91] give higher values (0.5 – 1 eV; the actual value depends on the tube diameter and chirality), which is in a good agreement with experimental values of $E_{m}^{(a)} \sim 0.8$ eV [138]. Very recent direct observations of the migration of individual point defects in nanotubes [29] and nano-scale graphite species [28] are also in line with the theoretical results. Interstitials (adatoms) inside SWNT and hollow cores of MWNTs are highly mobile, with the migration energy of 0.1-0.4 eV (depending on the diameter and chirality of the tube) [41]. Migration of interstitials in the open spaces between the adjacent shells in MWNTs seems to be similar to that in graphite, and further studies are required to determine the migration energy of interstitials in MWNTs more accurately, see Section 1.4.8.

![Multi-walled nanotube after electron irradiation at room temperature (a) and at 700°C (b). Courtesy of F. Banhart.](image-url)

Recent simulations [61] showed that the vacancy migration energy $E_{m}^{(v)}$ is above 1 eV, larger than $E_{m}^{(a)}$. Nevertheless, single vacancies should be mobile already at 200°C. Besides annihilating with interstitials, single vacancies will form di-vacancies which are practically immobile at temperatures under 1000°C, or disappear at the open ends of the tubes.

As for SW defects, the annealing should result in the restoration of the perfect atomic network, especially if an extra carbon adatom (which works as the catalyst for the transformation thus substantially reducing the defect annihilation barrier) is nearby [139].

It is important that the efficient annealing occurs only when the temperature is high during the irradiation. Irradiation at lower temperatures and subsequent annealing does not fully remove the radiation damage, probably due to low mobility of big defect clusters formed during low-temperature irradiation.
1.4.8 Relationship between point defects in nanotubes and those in graphite

The atomic structure of carbon nanotubes is closely related to that of graphite. As graphite is an important moderator material in fusion reactors, point defects in graphite have repeatedly been studied both experimentally [57,140,141] and theoretically [58–60, 87, 89, 120, 142, 143]. Based on the results of early experiments on defect migration in graphite, it was argued that the carbon interstitial forms no bonds with the atoms in the lattice, and it can easily migrate in the hollow regions between the graphene layers with an activation barrier of 0.1 eV [57]. Contrary to the above, recent theoretical calculations demonstrated that interstitials [120] and adatoms [87,136,143] form covalent bonds with atoms in graphene planes and diffuse with a migration barrier of around 1.5 eV [120] and 0.4 eV [87], respectively.

For vacancies, the interpretation of indirect experiments carried out mostly in the sixties assigned single vacancies a migration barrier of around 3 eV [57]. Again, the results of calculations differ, predicting a barrier of around 1.6 eV [59,142], much less than the experimental value.

The discrepancies in the migration energies come, on the one hand, from the uncertainties in the interpretation of the results of indirect experiments (for example, it is not clear which particular type of defects can be associated with the annealing peaks). On the other hand, the conventional DFT theory with the local density approximation (LDA) and generalized gradient approximation (GGA) functionals for exchange and correlations does not properly take into account van der Waals-type interactions between graphite layers (see the discussion in [144] and references therein), which may be important for defect migration in layered materials.

As SWNTs have a simpler structure than graphite, simulations and direct experimental probing of individual point defects in nanotubes by the TEM should provide lots of valuable information on the behavior of point defects in graphite.

1.5 Electron irradiation of carbon nanotubes

Effects of electron irradiation on the structure and properties of carbon nanotubes have been studied [30–33,38] mostly in the transmission electron microscope, as the TEM can not only create the damage in nanotubes by energetic (up to 1.25 MeV) electrons in a controllable manner but also monitor the irradiation-induced changes in situ. Moreover, as in modern electron microscopes with field emission guns the electron beam can be focused onto areas of several Angstroms, the nanostructures can selectively be modified on the atomic scale by displacing or removing atoms from pre-defined regions. In addition to the TEM, carbon nanotubes have been irradiated by energetic electrons in a Van der Graaff electron accelerator operating at 2.5 Mev [72].

1.5.1 Electron irradiation of free-standing single-walled carbon nanotubes

Early experiments [31] showed that SWNTs exposed to focused electron irradiation were locally deformed and developed neck-like features due to removal of
carbon atoms by knock-on displacements. Uniform irradiation of SWNTs [32] resulted in surface reconstructions and drastic dimensional changes, as a corollary of which the apparent diameter of the nanotubes decreased from 1.4 to 0.4 nm, and finally the tube broke, see Fig. 1.12. The reason for these transformations is saturation of dangling bonds at vacancies on the walls of the SWNTs created by energetic electrons, see Section 1.4.7.

Experimental and theoretical studies also demonstrated that the electron beam creates defects non-uniformly: when the electron energy is not very high (slightly above to the threshold energy) carbon atoms are most rapidly removed from surfaces lying normal to the beam direction [33–35]. For higher energies, large-angle scattering dominates because of a higher cross-section. The anisotropy in damage production was shown [35] to afford the ability to selectively modify the nanotube structure even with a uniform irradiation: for example, tangential irradiation of edge-on flattened nanotubes produced micron-long carbon ribbons [35].

Figure 1.12: Controlled electron irradiation of a single-walled nanotube segment bridged between a hole in a carbon grid. The diameter of the original nanotube (a) is approximately 1.4 nm. The tube has shrunk drastically in diameter during the irradiation. Image in (f) shows the smallest diameter (∼0.4 nm) that was visible before the tube broke (g). Reprinted with permission from Ref. [32], P. M. Ajayan, V. Ravikumar, and J.-C. Charlier, Phys. Rev. Lett. 81, 1437 (1998). Copyright (1998) by the American Physical Society.

1.5.2 Irradiation-induced links between single-walled carbon nanotubes in bundles

High dose electron irradiation of SWNT bundles in the TEM gave rise to gradual amorphization of the nanotubes with the irradiation dose [30]. At moderate doses, however, irradiation resulted in a dramatic increase (1-2 orders of magnitude) in the bundle bending modulus $E_b$, as measured by the AFM. As the bending modulus is related to the shear modulus (proportional to the force required to move a tube in the bundle with respect to other tubes), this was interpreted in terms of irradiation-mediated covalent bonds. Early empirical potential MD simulations [85] predicted formation of such bonds under ion irradiation, see Fig. 1.10(b), so one could expect that similar bonds could appear
due to interactions of the nanotubes with energetic electrons. The structure of the bonds was theoretically studied at length by \textit{ab initio} methods \cite{133}.

Experiments \cite{30} showed that at irradiation doses over $50 \times 10^{20} \text{ e/cm}^2$ the bending modulus started decreasing, which was understood in terms of the damage accumulation in SWNTs, and thus, a drop in the Young (axial) modulus of individual tubes \cite{97, 100}. It is interesting that the increase in the bending modulus was observed at not only high (200 keV) electron energies (above the threshold) but also at energies under the threshold (80 keV). This observation may be explained by the presence of SWNTs with small diameters in the bundle, and thus lower threshold energies required to displace C atoms and form links, see Section 1.4.4, or by cross-links originating from irradiation-mediated chemical reactions between nanotubes and carboxyl groups \cite{30}.

Another piece of evidence for irradiation-induced links between SWNTs in the fibers was obtained by measuring \textit{in situ} the electrical properties of nanotubes irradiated in the TEM \cite{44}. The resistivity of the irradiated SWNT-bundles assembled to a macroscopic fiber was measured as a function of irradiation dose. A minimum was found, which, similar to mechanical measurements \cite{30}, can be interpreted as an interplay between two effects of irradiation: formation of covalent bonds enhancing inter-tube conductance and amorphization of the sample at high doses, which decreases the conductivity of each tube.

1.5.3 \textbf{Electron irradiation of multi-walled carbon nanotubes}

Similar to SWNTs, electron irradiation of MWNTs at room temperature resulted in the formation of vacancies on their walls and eventual amorphization upon high-dose irradiation \cite{38, 45}, see Fig. 1.11(a). In general, MWNTs seem to be more stable under electron irradiation than SWNTs \cite{38} because the atoms sputtered from inner shells remain in the MWNT and Frenkel pairs created inside the MWNT can easily recombine. The irradiation-induced damage manifested itself in the deterioration of mechanical properties of MWNTs exposed to prolonged 2-MeV electron irradiation \cite{45}. It also affected the electronic properties of the tubes near the Fermi level, as assessed by electron spin resonance \cite{45, 46}.

High-dose irradiation of MWNTs at high (600$^\circ$C) resulted in very interesting effects. Fig. 1.13 shows the structural evolution of a MWNT under the electron beam. Intense irradiation (several hundred A/cm$^2$) led to almost spontaneous shrinkage of all shells and collapse of the tube. Surprisingly, all shells remained temporarily intact (no breakage or disintegration) although material was lost (the surface area was decreasing). However, when the collapse proceeded, the innermost shell finally disintegrated. During the collapse, an aggregation of material in the shape of irregular graphitic cages occurs in the hollow core just outside the irradiated area, Fig. 1.13(b-d). The initially cylindrical structure collapsed into a morphology of a double cone. As soon as the collapse was complete (the innermost tube had a diameter of a typical SWNT), an unexpected morphological evolution was observed, Fig. 1.13. Whereas the outer shells shrank but remained undamaged, the inner shells were successively broken until a SWNT in the center was left. It is always the innermost layer which breaks in such a way that the two halves form cones with closed caps. The cone from the innermost tube moved outwards (in axial direction), and the cones from the other shells move up. Eventually, the last remaining shell broke so
Figure 1.13: Morphological evolution of a multi-walled carbon nanotube under electron irradiation. An electron beam with a diameter of 15 nm and a beam current density of approximately 450 A/cm$^2$ was focused onto the central part of the tube. Irradiation time: (a) $t = 0$ (starting point); (b) $t = 150$ s; (c) $t = 300$ s; (d) $t = 800$ s. Specimen temperature: 600°C. Reprinted with permission from Ref. [41] F. Banhart, J. X. Li, and A. V. Krasheninnikov, Phys. Rev. B 71, 241408(R) (2005). Copyright (2005) by the American Physical Society.

Figure 1.14: Central part of a collapsing tube showing the successive loss of shells in detail. Electron beam diameter: 18 - 28 nm (increased deliberately from (a) to (d)); corresponding beam current densities: 155 - 65 A/cm$^2$; irradiation times: (a) $t = 0$ (starting point); (b) $t = 540$ s; (c) $t = 1400$ s; (d) $t = 2000$ s; specimen temperature: 600°C. The 3-shell tube in (a) was generated by transforming a bundle of SWNTs into a MWNT under electron irradiation. The caps closing the ends of the shells are arrowed. Reprinted with permission from Ref. [41]. F. Banhart, J. X. Li, and A. V. Krasheninnikov, Phys. Rev. B 71, 241408(R) (2005). Copyright (2005) by the American Physical Society.
that two separate multi-shell cones were left (not shown in the figures). Such a behavior was explained [41, 101] in terms of a lower stability of the inner shells under irradiation due to a higher curvature of the atomic network (see Section 1.4.4) and fast diffusion of carbon interstitials through the inner hollow in the axial direction.

Concurrently with the experiments [41, 101] on electron irradiation of MWNTs with many shells, qualitatively similar results [29] were obtained for double walled nanotubes at different temperatures, see Fig. 1.15. Efficient annealing of the radiation damage due to interstitial migration along the inner hollow indicated that carbon nanotubes can be used as pipes for effective transport of interstitial carbon and foreign atoms.

Figure 1.15: Sequential TEM images for the formation rates of the interlayer defects at different temperatures with the same time scale (0 to 220 s). (a) At 93 K, the defects due to electron irradiation are quite prolific, and the nanotube inside quickly damages due to the complex defects. (b) At 300 K, the nanotubes are more resistive but the defects can also be found frequently. (c) At 573 K, the defect formation can hardly be seen and the DWNTs are completely resistive due to the electron beam irradiation. The arrows indicate possible interlayer defects. Scale bar 2 nm. Reprinted with permission from Ref. [29]. K. Urita, K. Suenaga, T. Sugai, H. Shinohara, and S. Iijima, Phys. Rev. Lett. 94, 155502 (2005). Copyright (2005) by the American Physical Society.

1.5.4 Welding and coalescence of carbon nanotubes under electron irradiation

Observations of the saturation of irradiation-induced dangling bonds in carbon nanotubes, combined with the inherent ability of carbon atoms to form structures with different coordination of the atoms, opened new ways for electron-beam-assisted engineering of carbon nanotubes at high temperatures.

The coalescence of two parallel SWNTs under electron irradiation was demonstrated at 600 – 800°C [36]. These transformations were found to proceed due to vacancies via a zipper-like mechanism, imposing a continuous reorganization of atoms in individual tube lattices along adjacent tubes. The electron-beam-
induced coalescence of nanotubes may, in principle, be employed for improving on the control over the nanotube diameter distribution.

Irradiation of crossed SWNTs in the TEM was shown [42] to give rise to nanotube welding. Various stable “X”, “Y” and “T” junctions were created, see Fig. 1.16. Two crossed pristine tubes would not normally join, even at high temperatures, as the structure of the junction containing non-hexagonal rings and strongly distorted bonds is less stable than the two perfect tubes. However, irradiation-induced vacancies and energy gain by dangling bond saturation made it possible to weld the tubes together. This results suggest that it may now be possible to fabricate nanotube networks by growing crossed nanotubes or moving they mechanically followed by controlled electron irradiation at high temperatures. The use of a highly localized electron beam with diameters of several nanometers and high temperature annealing of the samples after irradiation should minimize the damage outside the junction area, which is particularly important for applications of SWNT-based circuits in nano-electronics. Simulations [114] showed that the welded nanotube structures should be mechanically stable in spite of many defects near the contact area.

Electron irradiation can also be used to fuse together the fullerenes inside carbon nanotubes (peapods) [145,146]. The resulting structures consisted of corrugated tubules nested inside the original SWNT. These carbon nanostructures exhibited pentagonal, hexagonal, heptagonal, and octagonal rings and resembled the theoretically proposed Haeckelite structures [147].

Besides carbon nanotubes, irradiation-mediated fusion of fullerenes was im-
1.5. ELECTRON IRRADIATION OF CARBON NANOTUBES

implemented inside boron-nitrogen nanotubes [148]. As a result, a carbon nanotube was obtained inside the BN nanotube. Because BN nanotubes are insulating, the use of the electron beam for producing such structures (a metal wire inside insulating) opens new ways for making complex nano systems with predetermined electrical properties.

1.5.5 Engineering carbon nanotube structures with a focused electron beam

The structure and the shape of nanotubes can be further tailored by electron irradiation with a focused electron beam (just a couple of nanometers in diameter) and at high temperatures.

MWNTs irradiated with an electron beam of the size roughly equal to the tube wall thickness were shown [43] to bend due to the removal of carbon atoms from one side of the tube 1.17. The bending angle could be controlled precisely by the irradiation dose. The changes in the shape apparently originated from the saturation of dangling bonds at the cut.

Figure 1.17: Multi-walled carbon nanotube under spatially-localized electron 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, (d) 11 min, (f) 15 min. Beam current density 10^3 A/cm^2. Courtesy of F. Banhart.

The irradiation of a SWNT bundle with an electron beam of 20 nm in diameter resulted [43] in the collapse of the bundle in the irradiated area followed by graphitization and transformation of SWNTs into a MWNT, see Fig.1.18. In such a way a coherent junction between SWNTs in the bundle and a MWNT can be created.

Experiments [40] also showed that bundles of SWNTs could be cut by the electron beam, see Fig. 1.19 either partly or completely. The cutting speed was obviously determined by the beam intensity, and surprisingly, by the existence of close cuts. For example, the cutting speed decreased when the cut
reached the tubes that had been cut from the other side of the tube, as in Fig. 1.19(d). As the ends of the tubes at the cuts are normally closed, this observation could be interpreted as an evidence for efficient migration of interstitials inside SWNTs: if the tube was closed by a cap, the interstitials could no escape from the irradiated area and thus the defect annihilation rate was higher. Note that the nanotubes were cut due to ballistic collisions of energetic electrons with nanotube atoms, but not by electron-beam-stimulated chemical reactions in the presence of gaseous species like water molecules, as in [149].

Other aspects of electron-beam engineering were addressed in [47, 48]. In particular, it was shown [47] that electron beam can be used to puncture carbon nanotubes with nitrogen molecules inside and to produce amorphous CN$_x$ islands. As for electron irradiation of nitrogen-doped nanotubes, very recent simulations [107] indicate that the dopant nitrogen atoms can be displaced more easily than the host carbon atoms. Thus spatially localized electron irradiation of N-doped nanotubes can be used for local atomic and band structure engineering by selectively removing N atoms from the predetermined areas. Likewise, this approach can also be used for the local atomic and band structure engineering of nanotubes with nitrogen-molecule-functionalized groups [150], and for B-C-N nanotubes [151, 152].

### 1.6 Ion irradiation of carbon nanotubes

Depending on the ion mass, the ions used in materials science for irradiation and implantation are traditionally split into two categories: light and heavy ions.
1.6. ION IRRADIATION OF CARBON NANOTUBES

Figure 1.19: Image series (a-c) shows the cutting of a gap in a bundle of SWNTs by moving a focused electron beam across the bundle. Cutting the second gap in that same bundle (d). Complete sectioning of the bundle (e). Courtesy of F. Banhart.

Normally H, He and sometimes Li ions are referred to as “light”, while ions of other chemical elements are treated as “heavy”. Another important parameter is the irradiation dose. One can define “low dose” as the dose corresponding to the situation when the defected regions created by different ions do not overlap. Conversely, “high dose” irradiation means that many ions hit the same microscopic area of interest.

1.6.1 Experiments on heavy ion irradiation of carbon nanotubes

High-dose irradiation

Early experiments on heavy ion irradiation of MWNTs with diameters of about 10 nm with 3 keV Ar ions followed by X-ray photo electron spectroscopy and TEM probing [16] demonstrated that the bombardment resulted in the appearance of carbon dangling bonds, which can be understood in terms of single- and multi-atom vacancies. A gradual amorphization of the carbon network was reported, and for maximum irradiation doses used (more than $10^{19}$ ions/cm$^2$) MWNTs with originally hollow cores transformed to nano-rods composed of amorphous carbon. The amorphization of MWNTs by 3 keV Ar ions was achieved in [19] with a much lower irradiation dose of $4 \times 10^{16}$ ions/cm$^2$.

Although the first experiments reported essentially destructive effects of irradiation on nanotubes, later works provided evidence that heavy ion irradiation can be used in a creative way.

Irradiation of arc-evaporated MWNTs with 30 and 50 keV Ga ions resulted in very interesting structural transformations in the nanotubes [7]: For 50 keV ions with doses of $\sim 10^{13}$ ions/cm$^2$ the outer shells of the MWNTs remained intact, while the inner layers reorganized into highly ordered pillbox-like nanocompartments with diameters of about 5 nm and of varying lengths between 2 and 20 nm, see Fig. 1.20. Increasing the dose to $10^{14}$ ions/cm$^2$ resulted in
the gradual disordering of the graphitic shells and destroyed the nano-capsules, while at doses of about $10^{15}$ ions/cm$^2$ the graphitic shells collapsed into the hollow, resulting in the formation a homogeneous amorphous rod. Irradiating nanotubes with 30 keV ions gave similar results, but at higher doses.

The formation of similar bamboo-like structures in MWNTs irradiated with 4 MeV Cl$^{2+}$ ions with a dose of $3 \times 10^{16}$ ions/cm$^2$ was reported [20] as well. In addition to the changes in the shape of the tubes, irradiation resulted in their swelling, as a result of which the average diameter of the tubes increased from 70 to 180 nm possibly due to intercalation of Cl atoms and due to defect-mediated changes in the atomic structure. Both Ga and Cl ion high dose irradiation fully amorphized the samples as evident from the TEM images, as well as from growing resistance of the tubes and increase in the area ratio of D-peak to G-peak in the Raman spectra [20].

Self-irradiation with 100 eV C$^+$ ions was used for making nanotube-amorphous diamond nano-composites [21] in which conducting mats of SWNTs were protected against wear by 50-nm amorphous diamond films. Experiments also indicate that magnetized-plasma ion irradiation can be used for encapsulating fullerenes [153] and intercalating cesium inside SWNTs [154] via irradiation-induced defects in the tube walls.

10 and 30 keV focused beams of Ga ions were shown [8] to be able to thin, slice, and alter the structure and composition of MWNTs at precise locations along the nanotube axis. This strategy of harnessing ion-beam-induced defect generation and doping could be attractive for modulating chemical and electrical properties along the nanotube length, and fabricate nanotube heterostructures and networks for device applications.

An interesting irradiation-assisted way for manufacturing nanotube networks consisting of perfectly straight and suspended structures was demonstrated in [12]. SWNTs grown suspended between pillars of Si/SiO$_2$ structures were
irradiated with 30 keV Ga$^+$ ions. The typical ions dose was around $1.5 \times 10^{14}$ ions/cm$^2$. The nanotubes were straightened by ion beam scans. In addition, the ion irradiation selectively removed nanotubes lying on the substrate, leaving the suspended nanotubes in place. Although ion irradiation induces structural modifications to nanotubes and introduces defects into the nanotube lattice, the form and dimensions of the nanotubes remained close to that of the original structures.

Irradiation-induced enhancement in the field emission properties of nanotubes was reported in [13]. Argon irradiation treatment straightened as-grown curly nanotubes, see Fig. 1.21, similar to Ga ion irradiation [12]. As a result, the local electric field was enhanced due to the increased aspect ratio and reduced mutual shield effect. Additional contribution may have come from irradiation-induced defects, which made nanotube effective surfaces more active, thus emitting more electrons.

![Figure 1.21: SEM images of nanotubes before (a) and (b) after Ar ion irradiation. Reprinted from Ref. [13]. D.-H. Kim, H.-S. Jang, C.-D. Kim, D.-S. Cho, H.-D. Kang, and H.-R. Lee, *Enhancement of the field emission of carbon nanotubes straightened by application of argon ion irradiation*, Chem. Phys. Lett. 378, 232 (2003), Copyright (2004), with permission from Elsevier.](image)

As for the beneficial effects of ion irradiation on nanotube electronic properties, spatially localized Ar ion irradiation (with doses up to $\sim 10^{16}$ ions/cm$^2$) of individual MWNTs deposited on SiO$_2$ substrates was used [10] to create a defective region which worked as a potential tunnel barrier for electrons in the MWNT. A fast increase in the tube resistance with the irradiation dose was reported. It was demonstrated that a double-barrier structure fabricated by such method can work as a quantum dot. However, the types of defect and their spatial distribution were not identified, although knowing this is important for understanding the Coulomb oscillations observed in the system and how the current flows through the damaged MWNT shells. Spatially localized ion irradiation was also used for the fabrication of a single-electron inverter in MWNTs [11].

As irradiation-induced defects normally increase the reactivity of nanotubes (e.g., due to dangling bonds at the surface defects), focused-ion-beam irradiation, followed by mild chemical treatment, was used to functionalize nanotubes.
at preselected locations \[9\]. The bombardment with Ga ions having energies of 10-30 keV and with irradiation doses of \(~ 10^{15} - 10^{17}\) ions/cm\(^2\) resulted in the desired effect. Controlled chemical modification was also achieved with 2 keV argon ions \[14\], but at much smaller doses of about \(~ 10^{13}\) ions/cm\(^2\). The lower doses may, however, give a comparable number of surface defects, as the production of defects at the nanotube surface should drop with increasing ion energy, see Section 1.4.1.

### Low-dose irradiation

Effects of single ion impacts on the atomic structure and properties of nanotubes can be studied by low-dose ion irradiation combined with other techniques which can detect signatures of irradiation-induced defects.

MWNTs dispersed on graphite substrate were irradiated with 30 keV ions with a dose of around \(10^{11}\) ions/cm\(^2\) \[18\]. STM measurements carried out under ambient conditions revealed hillock-like protrusion on the nanotube walls (Fig. 1.22), which were associated with individual vacancies, in agreement with the theoretical predictions \[81, 86, 106\]. Annealing in nitrogen atmosphere of the irradiated samples at 450\(^\circ\)C demonstrated that defects in nanotubes tend to heal already at moderate temperatures, which was in line with the TEM results \[38\].


Low dose irradiation of individual SWNTs with 120 eV Ar ions (this energy is just above the threshold to produce defects in SWNT, see Section 1.4.1) and electronic transport measurements on the irradiated nanotube made it possible to assess the effect of individual defects on nanotube conductance \[5\]. At such low energies, irradiation with Ar ions should result in the formation of single and double vacancies, which gave rise to a dramatic drop in the conductance of the nanotube. Theoretical transport calculations showed that mostly divacancies contribute to the resistance increase and that just a 0.03% of divacancies produced an increase of three orders of magnitude in the resistance of
a 400 nm long SWNT.

The impact of low-dose (∼ 10^{12} ions/cm^2) ion irradiation on bundles of SWNTs was experimentally studied as well [6]. The bundles were irradiated with an 500-eV Ar^+ ion beam followed by transport measurements. The results suggest that irradiation gives rise to current re-distribution between the damaged and undamaged tubes in the same rope, which can be interpreted as evidence for the formation of irradiation-mediated links between individual SWNTs in the bundle. The links appear to be of the same origin as the inter-tube links in electron-irradiated nanotube bundles [30, 44]. The formation of covalent bonds between bundled-up nanotubes under impacts of low energy (below 50 eV) CF^+_3 ions was also reported [15]. The cross-links, however, should appear only near the bundle surface at such low ion energies.

1.6.2 Light ions: Proton irradiation of carbon nanotubes

Several experiments [22–25] on irradiation of SWNTs with high-energy (a couple of MeV range) protons were recently carried out. Both purified SWNTs [22, 23] and those assembled as a nanotube “Bucky” paper (NBP) [155–157] representing a highly interconnected network of SWNT bundles [24] were irradiated. Effects of proton irradiation on nanotubes embedded into a polymer matrix were studied as well [25]. In addition to fundamental aspects of energetic proton interactions with highly anisotropic carbon-based nano-materials, the interest in the response of nanotubes to proton irradiation was stimulated by the possible use of nanotubes in space applications, in particular as components of solar cells [24].

SWNTs deposited onto TEM grids for subsequent analysis were irradiated [22] in air at room temperature with 3 MeV protons with doses ranging from 6 µC to 0.72 mC, or correspondingly, from \(1.2 \times 10^{13}\) to \(3 \times 10^{16}\) protons/cm^2 (the beam diameter was reported to be 4 mm). Evident morphological changes such as curving of SWNTs and formation of short pieces were observed at doses of about 0.1 mC. Further irradiation resulted in nearly full amorphization of the nanotubes (a significant fraction of the tubes were still present as pieces of different lengths). Based on the results of the experiments, it was concluded that for the typical near-Earth space condition during “quiet sun” periods (typical proton energies of around 1 GeV, much lower fluxes) SWNTs will undergo no detectable alterations for practically unlimited time.

A 0.5 µm-thick SWNT film and a similar one placed below a 16.75 µm Xe film were irradiated at 15 K with 1 MeV protons [23]. The maximum irradiation doses were \(9.6 \times 10^{14}\) and \(5.5 \times 10^{14}\) protons /cm^2, respectively. The analysis of the irradiated samples done by Fourier transform infrared and Raman spectroscopy evidenced formation of CH bonds and defects in nanotubes, accompanied by some changes in nanotube diameters.

Effects of proton irradiation on optical properties of SWNTs matrixed in poly(3-octylthiophene) were investigated [25] by an optical absorption technique. Two inter-band transitions were observed, at 0.71 and 1.28 eV in a sample that was subject to 2 MeV proton irradiation to fluences ranging between \(5.0 \times 10^{10}\) and \(5.6 \times 10^{15}\) protons/cm^2. The results indicate that proton irradiation to fluences as high as \(5.6 \times 10^{15}\) has little effect on the interband transitions in carbon nanotubes. However, small radiation-related degradation has been observed as judged by the broadening of the interband transition spectra.
and by the reduction of the radial breathing mode intensity observed by Raman scattering.

The radiation tolerance of NBP was also analyzed in the context of the application of nanotubes in space photovoltaic applications in combination with quantum dots [24]. Irradiation with 2 MeV protons caused the room temperature resistivity of the NBP samples to increase nearly linearly up to a fluence of $7 \times 10^{16}$ protons/cm$^2$. Based on the comparison of the irradiation-induced changes in NBP resistivity (the defects in the samples were not characterized at the microscopic level), it was concluded that the sensitivity of the nanotube paper falls between that of individual nanotubes and graphite. This was a somewhat unexpected result, as systems as NBP which are composed of radiation-soft components (recall that nanotubes are radiation-soft themselves: irradiation dose of $3 \times 10^{16}$ protons/cm$^2$ resulted in complete amorphization and fracture of SWNTs [22]). It was also concluded that the solar cells based on quantum dots and NBP paper should be five orders of magnitude more resistant to radiation damage than the conventional bulk solar cells.

As seen from the experimental results, irradiation doses $\leq 10^{17}$ protons/cm$^2$ should completely amorphize the samples. However, the estimates of the radiation damage in SWNT created by protons with such energies and doses using the TRIM code [74] give dpa (displacement per atom) values of around $10^{-4}$ [158]. This value means that on average, one atom out of 10,000 was displaced during irradiation. Obviously, this is not enough for sample amorphization, and the nuclear stopping can be excluded. The electronic stopping for 1 MeV protons is some 2-3 orders of magnitude larger than the nuclear one, but the nanotubes are excellent heat and charge conductors, so that the deposited energy should be quickly redistributed over the sample. Note that for the typical metals like copper irradiated with light ions the TRIM code gives dpa values [159] which are at least in qualitative agreement with the experiments. Although chemically reactive species (like water and oxygen radicals which appear due to irradiation) may be present in the system and play some role, similar to irradiation of nanotubes with low-energy electrons [149] or ultraviolet light [50], the precise mechanism of the damage creation by high energy protons is unknown at the moment.

### 1.6.3 Welding of nanotubes by ion beams

As discussed in Section 1.5.4, a focused electron beam can be used [42] for welding nanotubes together at high temperatures. As MD simulations [83] pointed out, ion irradiation combined with high-temperature annealing should also result in welding of crossed nanotubes, both suspended and deposited on substrates, see Fig. 1.23. For the latter, the optimum Ar ion energies were predicted to be about 0.5 keV, whereas the optimum irradiation doses should be about $10^{15}$ions/cm$^2$. Higher doses will result in a heavy damage of the carbon network [83].

The theoretical predictions were corroborated later on by experiments: Irradiation of overlapping nanotubes with 10 keV Ga ions with doses up to $10^{16}$ ions/cm$^2$ resulted in the welding of nanotubes [8], see Fig. 1.24. Similar results were obtained with 50 keV carbon ions [26], although the irradiation dose of $10^{15}$ ions/cm$^2$ used converted the tubes into amorphous rods. As the experiments [8, 26], were carried out at room temperature, irradiation of nanotubes at
higher temperatures and/or subsequent annealing should minimize the amount of damage in the nanotubes.

Figure 1.23: Two crossed carbon nanotubes before irradiation (a). Atomic networks of (10,10)&(12,0) and (10,10)&(10,10) nanotubes [panels (b) and (c) respectively] welded together by energetic Ar ions, as simulated [83] with the empirical potentials molecular dynamics method.

Figure 1.24: SEM micrographs of overlapping nanotubes marked A and B, (a) prior to irradiation, and after exposure to (b) $10^{16}$ and (c) $2 \times 10^{16}$ ions/cm$^2$ of 10 keV Ga ions; (d) an example of a nanotube network formed by several welds indicated by arrows; (e) SEM micrograph showing a nanotube welded to the edge of the SiN membrane (see the arrows) by exposure to $10^{17}$ ions/cm$^2$ of 30 keV Ga ions. Reused with permission from Ref. [8]. M. S. Raghuveer, P. G. Ganesan, J. D'Arcy-Gall, G. Ramanath, M. Marshall, and I. Petrov, Appl. Phys. Lett. 84, 4484 (2004). Copyright 2004, American Institute of Physics.
1.6.4 Ion-irradiation-induced links between nanotubes and substrates

As simulations predict [82,108], ion irradiation of supported nanotubes should result in the pinning of the nanotubes to metallic and graphite [82] substrates, as well as to Si [108] surfaces. This should happen through the formation of chemical bonds between the nanotube and substrate atoms near irradiation-induced defects (by saturating dangling bonds), thus increasing the nanotube-substrate adhesion.

MWNTs were experimentally welded to SiN substrates [8]. The experiments [160] also showed that electrical contact resistance of MWNTs deposited on gold contact fingers can be decreases by orders of magnitudes when the contact areas are selectively exposed to the electron beam in a SEM. The local focused electron beam irradiation was also reported [161] to make good thermal contacts between the nanotubes and platinum nanofilm sensors. Thus one may hope that ion irradiation will improve not only mechanical but also electronic/thermal properties at the interfaces between the tubes and the environment.

1.6.5 Irradiation-mediated doping of carbon nanotubes with foreign atoms

Chemical doping of nano-structured carbon systems such as carbon nanotubes, fullerenes and peapods is a possible route toward controllable modification of their structural, mechanical, and, first of all, electronic properties. Doping may be implemented by intercalating foreign atoms into the open space in the carbon network [162–164] or by substituting the host atoms with impurities [165–174].

As for substitutional doping, much attention has recently been given to the doping of nanotubes with boron and nitrogen atoms. This is a natural choice of the dopant, as B and N atoms are the neighbors of C in the Periodic Table and thus have roughly the same atomic radius as C, while they possess one electron less or more than C, respectively. Several methods based on arc-discharge techniques [168,175] and substitutional reactions [170] have been developed for doping. Unfortunately, instead of occupying the substitutional \( sp^2 \) position in the graphitic network, a substantial part of the dopant is chemisorbed [176] on the nanotube surface or binds to irregular carbon structures in \( sp^3 \) sites [168]. Problems with incorporating B atoms into the carbon lattice of nanotubes have also been reported [175]. All of these issues further limit the applicability of these techniques.

Low-energy ion-irradiation was suggested [98,99] as an alternative way to introduce B/N impurities into nanotubes. Ion beams have been used to implant \( N^+ \) ions into graphite [177] and fullerene solids [178], so in principle this same technique could be used for nanotube doping. Indeed, the simulations [98, 99] showed that up to 40% of the impinging ions can occupy directly the \( sp^2 \) positions in the nanotube atomic network. Overall, the results indicated that irradiation-mediated doping of nanotubes is a promising way to control the nanotube electronic and even mechanical properties due to impurity-stimulated cross-linking of nanotubes.

Doping of nanotubes with N atoms through irradiation was recently implemented experimentally [17]. SWNTs were bombarded with low energy (500 eV) \( N_2^+ \) ions. XPS experiments showed that the N 1s core level spectra for N-doped
nanotubes could be interpreted in terms of two peaks related to sp\(^2\) and sp\(^3\) hybridization of N atoms in the C network. AFM nanoindentation of the irradiated tubes also provided evidence for the appearance of sp\(^3\)-hybridized bonds, as manifested by an increase in hardness. Overall, the experimental results were in line with the theoretical predictions [98, 99].

In addition to the substitutional doping, MD simulations [104] also demonstrated that intercalation of K atoms into the open space of nanotubes can be achieved by means of irradiation. The formation of clusters from the implanted potassium atoms was studied as well. It was found that for MWNTs with 1-3 shells, the highest ratio of K atoms in clusters per total number of K ions should be obtained at irradiation energy of about 100 eV. Such low energies should also minimize the damage created in nanotubes by energetic ions.

### 1.6.6 Carbon nanotubes as masks against ion irradiation

Another quite interesting application of irradiation of nanotubes on metallic substrates has been reported. Experiments demonstrated that ion bombardment and nanotubes may be employed for fabricating metal nanowires using MWNTs as masks [27]. By irradiating with 300 eV Ar\(^+\) ions, a Au/Ti wire about 10 nanometers in width has been formed underneath a MWNT lying on a thin Au/Ti layer deposited earlier on a SiO\(_2\) substrate. [27] The key idea is illustrated in Fig. 1.25.

After forming the nanowire due to metal layer sputtering everywhere except for the area beneath the nanotube, the MWNT could be removed by an atomic force microscope (AFM) or dissolved. Because nanotubes are micrometer-long and nanometer-wide objects and since they can be positioned very accurately using the AFM by pushing them mechanically [179], the described technique may potentially be employed for developing a large and complicated network of metal nanowires.

A computational study [84] was done to estimate the theoretical limit for the minimum width of a metal nanowire, which could be produced using this method. MD simulations of Ar ion irradiation of MWNTs showed that the bombardment results in the sputtering of carbon atoms from the MWNT, formation of vacancies on the MWNT walls and interstitial atoms between the shells. High irradiation doses lead to the complete amorphization of the MWNT, but the amount of sp\(^3\) bonds is very small, which is in agreement with experimental results [16]. By estimating the sputtering yield from a MWNT (notice that the yield is lower for carbon than for typical metals) and taking into account the thickness of the metal layer, a universal equation was derived which for a given nanowire material allows one to estimate the theoretical limit on the minimum width of the wire as a function of the original thickness of the metal layer. It was shown that this technique potentially provides a better resolution than the present-day electron beam lithography, although a low AFM operation speed prevents mass production of metal wires using nanotubes as masks against ion bombardment.

This setup may also be used for spatially selective ion implantation into the parts of the sample which have not been covered with nanotubes. Thus, the threshold energy of incident ions (the maximum energy at which no energetic recoil hit the area below the nanotube) is an important characteristic. The threshold energy as a function of the MWNT outer diameter (number of shells)
was evaluated [84] for various MWNTs. The threshold energy was found to linearly grow with the number of shells, see Fig. 1.25(c). An analytical approximation was derived which makes it possible to estimate the minimum diameter of a MWNT needed to prevent the substrate below the MWNT from sputtering and ion implantation for a given energy of the incident ion.

Figure 1.25: Schematic illustration of the setup for using multi-walled nanotubes as masks against ion bombardment. Before irradiation a nanotube has been deposited on a thin metal layer on a SiO$_2$ substrate (a). Ion irradiation results in sputtering of metal atoms and nanotube amorphization. After irradiation the nanotube can be removed by AFM (b). Threshold energy of incident ions (the maximum energy at which no energetic recoil hit the area below the nanotube) as a function of tube outer diameter (number of shells) (c). Reprinted from Ref. [93] A. V. Krasheninnikov and K. Nordlund, *Irradiation effects in carbon nanotubes*, Nucl. Instr. and Meth. in Phys. Res. B 216, 355 (2004), Copyright (2004), with permission from Elsevier.

1.6.7 Channeling of ions in nanotubes

The tubular shape of carbon nanotubes, as well as their hollow cores, high aspect ratio and a low concentration of defects suggest another possible application for nanotubes: conduits for energetic ions.

This potential application of nanotubes is related to a phenomenon which is highly important for the present-day semiconductor technology [53,180]: channeling of energetic ions through solids. When an energetic ion moves nearly parallel to a major axis or plane in a single crystal, it can be steered down the open channel between the aligned rows of atoms, thereby avoiding violent collisions with the host atoms and giving rise to deeper implantation and less lattice disorder.

**Heavy ions**

The channeling of heavy ions with keV energies through MWNTs was theoretically studied [102,103,181] by MD simulations and within the framework of
the classic electromagnetic theory [182]. It was shown that under certain conditions on the tube alignment with respect to the ion beam and on ion energies, the ions can efficiently channel through the empty cores of the nanotubes. Suggestions were made for making a nanotube-based conduit for energetic ions, which should work as an aperture and allow one to manipulate ion beams at the nanoscale, see Fig. 1.26. Note also that nanotubes have been suggested as possible conduits for atoms and molecules with thermal energies [183–185]. Extensions to higher energies of the particles might also result in developing other promising applications in biology and materials science. The main experimental challenge would be the stability of the tubes under irradiation, as defect formation will result in the accumulation of the displaced atoms in the nanotube core, which will quickly block the tube for the ions.

![Figure 1.26: (a) Schematic representation of a beam of Ar ions colliding with a multi-walled carbon nanotube with an open end. Depending on ion energy, impact point, and angle $\Theta_1$, the ion hitting the inner shell of the tube can either remain in the core region or go through the shell. (b) The basic idea for a nanotube-based ion aperture. Reprinted with permission from Ref. [102]. A. V. Krasheninnikov and K. Nordlund, Phys. Rev. B 71, 245408 (2005). Copyright (2005) by the American Physical Society.](image)

**Light ions**

The motion of high-energy light ions (protons) through SWNTs has received even bigger attention [186–189] than heavy ions. The driving force for these studies was the possibility to use SWNT bundles for steering the beams of high-energy (GeV) protons, which would otherwise require cumbersome and expensive magnetic systems. However, despite an extensive theoretical analysis and first experimental results [190] it is not clear at all if nanotubes can in practice be used for this purpose, as the sample may quickly be destroyed by the beam as experiments on proton irradiation of SWNTs indicate, see Section 1.6.2.
1.7 Irradiated carbon nanotubes as high-pressure cylinders

Another very interesting irradiation-induced phenomenon in carbon nanotubes which was recently reported for nanotubes irradiated with both electrons [37] and ions [116].

Controlled electron irradiation of MWNTs was demonstrated to cause large pressure buildup within the nanotube cores that can plastically deform, extrude, and break solid materials that are encapsulated inside the core. It had been earlier shown [39] that closed-shell carbon nanostructures, such as carbon onions, can act as self-contracting high-pressure cells under electron irradiation, and that high pressure buildup in the onion cores can even induce graphite-diamond transformations, see Ref. [38] for a review. However, it was not obvious that high pressure can be achieved inside nanotubes, as the difference in the geometry (cylinder vs. sphere) may have been critical for pressure buildup.

MWNTs encapsulating Fe, Fe3C, or Co nanowires were irradiated [37] in a TEM with a field emission gun and an acceleration voltage of 300 kV at a temperature of 600°C. Figure 1.27 shows the evolution of a nanotube partly filled with a Fe3C nanowire under irradiation. The initial configuration is presented in Fig. 1.27(a) Irradiation of the section at the end of the wire leads to a non-uniform collapse of the tube. The hollow noncollapsed part of the tube fills up with graphitic filaments (Fig.1.27(b)). Carbon material migrates from the open side of the channel and aggregates at the end of the Fe3C wire by closing the inner hollow with graphene sheets. Therefore, the number of shells increases...
1.7. IRRADIATED CARBON NANOTUBES AS HIGH-PRESSURE CYLINDERS

locally. The tube now collapses in the region of the carbide crystal by deforming the crystal. The diameter of the Fe$_3$C wire decreases from 9 to 2 nm while the solid carbide is squeezed through the hollow core downward along the tube axis, as in an extrusion process. The final collapse of the tube pinches and cuts off the thinned wire (Fig. 1.27(b)). The compressive effect is also manifested in a decrease in lattice spacing between graphitic shells and in the encapsulated crystal.

Qualitatively similar results were obtained for Co crystals. Note that the collapse of the tubes and the extrusion of encapsulated material occurred only under electron irradiation, not under heating. Additional heating of the specimen by the electron beam was negligible because the inelastic energy loss of the electrons is low and nanotubes are excellent heat conductors, so the transferred energy could dissipate into the environment.

Atomistic computer simulations by the DFTB method and continuum theory modeling shed light on the origin of the pressure. As discussed in Section 1.2, knock-on displacements of carbon atoms due to energetic electron create vacancies and interstitials in the nanotubes. Single vacancies are mobile enough [61] to form di-vacancies (see also Fig. 1.6), which are energetically favorable over single vacancies. Di-vacancies do not essentially move even at 600°C, as the migration energy is more than 5 eV. On the contrary, carbon interstitial atoms between the shells of MWNTs are highly mobile and can easily migrate away from the irradiated region, so it was assumed that no interstitials were left in the irradiated area, and that only di-vacancies were present. Calculations of the atomic structure of free-standing (without encapsulates) nanotubes with various number of di-vacancies showed contraction of the nanotube due to the atomic network reconstructions, Fig. 1.28(b). For nanotubes encapsulating materials, this should exert pressure on the material inside. As carbon-carbon covalent bond is very strong, one can expect a substantial pressure buildup, before the tube breaks. Indeed, simulations showed that pressure inside irradiated nanotubes can be as high as 40 GPa, only an order of magnitude below the pressure in the center of Earth (~360 GPa) or the highest pressure that has been achieved in diamond anvil cells (~400 GPa). However, phase transformations in many materials are within this range. Moreover, the advantage of the present technique is that the individual nanometer-sized crystals can be deformed under high pressure, and the evolution of the system can be monitored with high spatial and temporal resolution, as the experiment is carried out inside the TEM. This technique can also be used for creating and studying new phases of materials which can exist only at the nano-scale and at high pressures.

Concurrently with electron irradiation of nanotubes with encapsulates, a similar in spirit experiment was carried out [116]. MWNTs with typical diameters of 20-30 nm and encapsulating nickel nanorods were irradiated with high energy (100 MeV) Au$^{+7}$ ions. TEM studies of the irradiated samples showed that irradiation resulted in a decrease in the interplanar spacing of nanotube walls and nickel (111) planes. The effect was relatively weak, as the irradiation dose was small (of the order of $3 \times 10^{13}$ cm$^{-2}$), and because irradiation was done at room temperature, which was not enough for efficient annealing of defects in nanotube walls, and thus high pressure was not generated. Contrary to Ref. [37], irradiation-induced defects in the metal rods were reported. This is particularly interesting, as the energy loss in the metal (through electronic stopping) was not high enough to produce defects in Ni, at least in a bulk system.
More studies are necessary to understand the mechanism of damage production in the nano-scale composite nanotube-metal systems.

1.8 Influence of defects on the nanotube properties

1.8.1 Mechanical properties

The atomic structure of MWNTs, SWNTs in bundles and other macroscopic forms of nanotubes like NBP is governed by two kinds of atom-atom interaction: short-ranged covalent bonding between the C atoms within the graphene planes and long-ranged van der Waals (vdW)-type interactions between atoms in different SWNTs or different shells in MWNTs. The covalent interaction is very strong, the carbon-carbon covalent bond in graphite and nanotubes is one among the strongest bonds known. At the same time, vdW interactions are three orders of magnitude weaker. Due to different types of interactions and highly anisotropic atomic structure, carbon nanotubes have anisotropic mechanical properties. The axial properties, such as Young modulus $Y$, are excellent.
(\(Y \sim 1\) TPa [3]), while the properties associated with the vdW forces (e.g., the bending modulus of a nanotube bundle [30]) are much worse. The strength of macroscopic materials is also very low, as tubes can easily slide with respect to each other.

1.8. INFLUENCE OF DEFECTS ON THE NANOTUBE PROPERTIES

... and thus, a noticeable drop in the Young (axial) modulus of in-

As shown in Section 1.4, both electron and ion irradiation results in the formation of defects in nanotubes. These defects, especially vacancies, have a deleterious effect – deterioration of axial mechanical properties of nanotubes, as computer simulations [97, 191–194] indicate. Experiments [30] showed that during electron irradiation with doses over \(50 \times 10^{20}\) e/cm\(^2\) the bending modulus started decreasing, which was understood in terms of the damage accumulation in SWNTs, and thus, a noticeable drop in the Young (axial) modulus of individual tubes [97, 100]. Simulations demonstrated that small vacancies (from 1 to three missing atoms) relatively weakly affect \(Y\) [97]. Due to quasi-one dimensional structure of individual nanotubes, the effect of vacancies on the tensile strength and critical strain of nanotubes proved to be much stronger (20-30 % [97, 191]). Interestingly enough, the theoretical fracture strength of nanotubes with point defects is still much higher than the experimental values for supposedly pristine tubes [195]. This discrepancy can be attributed [191] to the presence of large-scale defects, such as those that may arise from oxidative purification processes.

At the same time, irradiation may give rise to irradiation-induced covalent bonds between tubes, Fig. 1.10 so provided that the drop in the axial properties is not that big, the overall strength of the nanotube material may increase. Assuming that the axial mechanical properties remain roughly the same under moderate irradiation, formations of covalent bonds between nanotubes in a bundle would increase the mechanical properties of the bundle [100], in agreement with the experimental results [30]. Likewise, a small amount of defects
can increase the interlayer shear strength of MWNTs by several orders of magnitude [96], which would have a strong effect [109] on the failure of nanotubes by the sword-in-sheath mechanism. In agreement with theoretical predictions, very recent experiments [124] on the telescopic motion of MWNTs demonstrated that irradiation-induced single vacancies at the telescopic interface lead to an increase in friction, but annealing of defects restores smooth motion of the sliding shells.

Irradiation can also increase the tensile strength of macroscopic nanotube products, such as NBP [94, 95]. Due to a low density (or correspondingly, high porosity $\sim 80\%$ [156]) and weak interactions between the bundles, the experimentally measured tensile modulus, strength and strain to failure of the NBP mats proved to be several orders of magnitude worse [155, 157] than those for individual nanotubes. Simulations demonstrated that the stiffness and tensile strength of NBP and nanotube fibers [196–198] can substantially (several orders of magnitude) be improved by irradiation. Physically, an increase in stiffness is mainly due to irradiation-induced inter-tube covalent bonds at the bundle contact areas, Fig. 1.29. Thus, irradiation may have overall beneficial effect on the mechanical properties of nanotubes.

### 1.8.2 Electronic properties

As demonstrated in numerous theoretical studies [5, 199–205] even a small number of defect have a strong effect on electron transport in nanotubes due to their quasi-one dimensional structure. Experiments [5, 6] also indicate that irradiation-induced defects strongly affect the resistivity of the samples, which normally increases by several orders of magnitude, depending on the original sample perfection and the conductivity regime.

For macroscopic oriented SWNT ropes the effect of irradiation proved to be more complicated [44]: A minimum in resistivity as a function of irradiation dose was found, which was interpreted as a result of a twofold effect of the irradiation: the domination of covalent bond formation between tubes in a bundle due to broken bonds in the tube walls and the amorphization of the sample at high dose.

Irradiation-induced defects affect the local electronic structure of the tubes near the Fermi level, as assessed by electron spin resonance [45, 46]. As mentioned in Section 1.6.1, spatially localized Ar ion irradiation of individual MWNTs [10] creates defective regions which represent potential tunnel barriers for electrons in the MWNT. A double-barrier structure fabricated by such method can work as a quantum dot. Spatially localized ion irradiation was also used for the fabrication of a single-electron inverter in MWNTs [11].

Thus, defect, and thus irradiation, can also be used in a beneficial way to tailor the nanotube electronic properties and improve the functionality of the nanotube-based devices.

### 1.8.3 Magnetic properties

Observations of magnetism in various metal-free carbon systems [206–209] have stimulated much experimental and theoretical research work (Ref. [210] and references therein) on the magnetic properties of all-carbon systems. The driving force behind these studies was not only to create technologically-important,
light, non-metallic magnets with a Curie point well above room temperature, but also to understand a fundamental problem: the origin of magnetism in a system which traditionally has been thought to show diamagnetic behavior only.

The observed magnetism may originate from defects in the graphitic network such as under-coordinated atoms, e.g., vacancies [211, 212] or atoms on the edges of graphitic nano-fragments with dangling bonds either passivated with hydrogen atoms [213–215] or free [214, 216]. Structural defects, in general, give rise to localized electronic states, a local magnetic moment, flat bands associated with defects and thus to an increase in the density of states at the Fermi level, and eventually to the development of magnetic ordering. Magnetism may also originate from impurity atoms which are non-magnetic by themselves, but due to unusual chemical environment, e.g., due to bonding to defects in graphitic network, give rise to local magnetic moments, or from a combination of both.

Indeed, irradiation of graphite with protons [217] resulted in a significant magnetic signal, which was explained in terms of vacancy-hydrogen interstitial atom complexes [89]. High-energy (100 keV) nitrogen ion irradiation of nano-sized diamond (which is graphitized at high irradiation dose) followed by magnetic measurements on the doped samples showed ferromagnetic order at room temperature [218]. The magnetic moment observed was in a good agreement with the results of DFT simulations [105], which reported net magnetic moments at several N-interstitial defect configurations.

Theoretical calculations also provide evidence that various defects in nanotubes such as adatoms [219], vacancies both naked [220] and passivated with H atoms [221] may be magnetic. Thus, although magnetism in carbon nanotubes has never been observed (to the best of our knowledge), irradiation of nanotube samples with non-magnetic ions like H and N may result in magnetism, similar to other forms of carbon.

1.9 Conclusions and Outlook

This Chapter has summarized the recent advances in our understanding of interactions of nanotubes with beams of energetic particles. Because of the high anisotropy of the atomic network, and due to the ability of carbon atoms to form bonds of different hybridizations, irradiation of nanotubes results in many fascinating irradiation-induced phenomena which can readily be used for engineering of various carbon-based nanosystems. Based on a wealth of experimental and theoretical data, one can conclude that irradiation can have not only destructive but also beneficial effect on carbon nanotubes.

One can envisage that the most promising future applications of irradiation for processing carbon nanotubes would be the use of spatially-localized electron and ion beams for making arrays of inter-connected carbon nanotubes with different electronic properties, which should be very important for carbon-based electronics. Defected areas may deliberately be created to provide the desired functionality of the device. At the same time, the amount of the undesired damage can be minimized after making a device by high-temperature annealing or photo excitation-mediated healing of defects [222]. Ion irradiation may further be employed for nanotube doping by introducing impurities as an additional means to control electronic properties of nanotubes.

Irradiation should also increase chemical reactivity of nanotubes via surface
defects, especially vacancies. Thus different chemical groups can be attached to the nanotubes in the pre-selected areas. Vacancy-type defects in nanotubes are thought to be important for thermal dissociation of water [223], so that irradiated nanotubes may be used as catalysts.

Irradiation-mediated improvements in mechanical properties of macroscopic nanotube samples are expected. Another plausible application of irradiation, which have been discussed in the literature [15, 224, 225], is to improve mechanical properties of nanotube-polymer composite materials [226–228] by improving adhesion between polymers and nanotubes. It is well known that both electron and ion irradiation can create links between polymers chains. However, since the damage formation mechanism in the polymer matrix (predominantly electronic effects) is different from that in a nanotube, it is not quite clear yet whether similar links between broken polymer chains and nanotubes could be formed and what the mechanical characteristics of the sample could be.

Although overall the damage production under both electron and ion irradiation can be understood within the framework of the conventional theory of irradiation effects in bulk solids, many issues which still lack understanding should be addressed to implement in practice all the ideas discussed above. In particular, the mobility of irradiation-induced defects in MWNTs and nanotube bundles is still uncertain, although this matter is quite important for understanding not only damage annealing but also nanotube growth. The mechanisms of damage formation in nanotubes under high-energy proton irradiation should be studied in more detail. Studies on defects in nanotubes should shed light on magnetic properties and the origin of magnetism in carbon nano-structured systems.

1.10 Acknowledgments


The author is also indebted to the Academy of Finland for the support of the research described in this Chapter, and to the Finnish Center for Scientific computing for grants of computer time.
Bibliography


[70] W. A. McKinley and H. Feshbach, Phys. Rev. 74, 1759 (1948).


[190] Zh. Zhu et al., private communication.


