Atomic scale engineering of carbon nanotubes

Antti Tolvanen

Division of Materials Physics
Department of Physics
Faculty of Science
University of Helsinki
Helsinki, Finland

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ABSTRACT

Carbon nanotubes, seamless cylinders made from carbon atoms, have outstanding characteristics: inherent nano-size, record-high Young’s modulus, high thermal stability and chemical inertness. They also have extraordinary electronic properties: in addition to extremely high conductance, they can be both metals and semiconductors without any external doping, just due to minute changes in the arrangements of atoms. As traditional silicon-based devices are reaching the level of miniaturisation where leakage currents become a problem, these properties make nanotubes a promising material for applications in nanoelectronics.

However, several obstacles must be overcome for the development of nanotube-based nanoelectronics. One of them is the ability to modify locally the electronic structure of carbon nanotubes and create reliable interconnects between nanotubes and metal contacts which likely can be used for integration of the nanotubes in macroscopic electronic devices. In this thesis, the possibility of using ion and electron irradiation as a tool to introduce defects in nanotubes in a controllable manner and to achieve these goals is explored.

Defects are known to modify the electronic properties of carbon nanotubes. Some defects are always present in pristine nanotubes, and naturally are introduced during irradiation. Obviously, their density can be controlled by irradiation dose. Since different types of defects have very different effects on the conductivity, knowledge of their abundance as induced by ion irradiation is central for controlling the conductivity. In this thesis, the response of single walled carbon nanotubes to ion irradiation is studied. It is shown that, indeed, by energy selective irradiation the conductance can be controlled. Not only the conductivity, but the local electronic structure of single walled carbon nanotubes can be changed by the defects. The presented studies show a variety of changes in the electronic structures of semiconducting single walled nanotubes, varying from individual new states in the band gap to changes in the band gap width. The extensive simulation results for various types of defect make it possible to unequivocally identify defects in single walled carbon nanotubes by combining electronic structure calculations and scanning tunneling spectroscopy, offering a reference data for a wide scientific community of researchers studying nanotubes with surface probe microscopy methods.
In electronics applications, carbon nanotubes have to be interconnected to the macroscopic world via metal contacts. Interactions between the nanotubes and metal particles are also essential for nanotube synthesis, as single walled nanotubes are always grown from metal catalyst particles. In this thesis, both growth and creation of nanotube-metal nanoparticle interconnects driven by electron irradiation is studied. Surface curvature and the size of metal nanoparticles is demonstrated to determine the local carbon solubility in these particles. As for nanotube-metal contacts, previous experiments have proved the possibility to create junctions between carbon nanotubes and metal nanoparticles under irradiation in a transmission electron microscope. In this thesis, the microscopic mechanism of junction formation is studied by atomistic simulations carried out at various levels of sophistication. It is shown that structural defects created by the electron beam and efficient reconstruction of the nanotube atomic network, inherently related to the nanometer size and quasi-one dimensional structure of nanotubes, are the driving force for junction formation. Thus, the results of this thesis not only address practical aspects of irradiation-mediated engineering of nanosystems, but also contribute to our understanding of the behaviour of point defects in low-dimensional nanoscale materials.
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1 INTRODUCTION

Throughout the history of mankind, our technological development has been defined by our ability to create new materials and control their properties. During the last century, the technological advances have become more than ever dependent on the ability to control materials properties at extremely short length scales. Correspondingly, a completely new field of research concentrating on the atomic and molecular scale, nanoscience, often combining several traditional fields, has emerged to fulfil these needs. Tuning material properties at the nanoscale has opened a way to applications which, compared to traditional approaches, are cheaper [1], faster [2], stronger [3], lighter [4], smaller [5], have less friction or if required more (Refs. [6] and [7] respectively), and have fantastic colours [8], to name some. Especially appealing is the possibility to manufacture electronic devices at the atomic level, as the ever increasing packing density of transistors in microprocessors will inevitably lead to molecular transistor sizes during the following decades (as described by the Moore’s law [9]). Therefore, controlling material properties at the molecular and atomic level has been the subject of a vast amount of studies during the last quarter century.

Carbon, the fourth most abundant element in the universe, and one of the few known since antiquity, has a unique ability to form complicated molecules, which have lead to appearance of life in our corner of the universe. Since the discovery of fullerenes [10] (1985), and multi-[11] (1991) and single-walled [12] (1993) carbon nanotubes (CNTs), carbon has played a major part in the development of nanoscience. All these nano allotropes of carbon are based on the $sp^2$ hybridisation of electronic orbitals leading to “honeycomb” network of atoms (known as graphene [13]), where all atoms are connected to three neighbours. When curved, this network can form spherical fullerenes and cylindrical nanotubes. All of these structures can be found in ordinary soot when looked at with an electron microscopes. Due to this natural tendency to form nanostructures, carbon has become the constituting element of the prototype nanomaterials. Of carbon allotropes, CNTs are the most promising one for applications, even though recent discovery of graphene has shaken the sovereignty of CNTs. However, the potential applicability of carbon nanotubes due to their fascinating properties remain, as explained below.

CNTs have inherent nanosize; single-walled CNTs (SWNTs) have a diameter of $\sim 1$ nm. Their length depends on the synthesis method, varying from $\sim 50$ $\mu$m for arc discharge to typically some millimetres for chemical vapour deposition. Individual SWNTs with lengths up to 4 cm have been reported [14], and a recent method [15] proposes that SWNT fibres can be synthesised with any desired length. Although SWNTs can be thought of as molecules, they have a well defined periodic atomic structure, similar to crystalline solids. However, in contrast to crystals,
carbon nanotubes can be chiral, i.e. without mirror symmetry, a property usually found only in molecules. Changes in the chirality, from achiral to multitude of different chiralities, lead to minute changes in the atomic structure of CNTs making both metallic and semiconducting nanotubes existent without any external doping, which is a unique property among materials. In spite of the fascinating properties many difficulties need to be overcome to fully exploit the extraordinary properties of CNTs'. For example, current CNT growth methods allow control over the nanotube diameter, but offer no control over chirality and hence electronic properties. Furthermore, electronically transparent contacts are needed to link CNT based devices to the macroscopic world and nanotubes have to be arranged in reliable way in order to produce circuits.

This thesis presents studies on controlled atomic scale engineering of carbon nanotubes by introducing defects aiming at solving some of the remaining problems in nanotube applications. One way to introduce disorder and to modify the morphology or conductivity of a material is to use ion irradiation. Classical molecular dynamics (MD) simulations with analytic bond order potentials are a suitable method for understanding ion-nanotube interactions in experimental-like conditions. Timescales achievable by this method are limited to nanoseconds, but this is enough to describe the actual irradiation process. More accurate ab initio methods can be used to confirm that the atomic configurations of defect structures given by MD are reasonable, and also to study the local electronic effects of irradiation. The effect of longer time scales at finite temperatures can be taken into account by employing kinetic Monte Carlo (kMC) method, which gives information on non-local defect evolution. Combining these methods, experimentally testable information on defect formation is achieved. Furthermore, a combination of presented simulation methods and scanning tunneling microscopy/spectroscopy (STM/STS) experiments allows identifying defects from their electronic signatures, explaining new experimental phenomena, and proposing a method for tuning electronic properties of CNTs. In addition to directly changing the properties of the nanotubes, it is equally important to control the interface between CNTs and metal electrodes, which serve as contacts between the nanotube and its periphery. Transmission electron microscopy (TEM) offers the possibility of in situ engineering nanotube-metal particle junctions. However, electron irradiation raises a difficult problem of energetic electron-atom interactions, which with current computational possibilities have to be approximated by analytical calculations of defect formation probabilities based on electron-nucleus interactions [16]. In the studies presented in this work, the dynamics of defect creation by electron irradiation plays a minor role and the emphasis is on the energetics of the systems engineered in situ during transmission electron microscopy.
The results of this thesis demonstrate how the combination of atomistic simulations, particle irradiation, and atomic resolution microscopy can be used to plan and execute atomic scale engineering of carbon nanotubes. Furthermore, the results contribute to our understanding of the behaviour of point defects in low-dimensional nanoscale materials.

2 PURPOSE AND STRUCTURE OF THIS STUDY

The purpose of this thesis is to show how energetic particle irradiation can be used in engineering carbon nanotubes and carbon nanotube-metal nanoparticle compounds for future nanoelectronic device applications, and to extend the understanding of irradiation effects to low dimensional systems. Effects of both electron and ion irradiation are studied by computational methods, and in collaboration with several experimental groups.

This thesis consists of this summary and five research articles either published or accepted for publication in international peer-reviewed journals. In section 3, the necessary background information of carbon nanotubes required for understanding the results is presented. Section 4 describes the computational methods used in the studies and gives a short introduction to the experimental methods used in the collaborative papers published with experimentalists. Section 5 presents the results giving the substance to this thesis. Conclusions of this work are presented in section 6.

2.1 Summaries of the original publications

In publication I, production of different defects in SWNTs under ion irradiation is studied. As single and double vacancies have drastically different effect on SWNT conductivity, the ratio of single and double vacancies is selected as the decisive factor in the study. Publication II continues irradiation effect studies, but instead of defect production, it concentrates on local electronic effects of irradiation induced defects The DFT simulations are compared to STM/STS studies done by the experimental collaborators. In publication III, the observed SWNT growth from sharp metal tips in a transmission electron microscope is explained by changes in carbon solubility in metal nanoparticles as the geometry of these particles is modified during irradiation. Publication IV extends the related computational study to a larger variety of nanoparticle geometries. A model explaining the mechanism of nanotube-metal nanoparticle junction formation is presented in publication V.
Publication I: Relative abundance of single and double vacancies in irradiated single-walled carbon nanotubes,

Single and double vacancies (SV and DV) affect the conductivity of carbon nanotubes differently, making the interpretation of experiments on irradiation induced changes in conductivity impossible without exact knowledge of how many of these defects are produced. In this publication, the abundance of single and double vacancies produced by Ar ion irradiation is studied by MD simulations combined with kMC. The ratio of single and double vacancies is found to have a minimum at 0.5 keV giving the most destructive irradiation energy for SWNT conductivity. The maximum for producing more complex defects also lies near 0.5 keV. SV-DV ratio increases with irradiation energy, as mostly single vacancies are produced with higher ion energies. KMC simulations show that at room temperature and low irradiation energies (< 200 eV) mostly single vacancies are present in the system. This occurs as ad-atoms are mobile and recombine with vacancies, but the mobility of SV is too low for DV production by defect combination.

Publication II: Modifying the electronic structure of semiconducting carbon nanotubes by Ar$^+$ ion irradiation,

Based on the previous work, local electronic effects in semiconducting SWNTs of the most prolific defects produced by Ar ion irradiation are studied. In STM images, nearly all irradiation induced defects have nondistinctive features. In this publication, DFT simulations of the local electronic effects of these defects are combined with STS experiments with an aim to identify the defect types, abundance, and effects on local electronic structure. Electronic effects of defects are separated into three classes by features induced in the bandgap. Single vacancy, double vacancy and individual carbon ad-atom induce an almost constant dispersion band at the centre of the bandgap, bond rotation (i.e. Stone-Wales), triple vacancy and, ad-atom dimer *i.e.* inverse Stone-Wales defects cause modification of the band gap and neighbouring point defects introduce bands by their numbers. The simulations are used to recognise irradiation induced defects. Furthermore, the results are used to explain defect evolution in STM/STS, experiments and the possibility of using STM to engineer the local electronic structure is presented.
Publication III: Growth of Single-Walled Carbon Nanotubes from Sharp Metal Tips,

State-of-the-art transmission electron microscopy allows *in situ* atomic resolution imaging and manipulation of targets. In this publication, *in situ* nanotube growth from carbon saturated metal nanoparticles is reported when metal nanoparticle curvature is modified by the electron microscope. Computational results from MD simulations using analytical bond order potentials are used to explain the observations. In all spherical nanoparticles and nanorods studied, the formation enthalpy of interstitial carbon in the minimum energy configuration is increased as the radius of the nanoparticle decreases. This can be associated with the stress field created by the surface of the nanoparticle and acting on the interstitial carbon. Thus, when nanoparticle curvature is increased, carbon solubility is reduced and carbon precipitates, and when curvatures is decreased solubility increases leading re-ingestion of carbon into the nanoparticle. Even though carbon nanotube growth is usually modelled by surface diffusion of carbon on the catalyst particles, the presented observation require bulk diffusion as the main process.

Publication IV: Effect of iron nanoparticle geometry on the energetics of carbon interstitials,

Related to the computational results of the publication III, studies on carbon interstitial energetics in iron are extended to wider a variety of nanoparticle sizes, in α- and γ-phases of iron both in octahedral and tetrahedral interstitial configurations. Octahedral interstitial formation enthalpy is found to depend on the interstitial bond orientation with respect to the nanoparticle surface. In some cases, the difference in formation enthalpies of tetrahedral and octhedral interstitials is decreased suggesting enhancement of diffusion. In addition to nanoparticles, interstitial formation enthalpies for octahedral configuration in semi-infinite slabsystem is presented showing increase in solubility in the subsurface layer.

Publication V: Defect-induced junctions between single- or double-wall carbon nanotubes and metal crystals,
J. A. Rodriguez-Manzo, A. Tolvanen, A. V. Krasheninnikov, K. Nordlund, Arnaud Demortière and F. Banhart, *Nanoscale, accepted for publication*
Junctions between carbon nanotubes and metal nanoparticles are created in situ during electron microscopy. Computational results show that it is necessary to introduce vacancies into the nanotube in order to create the a covalent nanotube-metal junction. Using a theoretical model presented in the publication, it is shown that junction formation can be either endothermic or exothermic depending on the system. Ab initio simulations also show that the junction between the nanotube and the metal particle is covalent, which is essential for electronics applications.

2.2 Author’s contribution

The author of this thesis carried out all the MD simulations and analyses in publication I and all of the computational work presented in publication II. For publications III and V the author carried out most of the simulations, and all simulations in publication IV. In publications I and IV the author wrote the complete draft of the text. In publication II the author wrote the draft of the text excluding the computational details. In publications III and V, the author participated in writing the draft of the computational parts of the text, and devised the original theoretical explanations for the experimental results.

3 CARBON NANOTUBES

CNTs are cylindrical molecules, whose discovery in 1991 by Iijima [11] launched a vast amount of research on this allotrope of carbon. In this section, an introduction to CNTs is given, concentrating on the properties of isolated SWNTs, which are the most relevant for this thesis. First, the atomic structure of CNTs is introduced followed by remarks on the synthesis of these structures. Lastly, the extraordinary mechanical and electronic properties of CNTs are presented with examples of applications.

3.1 Atomic structure of carbon nanotubes

CNTs are molecules of pure carbon with the geometry of a cylindrically wrapped hexagonal carbon atom lattice. All carbon atoms in the nanotube have three nearest neighbours and the intrinsic geometry coincides perfectly with a graphene sheet – angular periodicity excluded. For this reason, it is usual to introduce CNTs as rolled-up graphene sheets, even though nanotubes do not actually form from graphene layers during synthesis. Curiously, the opposite has been
recently demonstrated [17]. If CNT’s ends are capped by hemifullerenes or if the diameter of the tube changes, 5-member rings (pentagons) have to be added to the hexagonal lattice to induce positive curvature, and 7-member rings (heptagons) for negative curvature.

Figure 1: Construction of the (8,3) nanotube form graphene lattice with lattice vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \). \( \mathbf{C}_h = 8\mathbf{a}_1 + 3\mathbf{a}_2 \) is the chiral vector making angle \( \theta \) with the zigzag direction. Points \( A \) and \( \tilde{A} \) are equivalent on underlying honeycomb lattice. Axial direction is presented by the line orthogonal to \( \mathbf{C}_h \).

The diameter of a CNT is determined by its chiral indices \((n,m)\) which are defined by the angular periodicity of the cylindrical honeycomb lattice (see Fig. 1.), i.e. two equivalent points on the underlying honeycomb lattice connected by the chiral vector

\[
\mathbf{C}_h = m\mathbf{a}_1 + n\mathbf{a}_2, \tag{1}
\]

where \( \mathbf{a}_i \) are the primitive translation vectors of the hexagonal lattice. From the law of cosines, the diameter \( d_t \) of the nanotube is

\[
d_t = \frac{\mathbf{C}_h}{\pi} = \frac{\pi}{\mathbf{a}}\sqrt{n^2 + nm + m^2},
\]

where \( \mathbf{a} = 2.46 \text{ Å} \) is the lattice constant of the honeycomb lattice. The angle \( \theta \) between \( \mathbf{C}_h \) and zigzag direction \( \mathbf{a}_1 \) of the honeycomb lattice is called chiral angle. By symmetry \( 0^\circ \leq \theta \leq 30^\circ \). Nanotubes with
$(n, 0) \iff \theta = 0^\circ$ are called zigzag tubes as the zigzag pattern of $a_1$ direction rotates around the nanotube perpendicular to its axis. Nanotubes with $(n, n) \iff \theta = 30^\circ$ are called armchair tubes after the armchair pattern along the circumference. Other possible combinations of $(n, m)$ lead to absence of mirror symmetry, and thus this kind of nanotubes are called chiral. Example structures of these different types are presented in Fig. 2. The chiral vector $C_h$ and translation vector $T$, $T \cdot C_h = 0$, define the unit cell of the nanotube. In addition to atomic structure and chiral symmetry, the chiral numbers $(n, m)$ define the electronic properties of the nanotubes as explained below.

Figure 2: Atomic structures of zigzag (a), armchair (b) and a chiral(c) SWNT.

### 3.2 Electronic properties of carbon nanotubes

One main interest in carbon nanotubes has arisen from their extraordinary electronic properties. Depending on their chirality, CNTs can be either metallic or semiconducting. Their high aspect ratio and low defect concentration (even as low as 1 defect per $4 \mu$m have been reported[18]) make them a perfect testbed for studies of conductivity in $1D$ systems. Extraordinary linear energy dispersion of low energy charge carriers in metallic nanotubes lead to exotic phenomena. In this introduction, a sketch of the basic theory behind these phenomena is given. For a more extensive presentation, see the reviews of Ando [19] and Charlier et al. [20].
The basic features of electronic properties of CNTs can be described by the tight-binding approximation on graphene. Even though graphene was synthesised only recently [13] its electronic properties have been studied for over 50 years [21]. This is because the interlayer spacing of graphite is large (3.37 Å) compared to intralayer atomic separation (1.42 Å), and intralayer conductance can be taken as a first approximation of the graphite conductance. In a similar manner for multi walled CNTs, the electronic properties are dominated by the electronic properties of the coaxial SWNTs forming the MWNT.

The graphene Brillouin zone is presented in figure 3. Graphene unit vectors \( \mathbf{a}_1 = a\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right) \) and \( \mathbf{a}_1 = a\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right) \), where \( a = \sqrt{3}a_{cc} \), lead to reciprocal lattice vectors \( \mathbf{b}_1 = b\left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right) \) and \( \mathbf{b}_2 = b\left(\frac{1}{2}, -\frac{\sqrt{3}}{2}\right) \), where \( b = \frac{4\pi}{a\sqrt{3}} \). High symmetry points \( \Gamma, M, K \) and \( K' \) are located at \((0,0)\), \((1,0)\), \( \frac{2\pi}{a}\left(\frac{1}{3}, \frac{1}{\sqrt{3}}\right) \) and \( \frac{2\pi}{a}\left(\frac{2}{3}, 0\right) \) respectively.

![Figure 3: Brillouin zone of graphene showing the high symmetry points.](image)

Carbon has four valence electrons forming four valence orbitals \((2s, 2p_x, 2p_y, \text{ and } 2p_z)\). Carbon-carbon bonds, called \( \sigma \) bonds, in graphene are formed by hybridisation of \( s, p_x \) and \( p_y \) (thus dubbed \( sp^2 \) hybridisation), making coplanar bonds between carbon and its three closest neighbours. These strong covalent bonds are responsible for the elastic properties of graphene and SWNTs. \( p_z \) orbitals perpendicular to the surface of graphene or nanotubes create delocalised \( \pi \) orbitals with their neighbours. The weak bonding of graphene sheets in graphite and between CNTs in nanotube bundle is due to the van der Waals interaction and interaction of \( \pi \) orbitals \([20; 22]\). \( \sigma \) bands lie high above and low below the Fermi level in graphene, and thus \( \pi \) bands located around the Fermi level define the conduction properties of graphene and nanotubes, except for extremely small diameters \([23]\).
The tight binding wavefunction for graphene can be written with normalised $2p_z$ free atom orbitals $X(r)$ as:

$$\Psi = \phi_1 + \phi_2 ,$$

where

$$\phi_1 = \sum_A \exp(2\pi i \mathbf{k} \cdot \mathbf{r}_A) X(r - \mathbf{r}_A) \text{ and}$$

$$\phi_2 = \sum_B \exp(2\pi i \mathbf{k} \cdot \mathbf{r}_A) X(r - \mathbf{r}_B),$$

where $A$ and $B$ denote the two atoms in the unit cell belonging to different sublattices. Starting from the time independent Schrödinger equation:

$$\hat{H} |\Psi\rangle = \epsilon |\Psi\rangle \text{ i.e.}$$

$$\sum_j \langle \phi_i | \hat{H} | \phi_j \rangle \langle \phi_j | \Psi \rangle = \epsilon \langle \phi_i | \Psi \rangle ,$$

one finds the usual matrix equation:

$$\begin{vmatrix}
\langle \phi_1 | \hat{H} | \phi_1 \rangle - \epsilon & \langle \phi_1 | \hat{H} | \phi_2 \rangle \\
\langle \phi_2 | \hat{H} | \phi_1 \rangle & \langle \phi_2 | \hat{H} | \phi_1 \rangle - \epsilon
\end{vmatrix} = 0 .$$

Solving $\epsilon$ from the determinant gives:

$$\epsilon = \frac{1}{2} \left[ H_{11} + H_{22} \pm \left( (H_{11} - H_{22})^2 + 4H_{12}^2 \right) \right],$$

where $H_{ij}$ are the matrix elements $\langle \phi_i | \hat{H} | \phi_j \rangle$. From symmetry $H_{11}=H_{22}$ and $H_{12}=H_{21}$ giving

$$\epsilon = H_{11} \pm |H_{12}| ,$$

where $H_{11}$ corresponds to electron hopping between nearest neighbours in the same sublattice, i.e. hopping from atom the $A$ to an atom $A'$, and $H_{12}$ corresponds to electron hopping from nearest neighbours on the lattice, i.e. hopping from the atom $A$ to an atom $B$.

$$H_{11} = \langle \phi_1 | H | \phi_1 \rangle = \sum_{A,A'} \exp(-2\pi i \mathbf{k} \cdot \mathbf{r}_A) \exp(2\pi i \mathbf{k} \cdot \mathbf{r}_{A'}) \int X^*(r - \mathbf{r}_A)HX(r - \mathbf{r}_A)d\tau, \quad (10)$$
for nearest neighbours $A$ and $A'$ in the same sublattice. Writing

$$E_0 = \int X^*(\mathbf{r}) H X(\mathbf{r}) d\tau \tag{11}$$

and

$$\gamma'_0 = \int X^*(\mathbf{r} - \sigma'_i) H X(\mathbf{r}) d\tau \tag{12}$$

equation 10 gives

$$H_{11} = E_0 - \gamma'_0 \sum_{\sigma'_i} \exp(-2\pi i \mathbf{k} \cdot \sigma'_i) \tag{13}$$

Writing

$$\gamma_0 = \int X^*(\mathbf{r} - \sigma_i) H X(\mathbf{r}) d\tau, \tag{14}$$

where $\sigma$ is the vector connecting nearest neighbours $A$ and $B$ on the lattice, $H_{12}$ is given by

$$H_{12} = -\gamma_0 \sum_{\sigma_i} \exp(-2\pi i \mathbf{k} \cdot \sigma_i) \tag{15}$$

over three nearest neighbours $\sigma_1 = a(0, \frac{1}{\sqrt{3}})$, $\sigma_2 = a(-\frac{1}{4}, -\frac{1}{2\sqrt{3}})$ and $\sigma_3 = a(\frac{1}{4}, -\frac{1}{2\sqrt{3}})$. Considering hopping between only the nearest neighbours and choosing $E_0 = 0$, one gets the dispersion relation

$$E^\pm(k_x, k_y) = \pm \gamma_0 \sqrt{1 + 4 \cos \sqrt{3} k_x a^2 \cos \frac{k_y a}{2} + 4 \cos^2 \frac{k_y a}{2}}. \tag{16}$$

At the corners of the Brillouin zone $\mathbf{K}$ and $\mathbf{K}'$, $\epsilon^\pm(\mathbf{K}) = \epsilon^\pm(\mathbf{K}') = 0$. Thus, the Fermi surface of graphene is zero dimensional and consists only of the points $\mathbf{K}$ and $\mathbf{K}'$. For this reason the term semimetal is used for graphene and graphite. Taylor expansion in the vicinity of $\mathbf{K}$ and $\mathbf{K}'$ leads to linear dispersion:

$$\epsilon^\pm(\mathbf{k} + \mathbf{K}) = \epsilon^\pm(\mathbf{k} + \mathbf{K}') = \pm \gamma |\mathbf{k}|, \tag{17}$$

where $\gamma = \frac{\sqrt{3} a \gamma_0}{2}$. The linear dispersion near $\mathbf{K}$ and $\mathbf{K}'$ plays an important role in the exotic electronic properties of graphene and carbon nanotubes.
The tubular form of SWNTs sets periodic boundary conditions along the circumference of the tube leading to quantisation of the circumferential wave vectors. In the axial direction, the wave vector remains continuous. For nanotubes with sufficiently large diameter, the band structure can be obtained by the so called zone folding approximation imposing this circumferential periodicity to the wavefunctions and a phase restriction i.e.:

$$\Psi(r + C_h) = \exp(i \mathbf{k} \cdot C_h)\Psi(r) = \Psi(r) \quad \text{and} \quad \exp(i \mathbf{k} \cdot C_h) = 1.$$  \hspace{1cm} (18)

Thus, the allowed energy levels are restricted to energy bands continuous in the direction of the tube axis ($\Gamma \rightarrow X$) and discrete around the circumference, with only the $\mathbf{k}$ vectors allowed that fullfill $\mathbf{k} \cdot C_h = 2\pi q$ as presented in Fig. 5 for the (5,5) armchair tube.

For graphene the semimetallic nature arises from the band crossing of the $\pi$ bands at $\mathbf{K}$ and $\mathbf{K}'$. For nanotubes a band crossing exists if

$$\exp(i \mathbf{K} \cdot C_h) = 1 \quad \text{or} \quad \exp(i \mathbf{K}' \cdot C_h) = 1.$$  \hspace{1cm} (19)
leading to the restriction \( n - m = 3N \), where \( N \) is an integer. If \( n - m \neq 3N \), the nanotube is semiconducting. In consequence, the electronic properties of CNTs are defined by the chiral numbers \( n \) and \( m \). Linear dispersion near \( \mathbf{K} \) and \( \mathbf{K}' \) is conserved in metallic nanotubes.

![Diagram of allowed k lines for (5,5) armchair tube](image)

**Figure 5:** Presentation of allowed \( \mathbf{k} \) lines for (5,5) armchair tube. The bands are indexed by \( q \) in \( \mathbf{k} \cdot \mathbf{C}_h = 2\pi q \). Only \( q > 0 \) bands indexed for visual clarity. \( \mathbf{X} \) is the boundary of the one dimensional Brillouin zone.

### 3.3 Synthesis

The most widely used synthesis methods of carbon nanotubes are laser evaporation (laser ablation), carbon arc discharge, and chemical vapour deposition. In laser evaporation, a quartz tube containing argon gas, and a graphite target containing nickel and cobalt are heated to 1200°C in a furnace. The graphite target is evaporated by intense laser pulses and the gas is carried among the inert argon outside the furnace to a collector at milder temperature where the nanotube growth begins. Cobalt and nickel clusters act as catalytic nucleation sites for nanotubes. Yield of this process can reach 70%, and the produce has highly uniform diameter distribution. On the downside, this method is clearly more expensive than CVD or carbon arc discharge.

First nanotubes reported by Iijima [11] were produced by the carbon arc discharge method (this method was commonly used to produce fullerenes). A potential difference of the order of 20 V is applied across carbon electrodes with micrometer scale diameters separated by \( \sim 1 \) mm in inert atmosphere (e.g. helium). Carbon atoms from the positive electrode are ejected into the negative electrode forming carbon nanotubes. In order to produce single walled nanotubes electrodes must contain some cobalt, nickel or iron as catalytic nucleation sites. Without catalysts, nested or multiwalled nanotubes are produced.
Chemical vapour deposition has become the de facto method of carbon nanotube synthesis. In this method, hydrocarbon gas containing a carbon precursor is catalytically decomposed on catalyst particles at high temperatures (e.g. CH\textsubscript{4} at 1100\degree C). Chemical vapour deposition is the cheapest method for carbon nanotube production and allows growing nanotubes directly on a substrate. Aligned nanotube forests can be grown and nanotube diameter can be controlled by controlling catalyst particle size [24]. As CVD allows continuous fabrication, it remains the most promising method for large scale production.

The actual growth process from the catalyst particle is hitherto unknown despite a huge body of research (see e.g. [25] and references within). This is an important open problem as, even though some control over diameter exists, the chirality of grown nanotubes can not be selected, and thus both metallic and semiconducting nanotubes are produced simultaneously. Furthermore, all SWNT growth methods use metal catalyst particles, motivating studies on carbon nanotube catalytic growth and carbon nanotube catalyst particle interactions.

### 3.4 Applications

The carbon sp\textsuperscript{2} bond is among the strongest atomic bonds. For this reason the mechanical properties of carbon nanotubes are extremely appealing for mechanical reinforcement applications. The Young’s modulus of carbon nanotubes, describing how easily the material is elongated under stress, is almost ten times larger than that of steel. Carbon nanotubes are also very resilient when they are bent. Instead of cracking, nanotubes buckle and can be straightened into original form. Fractures are avoided as there are no dislocation lines in nanotubes and stress of strong bending can be minimised by introducing curvature with pentagons into the hexagonal atomic network. Tensile strength, i.e. pressure needed to break the material, of carbon nanotubes is 20 times larger than that for steel. As nanotubes are currently too expensive for large scale applications such as reinforcing steel or concrete [26] in construction, the usual application is in expensive sports equipment where weight versus strength ratio is essential e.g. tennis rackets, baseball bats, bicycle frames and ice hockey sticks.

The high conductivity, nanoscale diameter and chemical stability of CNTs make them ideal candidates for electron emission. Field emission from nanotubes was first demonstrated by Rinzler in 1995 [27], leading to many experiments on possible applications since carbon nanotubes have very low threshold electric field for electron emission [28]. In 2001 Samsung manufactured a prototype display based on CNT field emission [29], but development of cheap large LCD panels for flat displays reduced the commercial appeal of this application. More promising application
is in LCD backlights where Samsung has shown extremely high contrast achieved by CNT based LED backlighting of LCD displays [30].

Many applications in energy storage have been envisaged utilising CNTs. Conventional carbon electrodes can be replaced by CNT electrodes improving the electrochemical intercalation of lithium leading to improvement in energy capacity, charging time, and lifetime [31; 32]. In the beginning of 2000, hydrogen storage in carbon nanotubes gathered substantial attention, but experiments have shown contradictory results [33]. Still, a realistic estimate of 8 wt% satisfies the applicability limit. Carbon nanotubes have also been proposed as the electrode material of supercapacitors [34]. Also applications in improving the properties of solar cells have been proposed [35; 36].

Electric conductance of carbon nanotubes is changed when molecules attach to the nanotube surface. Due to their high surface to volume ratio, CNTs are ideal for gas sensing applications. The response time of CNT gas sensors have been shown to be an order of magnitude shorter than conventional probes [37]. Due their high conductivity and inherent nanoscale, CNTs have been proposed as scanning probe instrument tips such as atomic force microscope and STM [38]. It is also possible to construct nanotweezers by attaching CNTs as tips of a two-electrode AFM [39].

The extraordinary electronic properties have motivated mass of research in nanoelectronics applications of carbon nanotubes. Semiconducting CNTs can be used in field effect transistors (FET) with high on/off ratio and fast switching [40; 41; 42; 43]. At cold temperatures, CNT FET has shown peculiar transport properties [44]. Even 50 GHz operation has been observed [45] and a theoretical limit of 130 GHz has been proposed [46]. Recently an extremely fast nanotube memory element was realised [2].

4 SIMULATION METHODS

Physics is the most fundamental of all sciences forming the base of all phenomena in existence. Eventhough many laws of physics, e.g. increase of entropy or local equivalence of gravity and acceleration, can be stated quite simply, the mathematical models constructed to give quantitative predictions get extremely complicated even for interactions between individual particles. Thus, making exact theoretical predictions from the most advanced, current, models is in most cases impossible.

Computational physics aims to solve this problem by making well-founded approximations of the systems to be studied and the interactions of their constituents and translating these approx-
imative models into a language processable by a computer. Harnessing the vast computational capabilities of modern supercomputers allows computational physicist to study systems with up to tens of millions of atoms interacting classically with each other, or to describe quantum mechanical interactions of molecules constituting even hundreds of atoms.

This section consists of short introductions to molecular dynamics with classical potentials and density functional theory based \textit{ab initio} simulations which are the main computational methods used in this thesis. Classical molecular dynamics allows the simulation of systems up to millions of atoms for nanosecond timescale. The accuracy is limited by the approximative interaction models. In contrast, \textit{ab initio} simulations can capture intricate details of the quantum mechanical interactions between the molecules, but the system sizes and time scales are many orders of magnitude smaller. However, also these methods are approximative due to the reasons mentioned above.

In the publications presented in this thesis, the computational methods were selected to capture the most essential aspects of each phenomena. When large systems and statistics were needed, classical methods were used, and when quantum mechanical aspects of molecular binding were essential, \textit{ab initio} methods were employed. In order to reach a more complete description these methods were combined.

### 4.1 Classical molecular dynamics

Molecular dynamics is a method for studying dynamical processes in of a closed system of particles. In classical molecular dynamics (CMD) Newtonian equations of motion are solved numerically, using known interactions between the particles. Molecular dynamics was originally developed in the late 1950’s by Alder and Wainwright for phase transitions and atomic vibrations in molecules [47; 48; 49].

The central approximation in most atomistic simulations is the Born-Oppenheimer approximation [50] separating nuclei and electrons in the molecular wavefunction. The basic principle behind this approximation is that the movement of electrons is fast enough to reach electronic equilibrium before the movement of nuclei can perturb the electron system. This means that the atomic interactions can be computed from static electron system and allows the description of atoms as single particles in classical molecular dynamics.

A rudimentary algorithm for molecular dynamics simulation can be presented as follows. First, the initial atomic positions are read in. Forces are calculated from the atomic positions, and
the atoms are moved to new coordinates predicted from the forces. After advancing the time by one time step, the forces are calculated from the new positions and so forth until the end of simulation time is reached. A predictor-corrector algorithm is often employed for improving the accuracy of the predicted state in the future timestep.

All classical MD simulations presented in this thesis were run using a simulation code PARCAS written by K. Nordlund [51]. In this code equations of motion are solved utilising a fifth order Gear predictor corrector algorithm (see e.g. Ref. [52]). A variable time step is used for efficient computation also ensuring small enough time steps for handling highly energetic particles as in irradiation events.

4.2 Interatomic potentials

A central factor in the accuracy of a classical molecular dynamics simulation is the interatomic potential. Avoiding quantum mechanical electronic structure calculations leads to a reduction in particle number (in realistic materials the number of electrons always greatly exceed the number of atoms) and computational complexity of interactions, but at the same time the information of atomic interactions is completely lost. Thus, the interatomic potential has to be built from a combination of physical postulates and empirical data.

Many different approaches have been used for constructing the interatomic potential. Pair potentials have the simplest functional form taking into account only the pairwise distance of atoms. Most simplest pair potential is the Lennard-Jones, named after J. E. Jones who suggested the addition of attractive and repulsive interactions in this form [53]:

$$V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right],$$

where $\epsilon$ and $\sigma$ are fittable parameters, giving good results for noble gases. This potential model has been used for many materials due its low computational costs, but it has very limited accuracy except for van der Waals-bonded systems.

A widely used improvement of the pair potential is the embedded atom method (EAM) developed in the 1980’s by Daw and Baskes [54; 55]. In this method, every atom of the system is added as an impurity atom into the electron density of the undisturbed system of all the other atoms based on Stott-Zaremba corollary [56]. Total energy $E$ of the system is given by a sum
of an electronic embedding energy functional $F_i$ and pair potential $\phi$:

$$E = \sum_i F_i(\rho_i(R_i)) + \frac{1}{2} \sum_{i,j} \phi(R_{ij}),$$  \hspace{1cm} (21)

where $\rho_i$ is the electron density of the host without atom $i$, and $R_{ij}$ is the distance between atoms $i$ and $j$. EAM gives reasonable results for noble gases and metals, but it can not describe materials with covalent bonds which have strong directional dependence.

Bond order potentials have the advantage over pair potentials and embedded atom method in their ability to take the bonding state of the atom into account. In the classical MD studies of this thesis, Tersoff-type bond order potentials [57] were used. The total energy $E$ of the system is given as sum over individual atoms $i$ as

$$E = \sum_i E_i = \frac{1}{2} \sum_{i \neq j} V_{ij},$$  \hspace{1cm} (22)

where

$$V_{ij} = f_C(r_{ij}) \left[ A \exp(-\lambda_1 r_{ij}) - B_{ijk} \exp(-\lambda_2 r_{ij}) \right],$$  \hspace{1cm} (23)

and $f_C$ is the cutoff function of the potential, $A$, $\lambda_1$ and $\lambda_2$ are positive constants with $\lambda_1 > \lambda_2$, and $B_{ijk}$ is the bond order parameter, which takes into account the favoured symmetry of the atomic bonding.

These potential models have been developed for modeling equilibrium, or near-equilibrium, properties of materials, and hence typically fail in strongly nonequilibrium situations. In this thesis, the emphasis of MD simulations is on irradiation studies where atomic interactions at small separations become extremely important, and the potentials have to be corrected by smoothly joining them to a short-ranged repulsive potential describing these interactions correctly [58].

### 4.3 Density functional theory

Density functional theory (DFT) is a formulation of quantum mechanics which can be efficiently implemented for many-particle ground state simulations. Most of modern quantum mechanical simulations of solid state properties, electronic structure, and chemical reactions are based on this method.
DFT is based on the Hohenberg-Kohn theorem [59], stating that the ground state energy can be written as a functional of state density and that this density minimising the energy functional will be the density of the ground state. The usual, and original, application is finding the ground state electron density for a system of interacting electrons in a static atomic potential in the spirit of Born-Oppenheimer approximation. This reduces the energy minimisation problem from a $3N$-variable problem to a 3-variable problem.

The Hohenberg-Kohn theorem implicates that the ground state energy of interacting electron gas in a static potential $v(r)$ can be written with minimal number of variables as

$$E = \int v(r)n(r)dr + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|} + G[n],$$

where $n(r)$ is the electron density and $G[n]$ is a universal functional of the density. For interacting electron gas it is natural to divide $G[n]$ as

$$G[n] = T_s[n] + E_{xc}[n],$$

where $T_s[n]$ is the kinetic energy of noninteracting electrons with density $n$ and $E_{xc}[n]$ is the exchange-correlation energy of the interacting system with density $n$. If $E_{xc}[n]$ is known, this leads to an exact solution of the ground state. However, the functional form of $E_{xc}[n]$ is generally unknown. For slowly varying $n$, the exchange-correlation energy can be approximated as $E_{xc}[n] = \int n(r)\epsilon_{xc}(r)dr$, where $\epsilon_{xc}r$ is the exchange and correlation energy of single electron in uniform electron gas of density $n$ [59]. Using this local density approximation (LDA), the ground state can be solved self-consistently as first shown by Kohn and Sham [60], leading to almost exact solution for slowly varying $n$. LDA works extremely well for bulk many materials, especially metals, but lacks in accuracy when studying molecules or nanostructures due to more abrupt changes in the valence electron density.

Local curvature effects can be taken into account in $E_{xc}[n]$ improving the solutions for more rapidly varying electron densities by the generalized gradient approximation (GGA), where $E_{xc}(n) = \int \Pi_i f (n_{\sigma}(r), \nabla n_{\sigma}(r)) dr$, where the product $i$ is over spins. Many different proposals for $f$ exist as such as Perdew-Wang (PW91) [61], Perdew-Burke-Ernzernhof (PBE) [62], Becke-Perdew (BP) [63; 64] and Lee-Yang-Parr (LYP) [65].

In publications II and V, Vienna Ab initio Simulation Package (VASP) [66] utilising plane wave basis sets was used for DFT calculations. Core electrons of atoms were approximated by the projector augmented wave (PAW) [67] method, where the optimisation of rapidly changing core states is avoided by using static core states. In publication II, PW91 GGA was employed...
allowing formation energy comparisons with previous results for some of the presented defect structures. The currently more widely applied PBE GGA was used in publication V. These exchange-correlation parametrisations are generally thought equivalent, although they yield different defect formation energies in some systems [68].

4.4 Simulation setup

The most essential features of the simulation setups used in the publications are reviewed in this section. The detailed descriptions can be found in the corresponding publications.

The irradiation response of nanotubes was studied in publication I using classical MD. Nanotubes of \( \sim 2000 \) carbon atoms were used as the target, with a few fixed atoms at the ends to avoid centre-of-mass movement. Irradiation area was minimised based on system symmetry to maximise the density of random non-equivalent irradiation locations. During each irradiation incident, i.e. the first 5000 fs, Berendsen temperature control [69] was used at the periodic cell borders to avoid spurious effects of reflected or periodic heat waves. With the periodic setup, simulation system size could be reduced as the temperature control area doubles, leading to realistic heat conduction away from the incident area. Atoms relevant to the irradiation response were simulated as the NVE ensemble. After the actual irradiation event the system was slowly cooled down to 0 K. The resulting defects were characterised by a combination of ring analysis based on prime ring algorithm [70] and a heuristic algorithm identifying the defects by the local changes they induce in the ring structure of the hexagonal network given by the ring analysis. The annealing of defects at macroscopic timescales was included by kMC simulation as presented in Ref. [71].

In the \textit{ab initio} simulations of publication II, periodic supercells of 80 – 240 atoms were used. A comparison with the experimental STM/STS was done by evaluating the local density of states in a neighbourhood of atoms corresponding to STM tip’s interaction area on a line parallel to the tube axis. The atomic and electronic structures of SWNTs with irradiation induced defects were studied by \textit{ab initio} DFT simulations as introduced in Sect. 4.3 and Sect. 4.4 using the VASP simulation package. In order to compute defect induced changes in the electronic structure of SWNTs, information on the excited states of the system is needed. This is known to be problematic within DFT calculations, as DFT is inherently a ground-state theory and exited-state properties can not be rigorously deduced from the given ground-state. Especially, the band gap of various semiconductors is underestimated with LDA or GGA exchange and defect induced states may be predicted to wrong positions in the band gap [72; 73; 74; 75]. Many theoretical approaches [72; 73] aimed at solving this problem exist, but the improved accuracy
of these methods comes with too great computational cost for the systems studied (e.g., the GW approximation [76] and hybrid functionals [65]) or require additional approximations as in the the LDA+U method [77]. In our simulations, DFT-GGA method used gave a reasonably accurate band gap of 0.74 eV for the (10,0) nanotube studied, compared to the experimental value 0.9 eV [78].

Classical molecular dynamics simulations of publications III-V included iron nanoparticles interacting with individual carbon nanotubes and carbon atoms. In the energetics studies of publications III and IV, carbon interstitials were placed in the minimum energy and saddle point configurations inside an iron nanoparticle in vacuum. System sizes from \( \sim 10 \) to \( \sim 50000 \) atoms were used. Classical potentials allow the systematic study of large variety of nanoparticle sizes within the same method.

Metal nanoparticle-nanotube interactions presented in publication V were simulated both with classical and \textit{ab initio} methods. With the latter, the supercell size was selected to include enough vacuum to avoid mirror interactions in periodic systems. When the atomic configurations were optimised with classical MD, the systems were annealed using the Berendsen thermostat to avoid metastable configurations.

5 ATOMIC RESOLUTION MICROSCOPY

As most of the publications presented in this thesis are collaborative projects with experimentalists a brief introduction on the related experimental methods is given below. Both scanning tunneling microscopy (STM) and Transmission electron microscopy (TEM) can achieve atomic scale resolution. STM is a nonintrusive method allowing the imaging of sample topography and probing the local electronic structure. TEM gives atomic resolution structural information on samples and can be used to modify the atomic structure by displacements caused by electron knock on collisions with atoms.

5.1 Scanning tunneling microscopy and spectroscopy

Scanning tunneling microscopy is currently the only probing method that gives information on the topography and electronic structure of samples with atomic scale resolution. It was developed by Binnig and Rohrer in 1981 [79] and has become a widely used experimental technique in the studies of nanosystems.
The basic idea behind STM is quantum mechanical tunneling of electrons through vacuum when a narrow tip is placed close to the sample and a bias voltage is applied between the two systems. With constant bias voltage, the tunneling current depends on the distance between the tip and the sample surface. Starting from a simple time independent one dimensional model, tunneling of electrons between a STM tip and the sample can be described by single electron tunneling through rectangular potential barrier as presented in Figure 6. Solving the Schrödinger equation results in a transmission coefficient

\[ T = \frac{16k^2\kappa^2}{(k^2 + \kappa^2)^2} \exp(-2\kappa z), \]  

(26)

where \( k = \sqrt{2mE/\hbar^2} \) and \( \kappa = \sqrt{2m(V - E)/\hbar^2} \) for an electron with kinetic energy \( E \) through effective barrier \( V - E \) with width \( z \). The exponential dependence of transmission from barrier width, i.e. tip distance, \( z \) leads to the high height resolution of STM.

Figure 6: Sketch of one dimensional energy diagram of tip-vacuum-sample system. a) For zero applied bias voltage \( U \) Fermi levels of the tip and the sample are aligned. When bias voltage is applied energy levels are shifted upward b) or c) downward by \( e|U| \) depending on the polarity of the bias voltage.
The most important feature of STM for the results of this thesis is the possibility of performing scanning tunneling spectroscopy (STS). In STS, the STM tip is kept at a constant position, while the bias voltage is swept.

A more accurate treatment of STM setup as presented by Tersoff and Hamann [80], leads to

$$\frac{dI_t}{dU} \propto e \cdot \rho_t(0) \cdot \rho_s \cdot T,$$

(27)

where $e$ is the electron charge, $I_t$ is the tunneling current, $\rho_t(0)$ the tip DOS at Fermi level, $\rho_s$ the LDOS of the sample, and $T$ the tunneling coefficient. The proportionality of $dI_t/dU$ to the LDOS allows the local electronic structure of the sample to be probed by STS. For an exhaustive review of STM theories see Ref. [81].

## 5.2 Transmission electron microscopy

Transmission electron microscopy is a technique of taking a “photograph” with electrons. A beam of electrons is transmitted through a thin sample and focused on a fluorescent screen, photographic film, or CCD sensor. Resolution of an optical imaging system is limited by diffraction to the wavelength of visible light $\sim 500$ nm. An electron with a typical energy of 200 keV in the electron beam of TEM has a wavelength of 2.5 pm, setting the theoretical limit for imaging resolution much below atomic lengthscales. Due to various technical problems, the actual resolution is about 1 Å. However, high energy of the electrons in a TEM beam also damage the sample under imaging. Modern high resolution TEMs may reach atomic resolution of carbon nanostructures at only 80 keV, but this is extremely difficult at best. On the other hand, atomic displacements caused by the electrons in a TEM also offers the possibility to induce vacancies to the sample at atomic precision.

Due to the extremely short wavelength of the high energy electrons, their interactions with the sample are practically limited to knock-on collisions with the sample nuclei [16]. From relativistic mechanics, the maximum energy transferred to a sample nucleus of mass $M$ by incident electron of energy $E$ is

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

(28)

where $m$ is the electron mass and $c$ the speed of light. The minimum energy that has to be transferred to a target atom in order to produce a vacancy-interstitial pair which does not spontaneously recombine is called the threshold energy $E_{\text{thr}}$, a quantity similar to the escape
velocity required for a rocket to overcome earth’s gravitational field after its engines have shut down. By inserting $E_{\text{thr}}$ to equation 28 as $T_{\text{max}}$, the required irradiation energy $E$ can be solved. For a carbon atom in SWNT, $E_{\text{thr}} = 17$ eV corresponding to $E \sim 86$ keV. The number of vacancies produced during experiment can be evaluated by the displacement rate $p$ given by

$$p = \sigma j,$$

where $\sigma$ is the displacement cross section and $j$ the beam current density. The analytical expression for displacement cross section in Mott scattering of relativistic electrons from atoms (i.e. nuclei), as first presented by McKinley and Feshbach in 1948 [16] can be written as

$$\sigma = \frac{4Z^2E_R^2}{m^2c^4} \left( \frac{T_{\text{max}}}{E_{\text{thr}}} \right) \pi a_0^2 \left( \frac{1 - \beta^2}{\beta^4} \right) \left\{ 1 + 2\pi\alpha\beta \left( \frac{E_{\text{thr}}}{T_{\text{max}}} \right)^{\frac{1}{2}} \right\}$$

$$- \frac{E_{\text{thr}}}{T_{\text{max}}} \left[ 1 + 2\pi\alpha\beta + \left( \beta^2 + \pi\alpha\beta \right) \ln \left( \frac{T_{\text{max}}}{E_{\text{thr}}} \right) \right],$$

where $Z$ is the atomic number of the displaced atom, $E_R$ Rydberg energy, $a_0$ Bohr radius, $\beta = \frac{v}{c}$ and $\alpha = \frac{Z}{137}$. In Fig. 8 the displacement rates $p = \sigma j$ of carbon atoms for various displacement thresholds are presented as a function of electron energy with current $j = 10 \text{ A cm}^{-2}$. An important feature of the displacement rate is the nonlinear dependence on the displacement threshold.
Figure 8: Displacement rate of carbon by an electron as a function of the electron energy $E$.

Beam current density of $10^{-50} \text{A cm}^{-2}$, close to the typical experimental beam current densities, was used giving an order of magnitude estimate for typical experimental beam current densities of $10 - 50 \text{A cm}^{-2}$. Order of magnitude higher current densities are attainable when TEM is used intentionally to induce damage locally.

Approximating that displacement threshold of a carbon atom in SWNT $\sim 17 \text{eV}$ is roughly reduced to $\sim 11 \text{eV}$, when one of the three bonds is missing, displacement rate doubles at 200 keV indicating that defects act as seeds for degradation of the structures. For more extensive treatment of electron irradiation damage in carbon nanotubes, see e.g. Refs. [82; 83; 84; 85].

6 ATOMIC SCALE ENGINEERING OF CARBON NANOTUBES

Applications of nanoscience can be divided roughly into two classes – functionality achieved in macroscopic systems due modifications of the material properties at the nanoscale and func-
tional nanoscale systems. Within the latter class, one faces the problem how to modify the material properties at nanoscale, which in practise is atomic scale modification. Two possibilities exist. The “easy” approach is to develop a system which self-assembles into a functional nanostructure. In essence, this means that one can pour the ingredients (atoms, molecules) of the nanodevice into a test tube, shake-and-bake and get a working device. This method would be easily scalable to mass production, but unfortunately it works only in some limited cases [86]. For most of the conceivable applicable nanostructures, it remains science fiction.

The other approach is to explicitly modify the atomic configuration of the nanostructure. However, it requires extreme sophistication of the tools used to modify the atomic structures, tweezers so small to move an atom do not exist.

One solution to atomic scale engineering is irradiation. The usual association of irradiation is its harmful effects on materials. Still, long traditions of using irradiation in a beneficial manner exist. One could even say, that modern semiconductor industry and the production of microprocessors would not exist without irradiation, since ion beam doping of the materials is essential to their functionality. Irradiation by energetic particles, such as electrons and ions, offers a method to locally induce damage, i.e. modify the atomic structure of nanomaterials. Localized ion irradiation of carbon nanotubes has been shown to result in the formation of quantum dots [87; 88] and inverters [89]. Both electron and ion irradiation can be used as tools to cut nanotubes [90; 91] and weld carbon nanotubes and nanostructures together [90; 92; 93; 94; 95], giving the possibility of creating interconnects between active components, such as transistors implemented of semiconducting nanotubes.

In the studies presented below, both electron and ion irradiation mediated engineering of nanotubes are presented. Publications I and II address the effects of ion irradiation on carbon nanotubes and describe how ion irradiation can be used to locally modify the electronic structure of carbon nanotubes. Publications III-V concentrate on defect production by transmission electron microscopy as a tool for atomic scale engineering of carbon nanotube – metal nanoparticle compounds.

6.1 Irradiation effects on carbon nanotubes

Irradiation response of macroscopic materials has been studied for decades. The original motivation was the development of fission and fusion reactors [96], where the materials have to stand a hostile radiative environment. It is well known that irradiation deteriorates materials
by creating defects. When irradiation is used on purpose, as in ion implantation of semiconductors, this leads to unwanted side effects as the implanted ions create a large number of lattice defects.

Momentum and energy transfer of an energetic particle (here ion or electron) to the target is mediated through different channels. The most important primary radiation effects are displacement of atoms inside the target or atom sputtering from the surface, electronic excitations, bond breaking, phonon generation, and emission of photons and secondary electrons. These different mechanisms have different cross sections in different materials, irradiation energies and particle types. In carbon nanotubes, which are either metallic or small gap semiconductors, and have high heat and charge conductance, the irradiation effects are dominated by knock-on atom displacements [82]. Some of the bulk, such as cascades, are practically non-existent as carbon nanotubes have either large surface-to-volume ratio (MWNTs) or have only surface atoms (SWNTs). Specific details of ion and electron irradiation effects in SWNTs are presented in the following sections.

Irradiation response of nanostructures is an interesting problem as the behaviour of nanostructures under irradiation differs from that of bulk materials. The most simple reason for this is the extremely small size and/or reduced dimensionality of nanostructures. The energetic particle penetrating a bulk target leaves all of its kinetic energy to the target, but may pass through a nanostructure, losing only a small part of its energy. In the extreme case of graphene, which is truly a two dimensional material, the target may be considered in some cases practically transparent to an energetic ion [97]. On the other hand, irradiation of zero dimensional targets, such as fullerenes or metal nanoparticles, may lead to melting, as the extreme local heating induced by the incident ion can not propagate and dissolve in the target.

Even within nanomaterials, the $sp^2$ bonded carbon nanostructures are special under irradiation. The hexagonal graphitic network of carbon atoms can reorganise after an irradiation incident. Bonds around vacancies reconstruct minimising the number of dangling bonds and the destructive effects of irradiation are minimised. [98] Example of this bond reconstruction by lattice recombination is presented in Fig. 9, where the atomic configuration of a single vacancy (SV) is presented. A displacement of a single atom from the hexagonal network leads to three atoms with only two neighbours. Due to the $sp^2$-hybridisation, it is energetically favourable for the atoms to have three neighbours even if some local deformation of the atomic structure is needed. In SV, two of the three undercoordinated atoms form new bonds with each other, leaving only a single atom undercoordinated. Due to the reconstruction, the radius of the nanotube is locally slightly decreased. It has been shown that, owing to this effect, carbon nanotubes subjected to electron irradiation can be used as high-pressure cylinders and nanoextruders [99].
Defects are not only essential in irradiation studies or defect engineering, but exist also in pristine nanotubes. Ion irradiation offers a possibility to study also the effects of these intrinsic defects by locally creating defects with predictable atomic configuration on a defect free section of a nanotube. Naturally, for this approach, accurate information on the defect production under ion irradiation is necessary.

6.2 Tailoring local electronic structure and conductivity of SWNTs

As described above, electron and ion irradiation can be used in a variety of applications. Electron and ion bombardment produces always (unwanted) irradiation-induced damage as a side-effect. Even a small number of defects may dramatically change the conductance of nanotubes, and hence considerable amount of attention has been paid to electronic transport in defected SWNTs [43; 100; 101; 102; 103]. Computations of electron transport in defected nanotubes has been conducted as follows [100; 102]: first transport over single defect systems are calculated, and these results are summed and averaged over a distribution of defects. Naturally, not only the structures of individual defects are important, but also the defect distribution created in the experimental setup. It has also been demonstrated that intrinsic defects in SWNT source-drain-
gate devices can induce resonant back-scattering [104; 105] leading to quantum dot devices at low temperatures, as well as high gate sensitivity at the defect position [18].

Previous studies have shown that single and double vacancies (SV and DV) and carbon adatoms (CA) are the most prolific defects which appear in SWNTs under ion irradiation [106]. Theoretical insight have been given to defect formation under ion irradiation [107; 108; 109; 110] and estimates have been given on the total irradiation damage in terms of coordination differences from pristine nanotubes [107; 110] but the exact ratio between concentrations of different defects has stayed unknown. This information is critical to conductance calculations, as SVs and DVs have very different effects on the electronic transport properties [100]. Where SV are known to have a minor effect on conductivity, DVs are known to destroy the conductivity providing an increment of three orders of magnitude to the resistance with a concentration of only 0.03% of DVs.

In publication I defect production was studied by simulating the effects of Ar ion irradiation on SWNTs. Using the simulation setup presented in Sect. 4.4 (8,8), (10,2), and (12,0) SWNTs were irradiated with Ar ion energies ranging from 25 eV to 3.0 keV. Under experimental conditions, the irradiation events are located at random positions on the target within the beam diameter. Thus considerable amount of statistics is needed for a realistic estimate of defect production. In this case, 300 irradiation events per energy were studied, giving reasonably small uncertainties. Average number of defects produced in a (8,8) SWNT per ion impact is presented in Fig. 10. Difference in the abundance of different defects can be seen from the results. Number of carbon adatoms (CAs) with respect to produced defects is highest at the low energies. With irradiation energies of 2 – 5 keV, production of SVs dominate, saturating to 0.8 vacancies per ion impact at 10 keV. The total number of defects reaches its maximum at 0.7 keV, number of DVs at 0.5 keV, and number of other (e.g. multivacancy) defects at 1.0 keV. Number of multivacancies remains below 10 % for all ion energies. Two channels for producing multivacancies exist; either the ion hits the side of the tube, thus interacting with multiple carbon atoms on its path, or carbon recoils in approximately tangential direction in the tube, producing secondary displacements. With the studied irradiation energies, the latter is more rare, but it can have substantial effect when irradiation energies rise to 0.1 MeV and above [97].

The system temperature in these simulations was chosen to be zero, as previous studies have shown that defect production is essentially the same at zero and room temperatures. By contrast, defect evolution is dependent on temperature, and in order to get a better estimate for the defect distribution in experimental conditions, this point has to be addressed. Problematically, MD or even accelerated [111; 112; 113] MD simulations can not achieve the time scales needed
Figure 10: Average number of defects produced per Ar ion impact as functions of energy. Markers pointing the simulation results are connected by lines for guides for the eye.

for annealing of non-local irradiation-induced defects. A typical example of such non-local configuration is presented in Fig. 11, where an SV was produced on impact and the kicked-out atom was bonded on the opposite side of the nanotube. In order to tackle this problem, the kMC method [114] was applied. In the kMC method a fixed lattice of atoms is assumed, on which the defects are allowed to migrate via temperature activated events. Irradiation induced defects were allowed to migrate up to a simulation time of 10 s. The kMC simulations showed that CAs inside the nanotube are extremely mobile even at room temperature, and all of them quickly recombine with vacancies while vacancies remain in the system. CAs outside the nanotube are less mobile and within the simulation time (10 s) ≈ 5 % of recombine with the vacancies. At
400°C, all CAs are annihilated. For these reasons, it is expected that almost all of the CAs recombine with vacancies during several hours after irradiation.

Complete CA-vacancy recombination is not possible, as substantial amount of the atomic recoils are sputtered away from the system, except for the lowest irradiation energies (25 – 75) eV. The kMC simulations show a decrease of 20 % in the numbers of SVs and DVs at 400°C. Due to smaller number of sputtered atoms, this effect is stronger at lower irradiation energies. Moreover, SVs are not mobile enough [115] at room temperature to coalesce into DVs within the low dose irradiation limit. A high ratio between SV and DV is essential if ion irradiation is to be used in the engineering of SWNTs, e.g. defect induced welding of CNTs as observed in TEM [116], without destroying the conductivity. On the other hand, if resistance is to be increased or electron localisation effects are desired, this ratio has to be minimised. Results for \( N_{SV}/N_{DV} \) from combined MD and kMC simulations for irradiation of (8, 8), (10, 2), and (12, 0) SWNTs at zero temperature and for (8, 8) also in room temperature and 400°C are plotted in Fig. 12. Annealing at finite temperatures slightly increases the ratio as the recombination of CAs with DVs produces SVs. At 400°C the ratio is increased by \( \sim 20 \% \) and at room temperature \( \sim 10 \% \) for low ion energies. For higher ion energies, the effect is weaker, as

![Figure 12: Ratio of the number of single to double vacancies \( N_{SV}/N_{DV} \) for (8, 8), (10, 2) and (12, 0) SWNTs at zero temperature. Effect of annealing in finite temperatures obtained by the kMC simulations for (8, 8) SWNT are also shown.](image)
almost all of the CAs are sputtered away. Irradiation energies below 0.1 keV seldom produce DVs as the maximum impact energy approaches the DV production threshold. Moreover, the number of CAs in the system is increased leading to recombination of the small amount of DVs to SVs, and thus $N_{SV}/N_{DV}$ goes to infinity. At energies 0.4 to 0.7 keV, the ratio is minimal and saturates to $\sim 3$ as irradiation energy is increased.

These results show that energy selective irradiation can be used either to control the effects of irradiation on SWNT conductivity, and also to give information on the finite time and temperature effects on defect annealing after irradiation. Furthermore, the simulations give the abundance of the most typical defects and defect clusters, such as SVs, DVs, triple vacancies (TV), CAs, CA dimers, Stone-Wales defects [117] and combinations of the previous, created during irradiation used for further analysis presented below.

The effects irradiation induced defects have on the local electronic structure of semiconducting SWNTs are studied in publication II. In addition to showing what kind of modifications of electronic structure are possible via irradiation, this information is essential for the identification of irradiation induced defects with STM/STS.

An example of STM/STS scan of a 50 nm long segment of a semiconducting SWNT with chiral indices (2, 9) or (2, 10) irradiated with 200 eV and 1.5 keV Ar ions is presented in Fig. 13. Common feature of irradiation induced changes in the LDOS is the appearance of new states in the band gap and/or minor changes in the band gap width and state density near the valence and conduction band edges. Experiments presented in publication II show that with 200 eV irradiation, well-defined single or multiple peaks appear in the band gap. 1.5 keV irradiation produces more often complicated, and spatially more dislocalised, electronic changes. This is in agreement with the results of publication I; the number of large multivacancies is increased at higher irradiation energies relative to the total number of irradiation induced defects.

In simulated STM images the signatures of individual defects are protrusions as indicated in numerous studies [118; 119; 120; 121; 122]. The geometry of the protrusions in the simulated STM images may vary making it possible in theory to distinguish the defect structures [119; 123] but from experimental images this is rarely possible due to convolution effects. Instead of comparing simulated and experimental STM images, the STS spectra in a defected area can be compared to simulations, making the identification of defects possible.

The most prolific irradiation induced defects give rise to new states and the defects can be classified in three different categories according to their experimentally detectable features. The first class of defects induce a single peak in the band gap. Second class of defects change
Figure 13: STM/STS scans of a semiconducting SWNT irradiated with 200 eV and 1.5 keV on the left and right panels respectively. **Left:** a) STM topography image of the nanotube. Here defects can be seen as protrusions. b) Detailed image of the defect sites and dI/dV scan recorded along the dashed horizontal line. c) Another example of STS scan where multiple localised peaks are found in the band gap. **Right:** a) and b) Topography images and the corresponding dI/dV scans recorded along the horizontal dashed lines. Courtesy of Gilles Buchs, EMPA, Switzerland and Kavli institute of nanoscience, The Netherlands.

The width of the band gap by inducing new states near the band edges. Third class of defects give rise to multiple peaks inside the band gap. Examples of simulated results for defects belonging to each category are presented in Fig. 14. Even though the features each category of defects induce inside the band gap are quite similar, the features outside the band gap offer the possibility to distinguish these defects from each other. For example both the Stone-Wales defect and inverse Stone-Wales defect (adatom dimer) both reduced the bandgap of (10,0) nanotube by 32 %, but the first induces new states of high density in the conduction bands, whereas for the latter they appear in the valence bands, as seen in Fig. 15.

As a conclusion, ion irradiation can be used to control the conductivity of SWNTs by selective production of DVs. Alternatively, the harmful effect of DVs can be avoided when irradiation is used to induce morphological changes and self-organisation as in nanotube welding. Ion irradiation can give rise to rich family of features in the bandstructure of SWNTs and the
A combination of *ab initio* simulations and STM/STS measurements can be used to identify the defects accurately.

**Figure 14:** Reconstructed atomic structures of double vacancy (top), triple vacancy (middle) and two adatoms (bottom), band structures ($\Gamma - X$), local densities of states and STS spectra.

**Figure 15:** Simulated STS spectra of Stone-Wales defect (left) and inverse Stone-Wales *i.e.* CA dimer (right).
6.3 SWNT metal nanoparticle interactions under electron irradiation

Metal particles are the key ingredient in the synthesis of carbon nanotubes. Moreover, metal particles can be utilised as links between the nanotube and its surroundings. Thus, studies of carbon nanotube-metal nanoparticle compounds are essential for nanotube applications and for better understanding the nanotube growth. Recent in situ electron microscopy studies have clarified nanotube growth from catalyst particles [124; 125; 126; 127; 128]. The most widely accepted growth mechanism for SWNTs is the vapour-liquid-solid theory [129; 130]. Although some experiments indicate that bulk diffusion of carbon atoms through the catalyst particle may occur [126; 128], surface diffusion model has been favoured in recent studies [131; 132]. In publication III, in situ TEM observations of nucleation and growth of SWNTs are explained by carbon interstitial energetics in metal nanoparticles. The growth of the SWNTs is induced by high surface curvature of the metal nanoparticle (see Fig. 16).

Figure 16: A) - D) A SWNT grows from a sharp Ni tip that was created by thinning Ni nanowire up to breaking point. SWNT growth is observed while the metal tip remains sharp. E)-H) After the metal tip curvature is reduced SWNT is re-ingested into the now blunt Ni particle. The image series was taken from a MWNT-Ni structure irradiated at 470°C. Scale: 5 nm. From publication II.

Curvature induced growth observation presented in Fig. 16 poses the questions what is the growth mechanism of SWNT in these observations? In order to answer the question posed, carbon interstitial energetics was studied as the theoretical part of publication III and was
sextended in publication IV. The main ingredient of the presented growth process is the solubility of carbon in metal nanoparticles. Previous studies have proposed both decreased [133] and increased [134] carbon solubility in metal nanoparticles. In the simulations presented in publications III and IV, the reduction of solubility as the surface curvature is increased was confirmed taking into account the actual atomic structures of nanoparticles, surface orientations, etc. in spherical and cylindrical iron nanoparticles both in the FCC and BCC phases.

Carbon interstitials in iron can be in octahedral or tetrahedral configuration (see Fig. 17). The octahedral configuration is the minimum energy configuration whereas the tetrahedral configuration is the saddle point of bulk diffusion [135].

![Figure 17: Octahedral and tetrahedral interstitial sites in FCC and BCC iron.](image)

The formation enthalpy $H_f$ of carbon interstitials was calculated from:

$$H_f = E_{Fe+C} - E_{Fe} - E_{\text{graphene}}, \quad (31)$$

where $E_{\text{graphene}}$ is the energy per atom in graphene and $E_{Fe+C}$ and $E_{Fe}$ are the energies of the system with/without C interstitial. As the energy of an isolated C atom is zero in the empirical interaction model, $E_{\text{graphene}} = 7.375$ eV/atom coincides with the cohesive energy of graphene. Formation enthalpies of octahedral carbon interstitials in spherical and cylindrical FCC iron nanoparticles of 5 – 25 Å radii are presented in Fig. 18. A systematic increase in formation enthalpy implicates the reduction of solubility with decrease of metal particle size, i.e. increase of surface curvature. In experimental setting of publication III (see Fig. 16) the reduction of nanorod radius from large ($\approx 3.0$) nm to small ($\approx 1.5$) nm at 470° C temperature (as in the experiments) leads to reduction of carbon concentration by factor of $\exp(\Delta H_f/kT) \approx 5$, when $\Delta H_f \approx 0.1$ eV. If the metal particle is initially saturated with carbon, this explains why carbon is precipitated from the nanoparticle into a nanotube. When the nanoparticle geometry changes from a sharp to blunt tip, the process is reversed and carbon atoms of the nanotube can be re-ingested back to the nanoparticle.
The formation of junctions between MWNTs and transition metal particles under electron irradiation has been demonstrated in recent studies [136; 137]. These junctions show covalent bonding, high resistance against fracture, and Ohmic conductance. The atomic level mechanism of junction formation has remained unknown. In publication V, the junction formation was explained by combination of electron microscopy and simulations. It was shown that irradiation induced defects are necessary for this process.

An example of an intermediate state of SWNT-iron nanoparticle junction formation is presented in Fig. 19. When electron irradiation induces defects to a carbon nanotube, vacancies and the associated dangling bonds are created. These bonds may interact with the nearby iron particle, leading to bonding between the two systems and reduction in total energy of both. In extreme
case, the nanotube is completely cut by electron beam and the ends of the cut nanotube
form bonds with the metal. The covalent nature and the energy gain from a junction formed
between a cut nanotube and iron nanoparticle is presented in Fig. 20. Energetics of the junction

Figure 20: **Left:** Electron density of a (7, 0) SWNT-Fe\textsubscript{116} particle junction as revealed by
DFT calculation. **Right:** The same system calculated by analytical potential method. The
atoms are coloured according to the difference in potential energy of the atoms in the junction
configuration compared to the isolated nanotube and metal particle.

formation between SWNT and metal nanoparticle is presented in Fig. 21. As DVs have low
formation energy [115] and appear easily under electron irradiation due to recombination of
SVs, the energy increase associated with isolated defects can be estimated as the number of
DV times DV formation energy (about 5 eV). During junction formation, all vacancies can be
assumed to form a big cluster just under the particle (spherical intersections with increasing
overlap with the nanotube) leading to lowered energy with respect to isolated vacancies. The
interaction of the metal particle with the defected tube lowers the energy of the system as
indicated by the black curve in the figure.

A simple model can be constructed assuming junction formation between a nanotube cut cleanly
to two halves and a metal particle. The difference in total energies $\Delta E_{\text{tot}}$ between the initial
system containing separated nanotube and metal nanoparticle and the final system of metal
particle bonded in between the two halves of the nanotube can be approximated within this
model as

$$\Delta E_{\text{tot}} = N_{db}(E_{C-M} - E_{sp^2}) + N_{surf}(E_{M-C} - E_{surf}),$$

(32)

where $N_{db}$ is the number of dangling bonds in the cut nanotube, $E_{C-M}$ is the energy of carbon
atom at the end of nanotube bonded with metal atoms, $E_{sp^2}$ is the nanotube cohesive energy
($\approx -7.3$ eV), $N_{surf}$ is the number of metal atoms bonding with the nanotube ($\approx N_{db}$), $E_{M-C}$
is the average energy of a metal atom bonding with carbon, and $E_{surf}$ is the energy of a
metal atom at the surface of the nanoparticle. DFT and analytical simulations show that
$E_{C-M} - E_{sp^2} \approx -E_{M-C} - E_{surf}$. Thus, the $\Delta E_{\text{tot}}$ is close to zero and the process may be
slightly endothermic or exothermic depending on the metal particle size and atomic species, as presented in publication V.

Figure 21: Energetics of SWNT-iron nanoparticle compound during junction formation. The upper curve (open squares) gives an estimate of the energy required to create the indicated number of isolated divacancies in (10,0) nanotube. The curve with full squares shows the energy change of the nanotube when the same number of atoms is displaced under the metal particle to form a big vacancy cluster as given by the analytical potential. The curve with open circles corresponds to energy released due the adsorption of the metal particle on the vacancy cluster. The difference between the energy required to cut the tube and the released energy due the interaction is presented by the full circles. The dashed red horizontal line corresponds to the energy needed to cut the tube in two halves. The total number of carbon atoms is same in all systems.
The results of this section show that electron irradiation can be used as a tool in formation of carbon nanotube-metal nanoparticle compounds, which may be the most important material systems in future nanotechnology applications. The presented simulation results can explain novel observations and give insight to the physical processes behind these observations.

7 CONCLUSIONS

In this thesis, atomistic simulations of the response of CNTs to ion and electron irradiation have been carried out at various levels of sophistication. It has been suggested how irradiation can be used for atomic scale engineering of CNTs. The simulation results were compared to and proved by the experimental data obtained during the collaboration with several experimental groups. The following most important results were obtained. (i) The local electronic structure of semiconducting SWNTs can be modified by ion irradiation in a controllable manner; (ii) Changes in the conductivity of CNTs can be controlled by energy selective irradiation; (iii) The solubility of carbon interstitial atoms in metal nanoparticles depends on the particle size, which explains the observations of CNT growth of CNTs under irradiation of carbon-metal systems in a TEM; (iv) The formation of CNT-metal nanoparticle junctions under electron irradiation is driven by defect formation.

The response of carbon nanotubes to ion irradiation was studied by a combination of classical MD and DFT simulations. The dynamical process of defect formation was studied by employing analytical potentials. The ratio of SVs and DVs, which are the most abundant irradiation-induced defects in CNTs and have very different effects on SWNT conductivity, was shown to be irradiation energy dependent. Irradiation-induced defects were found to cause a variety of changes in the electronic structures of semiconducting SWNTs, varying from individual new states in the band gap to changes in the band gap width. The extensive simulation results for various types of defect make it possible to unequivocally identify defects in SWNTs by combining electronic structure calculations and STS, offering a reference data for a wide scientific community of researchers studying nanotube with surface probe microscopy methods. Because of the nonintrusivity of this method it is suitable for measurements of of SWNTs in studies of electronics applications, e.g. transistors and memory elements, in which charge localisation at defects is of importance due to possible hysteresis effects.

The growth of SWNTs practically always include a metal catalyst particle. Surface curvature and the size of metal nanoparticles was demonstrated to determine the local carbon solubility in these particles. The reduction of solubility with reduction of size, i.e. increase of surface
curvature, was used to explain the growth of CNTs from a metal particle when the particles' surface curvature was changed in the TEM. The experimental results of publication III suggest that the observed CNT growth was dominated by bulk diffusion of carbon atoms at high curvature areas of the metal particles. The final confirmation of this conclusion is an intriguing detail and needs more studies.

Covalent bonds between the CNT and metal nanoparticle are crucial for Ohmic contacts, which enable the application of CNTs extraordinary electronic properties. The junctions between CNTs and metal particles were recently manufactured in a TEM, but the mechanism of junction formations remained unclear. The results of the simulations presented in this thesis showed that the structural defects created by the electron beam and efficient reconstruction of the nanotube atomic network are the driving force for junction formation and that in these junctions CNTs are covalently bonded to the metal particle. The microscopic mechanism of junction formation was explained by a model based on the energetics of atomic bonds between carbon and metal atoms.

To conclude, ion and electron irradiation was shown to be an effective, and essential, tool for atomic scale engineering of CNTs. This thesis has given insight into irradiation induced effects in CNTs, and the results substantially contribute to our understanding of the behaviour of point defects in low-dimensional nanoscale materials.
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