Computational Materials Science 138 (2017) 49–57

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Electronic transport in metallic carbon nanotubes with mixed defects within the strong localization regime

Fabian Teichert [a,c,d,*], Andreas Zienert [b], Jörg Schuster [c,d], Michael Schreiber [a,d]

[a] Institute of Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany
[b] Center for Microtechnologies, Chemnitz University of Technology, 09107 Chemnitz, Germany
[c] Fraunhofer Institute for Electronic Nano Systems (ENAS), 09126 Chemnitz, Germany
[d] Dresden Center for Computational Materials Science (DCMS), TU Dresden, 01062 Dresden, Germany

ARTICLE INFO

Article history:
Received 2 February 2017
Received in revised form 31 May 2017
Accepted 1 June 2017

2010 MSC:
82D77
82D80
82B44
82B80
81V99

Keywords:
Carbon nanotube (CNT)
Defect
Density-functional-based tight binding (DFTB)
Electronic transport
Recursive Green's function formalism (RGF)
Strong localization

ABSTRACT

We study the electron transport in metallic carbon nanotubes (CNTs) with realistic defects of different types. We focus on large CNTs with many defects in the mesoscopic range. In a recent paper we demonstrated that the electronic transport in those defective CNTs is in the regime of strong localization. We verify by quantum transport simulations that the localization length of CNTs with defects of mixed types can be related to the localization lengths of CNTs with identical defects by taking the weighted harmonic average. Secondly, we show how to use this result to estimate the conductance of arbitrary defective CNTs, avoiding time consuming transport calculations.

1. Introduction

Carbon nanotubes (CNTs) offer a large variety of properties [1–3], which can be very useful for future electronic devices. One of them is the very high conductance in the ballistic regime [4] that makes CNTs attractive for metallic interconnect systems [5–8]. Although research on CNTs has continued for many years since their discovery in 1991 and clean CNTs approaching the theoretical conductance limit can be produced under well-defined laboratory conditions [9], current CNT-based devices at the wafer level which means a fast and reproducible fabrication are still not reaching that limit. One reason is the strong impact of defects [10,11], which cannot be avoided during production processes at the wafer level [12–16], whether physically introduced like vacancies or chemically initiated like functionalizations. They can, e.g., be caused by ion collisions within a gas atmosphere, by electron beam treatments, or within organic solutions, which are necessary steps for the fabrication of devices with difficult three dimensional geometries. Thus, understanding the influence of these defects on electronic transport properties of CNTs is a necessary step towards their integration into microelectronic devices.

The present work approaches this subject at the theoretical level. On the one hand, the size of such mesoscopic systems is of the order of hundred thousand atoms, and on the other hand, a statistical description with large ensembles has to be considered. This is very time-consuming despite the availability of high performance computer resources and good scaling low-level methods.

In the past, most theoretical work in the field of quantum transport simulations focused on the properties of single selected CNTs, like it was done for vacancies [17–21], substitutional atoms [22,23]

* Corresponding author at: Institute of Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany.
E-mail address: fabian.teichert@physik.tu-chemnitz.de (F. Teichert).

http://dx.doi.org/10.1016/j.commatsci.2017.06.001
0927-0256/

and functionalizations [23–27]. For this purpose, different electronic structure methods were addressed, from tight binding (e.g. [22]) to density functional theory (e.g. [18,23]). These investigations showed that the conductance depends exponentially on the CNT length, what was also verified by experiments [13]. This is an indication of the strong localization regime, which is also present in case of random Anderson disorder [28,29]. But this regime does not only exist in CNTs. Also other materials can exhibit Anderson disorder, e.g. silicon nanowires [30], showing that strong localization is an interesting and important transport regime in quasi-one-dimensional structures.

Beyond the properties of single selected CNTs, a further description and quantification of the strong localization regime for different CNTs is necessary. Flores began a systematic study by calculating the localization length for three metallic armchair CNTs [19]. In a previous investigation [31], we continued these calculations for more CNTs to determine the diameter dependence. Therein, we discussed CNTs with one type of defect. In the following, we extend this work by calculating electronic transport properties of defective CNTs with defects of different types within one CNT. Bringing all results together, we develop and explain a model for estimating the conductance of metallic CNTs with arbitrary diameter and an arbitrary number of different types of defects.

2. Theoretical framework

Electronic transport through mesoscopic systems can be described by quantum transport theory, which is done here in the equilibrium limit [32]. The conductance formula in the limit of a small bias was introduced by Landauer and Büttiker [33]:

$$G = -\mathrm{G}_0 \int_{-\infty}^{\infty} \mathcal{T}(E) \frac{\mathrm{d}f(E)}{\mathrm{d}E}\,\mathrm{d}E. \tag{1}$$

$\mathrm{G}_0 = 2\mathrm{e}^2/\mathrm{h}$ is the conductance quantum, $\mathcal{T}(E)$ the transmission function, and $f(E)$ the Fermi distribution, where the effect of temperature is included.

The transmission function can be calculated via the Schrödinger equation in a matrix representation and its Green's function. For this purpose, the whole (infinite) CNT is treated as a device. That means, it is divided into three main parts: the (finite) central region C, containing all the defects, and two (half infinite) electrodes L and R, as shown in Fig. 1(a). Each part is described by Hamiltonian matrices $\mathcal{H}_\mathrm{L}/\mathcal{H}_\mathrm{C}/\mathcal{H}_\mathrm{R}$ and the coupling by similar matrices $\tau_\mathrm{LC}/\tau_\mathrm{CR}$. The coupling τ_LR can be neglected if the distance between the electrodes is large enough. The electronic properties are calculated via the Green's function of the central region

$$\mathcal{G}_\mathrm{C} = [(E + \mathrm{i}\eta)\mathcal{S} - \mathcal{H}_\mathrm{C} - \Sigma_\mathrm{L} - \Sigma_\mathrm{R}]^{-1}. \tag{2}$$

$\Sigma_\mathrm{L} = \tau_\mathrm{CL}\mathcal{G}_\mathrm{L}\tau_\mathrm{LC}$ and $\Sigma_\mathrm{R} = \tau_\mathrm{CR}\mathcal{G}_\mathrm{R}\tau_\mathrm{RC}$ are the self-energy matrices, which lead to an energetic shift due to the coupling to the electrodes. The Green's functions of the electrodes $\mathcal{G}_\mathrm{L/R}$ themselves can be calculated with the renormalization decimation algorithm (RDA), which is a fast iteration process [34,35]. η is a small value for numerical stability, which shifts the singularities from the real axis into the complex plane.[1] $\mathcal{S}$ is the overlap matrix, which is present in cases where the representation is done in a non-orthogonal basis. Altogether, this can be used to obtain the transmission function

$$\mathcal{T}(E) = \mathrm{Tr}\left(\Gamma_\mathrm{R}\mathcal{G}_\mathrm{C}\Gamma_\mathrm{L}\mathcal{G}_\mathrm{C}^\dagger\right). \tag{3}$$

$\Gamma_\mathrm{L/R} = \mathrm{i}(\Sigma_\mathrm{L/R} - \Sigma_\mathrm{L/R}^\dagger)$ are broadening matrices, which lead to an energetic broadening of each state due to the coupling to the electrodes.

[1] We use $\eta = 10^{-7}$ for calculating $\mathcal{G}_\mathrm{C}$ and $\eta = 10^{-4}$ for calculating $\mathcal{G}_\mathrm{L/R}$ via the RDA.

In the following we want to treat CNTs of mesoscopic lengths with more than hundred thousand atoms in the defective central region, where the direct inversion (2) is too time-consuming. Fortunately, when using a representation with localized basis functions, $\mathcal{H}_\mathrm{C}$ is block-tridiagonal. The central region of our device can be subdivided into M parts, where only neighbored parts are directly coupled, as shown in Fig. 1(b). This simplifies (3) to

$$\mathcal{T}(E) = \mathrm{Tr}\left(\Gamma'_\mathrm{R}\mathcal{G}_{M1}\Gamma'_\mathrm{L}\mathcal{G}_{M1}^\dagger\right). \tag{4}$$

$\mathcal{G}_{M1}$ is the lower left block of $\mathcal{G}_\mathrm{C}$. Its dimension is a factor M smaller. In the same way, Γ'_L (Γ'_R) is the upper left (lower right) block of Γ_L (Γ_R). With the usage of the recursive Green's function formalism (RGF) [36], $\mathcal{G}_{M1}$ can be calculated very efficiently within linearly scaling time $t = \mathcal{O}(M)$, which makes it possible at all to compute electronic transport properties of mesoscopic CNTs. For this purpose, narrowing the cells in Fig. 1(b) lowers the computation time, which has to be taken into account when choosing these cells.

The following computations are performed neglecting phonon effects. In the limit of a small bias, optical phonons have short coherence lengths of 180 nm [37], but also high energies above the thermal fluctuations. They are not excitable. Acoustic phonons have small energies of the order of thermal fluctuations and can be excited. But their coherence length of 2400 nm is much larger. Therefore, inelastic scattering is not dominant for systems shorter than this length. Beyond the following study, dephasing due to phonons can be included phenomenologically with the Büttiker probe model [38,39]. Here, the electron-phonon coupling strength is a parameter, which has to be assumed or calculated separately. An additional self-consistency iteration cycle is necessary, raising the computation time. E.g. the conductance of disordered graphene has been determined in this way [39]. Ab initio calculations of phonon modes and their influence on electron transport can also be done directly [40,41], but are even more challenging.

3. Modeling details

For the transport calculation, the electronic structure is described by a density-functional based tight binding model (DFTB) [42,43]. We use the 3ob parameter set, which is a non-orthogonal sp^3 basis developed for organic molecules [44,45]. The cutoff for the distance-dependent TB hopping energy integrals and the overlap integrals is chosen twice the carbon-carbon distance. Beyond this distance, the matrix entries are sufficiently small to be neglected. This cutoff is also favorable, because it leads to not more than third-nearest-neighbor interactions.

We analyze two different types of metallic CNTs, the (5,5)-CNT and the (10,10)-CNT, in combination with three different defect types (see Fig. 2): the unpassivated monovacancy (MV), where one carbon atom is removed, the passivated monovacancy, where one carbon atom is removed and the dangling bonds are saturated with hydrogen, and the divacancy (DV), where two neighboring carbon atoms are removed. The latter can be present in two different orientations: perpendicular to the tube axis ($\mathrm{DV}_\mathrm{perp}$) or diagonal ($\mathrm{DV}_\mathrm{diag}$). The length of the MV is equal to the length of the unit cell (UC). The length of the MV_3H and the $\mathrm{DV}_\mathrm{perp}$ is three times the length of the UC. For the $\mathrm{DV}_\mathrm{diag}$ two cases have to be considered. The length of the one shown in Fig. 2 is three times the length of the UC. Another one, which is mirrored, has four times the length of the UC, because half a UC has to be added at each side to get correct connections to the rest of the CNT. Because the defect cells (except the MV) are larger than the TB cutoff, they can be further divided into smaller cells to speed up the RGF algorithm.

A realistic structure is obtained by performing a geometry optimization of the ideal unit cell. Afterwards, the hydrogen atoms and the whole DV defect cell are also optimized. Finite size effects are