CNT-Metal Interconnects: Electronic Structure Calculations and Resistivity Simulations

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Cluster approach based on the multiple scattering theory formalism, realistic analytical and coherent potentials, as well as the effective medium approximation (EMA-CPA), can be effectively used for modeling of nano-sized systems. This allows us to calculate the dispersion law \( E(k) \), the electronic density of states, the conductivity, etc. The multiple scattering problems are stated for radial (e.g., quantum dots) and axial (e.g., nanowires, nanotubes) symmetry approaches. Basic attention is paid now for applications on carbon nanotubes (CNTs) of various morphology which possess the unique physical properties in nanoelectronics, e.g., contacts of CNTs with other conducting elements of a nanocircuit which can be promising candidates for interconnects in a high-speed electronics. The main problems solving for resistance in nanotube junctions with metal particles appear due to the influence of chirality effects in the interconnects of single-wall (SW) and multi-wall (MW) CNTs with the fitting metals (Me = Ni, Cu, Ag, Pd, Pt, Au) for predefined CNT geometry. Using the model of ‘effective bonds’ developed in the framework of presented approach and Landauer theory, we can predict the resistivity properties for both SW and MW CNT-Me interconnects. We have also developed the model of the inter-wall interaction inside the MW CNTs, which demonstrates the possible ‘radial current’ losses.

**Keywords:** Carbon Nanotubes, SW and MW Morphology, Junction Between the CNT and Metal Substrate, Multiple Scattering Theory, Electronic Structure Calculations, Resistance of CNT-Me Contact, Inter-wall Transparency in MW CNTs.

**1. INTRODUCTION**

The miniaturization of electronic devices, a high integration level, an increase of the operation frequencies and power densities are required to overcome the disadvantages of a nowadays microtechnology, including the use of adequate materials and innovative chip interconnects. Carbon nanotubes (CNTs) attract permanently growing technological interest, due to their unique physical properties, for example, as the promising candidates for nano-interconnects in a high-speed electronics. The main aim of the current study is the implementation of the advanced simulation models for a proper description of the electrical resistance for contacts between the CNTs of different morphologies and the metallic substrates of different nature. An adequate description of the nanotube chirality is one of the key points for the proper simulations on electric properties of CNT-based nanoelectronic devices.

The resistance of contact between an arbitrary CNT and a metallic catalytic substrate can considerably exceed that observed separately in the nanotube and metal. The conductance between real metals and CNTs still occurs, however, mainly due to the scattering processes, which are estimated to be rather weak. Figure 1 represents the contacts between a CNT and both substrates, as a prototype
nanodevice. This is a main subject of our current research and modeling. The toroidal region (CNT-Me) is the object of a nanoscopic approach responsible for the main contribution to the resistance. As to the nanotube itself and to the metallic substrate, their resistances may be considered as macroscopic parameters.

The electronic structure for the CNT-Me interconnect can be evaluated through the electronic density of states (DOS) for a carbon-metal contact considered as a ‘disordered alloy,’ where the clusters containing both C and Me atoms behave as the scattering centers. The computational procedure developed by us for these calculations is based on the construction of cluster potentials and the evaluation of both scattering ($S$) and transfer ($T$) matrices.

The general model of multiple scattering with the effective media approximation (EMA) for condensed matter based on the approach of an atomic cluster is presented in Figure 2. So far, the cluster formalism was successfully applied for Cu metal, as well as for semiconductors, both elemental (Ge and Si) and binary (As, Se).


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2. A MULTIPLE SCATTERING THEORY AND AN EFFECTIVE MEDIUM APPROACH FOR CNT SIMULATIONS

2.1. Electronic Structure Calculations

The resistivity can be considered as a scattering problem, where the current carriers participate in the transport, according to various mechanisms based on the presence of scattering centers (phonons, charge defects, structural defects, etc.), including a pure elastic way, called ballistic (Matsissen rule). The scattering paradigm is presented in Figure 3. The computational procedure developed to perform these calculations is based on the construction of the cluster potentials and the evaluation of the S- and T-matrices for scattering and transfer, respectively. This allows us to realize the full-scale electronic structure calculations for condensed matter (‘black box’), where influence means a set of electronic ‘trial’ energy-dependent wave functions $\Psi_{in}(r)$ and response $\Psi_{out}(r)$ gives the sets of scattering amplitudes corresponding to the possible scattering channels for any ‘trial’ energy. This allows us ‘to decrypt’ the electronic spectra of a ‘black box.’

We consider a domain where the stationary solutions of the Schrödinger equation are known, and we label them by

$$\psi_{in}(r) = \phi_k(r) = \exp(ikr) \quad (1)$$

The scattering of ‘trial’ waves, in the presence of a potential, yields the new stationary solutions labeled by

$$\psi_{out}(r) = \psi_k^{(\pm)}(r) \quad (2)$$

for the modified Schrödinger equation $\hat{H}\psi^{(\pm)}_k(r) = E\psi^{(\pm)}_k(r)$. An electronic structure calculation is considered here as a scattering problem, where the centers of scattering are identified with the atoms of clusters.

The first step of modeling is the construction of potentials, both atomic and crystalline, which is based on the analytical Gaspard’s potential of a screened atomic nucleus and $X_a$ and $X_{ab}$ presentations for the electronic exchange and correlation, using the LDA (Local Density

**Fig. 1.** A model of CNT-Me interconnect.

**Fig. 2.** A multiple scattering problem for the system of clusters as a multiple scattering model of condensed matter: a strategy of calculations on fundamental properties of condensed medium described within the effective media approximation.

**Fig. 3.** The scattering paradigm: Influence (In) and Response (Out).
Approximation). Figure 4 shows both atomic and crystalline potentials for carbon as compared to the Hartree-Fock atomic potential. Then, we apply the so-called muffin-tin approximation (MTA) for potential models.

To obtain the electronic structure, the calculations on scattering properties are necessary, generally, in the form of $S$- and $T$-matrices (Fig. 2). These calculations start with the definition of the initial atomic structure, to produce a medium for the solution of the scattering problem, for a trial electronic wave. The results of potential modeling and phase shifts in the framework of the MTA-approximation are presented elsewhere.

The formalism used here for calculations on the electronic structure is based on the CPA approach, the multiple scattering theory and the cluster approach. As a first step, we postulate the atomic structure at the level of short- and medium-range orders. As a second step, we construct a "crystalline" potential and introduce the muffin-tin (MT) approach. This is accomplished by using the realistic analytical potential functions.

The scattering paradigm for the simplest cases of spherical-symmetrical potentials (elastic scattering) looks as:

$$\psi_{\text{el}}(r) = e^{ikz} + f(\theta) \frac{e^{ikr}}{r} \quad \text("liquid metal" model) \quad (3)$$

and

$$\psi_{\text{el}}(r) = e^{ikz} + f(\theta, \varphi) \frac{e^{ikr}}{r} \quad \text(spherical cluster model) \quad (4)$$

Then, the electronic wave scattering problem is solved, and the energy dependence of the scattering properties for isolated MT scatterers is obtained, in the form of the phase shifts $\delta_{\text{el}}(E)$, and the $T$-matrix of the cluster is found as a whole. The indices $l$ and $m$ arise, as a result of expansions of the functions as Bessel’s functions $j_l$, Hankel’s functions $h_l$, and spherical harmonics $Y_{lm}$.

The paradigm of scattering theory and the developed strategy of simulation of CNTs electronic properties uses the generalized scattering condition for the low-dimensional atomic structures of condensed matter (Quantum Scattering in $d$-Dimensions):

$$\phi_k^{(\pm)}(r) \propto \phi_k(r) + \phi_k^{(\pm)}(\Omega) \exp(\pm ikr) \frac{1}{r^{(d-1)/2}} \quad (5)$$

where $\Omega$ describes the integrated space in angular units while the superscripts ’+’ and ’−’ label the asymptotic behavior in terms of $d$-dimensional waves:

$$\frac{\partial \sigma_{\alpha \beta}}{\partial \Omega} = \frac{2\pi}{\hbar^2} \left| \langle \phi_{\alpha} | \hat{V} | \phi_{\beta} \rangle \right|^2 \rho_d(E) \quad (6)$$

where $d$ is the atomic structure dimension.

The scattering model for a cylindrical atomic cluster allows us to calculate below the CNTs electronic structure for various diameters and chiralities.

### 2.2. Calculations of Conductivity and Resistance

The calculations of conductivity are usually performed using Kubo-Greenwood formula:

$$\sigma(E) = \frac{\pi \hbar}{4e^2} \int \left[ f(E) - f(E + \hbar \omega) \right] |D_{\alpha \beta}(E)|^2 \rho_d(E) \times \rho(E + \hbar \omega) \, dE \quad (7)$$

where $\omega$ is a real frequency parameter of Fourier transform for the time-dependent functions, $f(E)$ the Fermi-Dirac distribution function, $D_{\alpha \beta}(E) = \int \langle \phi_{\alpha} | \hat{V} | \phi_{\beta} \rangle \, dE$, where $\langle \phi_{\alpha} | \hat{V} | \phi_{\beta} \rangle = A \exp(iKR)$ and $K$ is the complex wave vector of the effective medium. The dispersion function $E(K)$ determines the properties of the wave function $\Psi(E,K)$ upon the isoenergy surface in $K$-space.

For static conductivity ($\omega = 0$ and $T = 0$, Eq. (7) gives the Drude-like formula:

$$\sigma_{\text{el}}(K) = \frac{e^2 n^*}{m^*} \tau \quad (8)$$

where $n^*$ is the effective electron density, with a relaxation time $\tau \approx 1/v_0$, $l(T)$ is the free path while a heat velocity is $v_0 = (3kT/m^*)^{1/2}$. The effective electron mass can be defined using the dispersion law:

$$m^* = (\partial^2 E/\partial K^2)_{\text{el}}^{-1} \quad (9)$$

where $K_{\text{el}}$ is a modulus of the real part $K$ vector.

There exist some ideas to estimate the conductivity in static and frequency regimes taking into account the temperature effects. However, in the case of CNT, we must consider not only the diffusive mechanism of conductivity, but also the ‘so-called’ ballistic one. This is an evident complication in the interpretation of electrical properties of CNTs and related systems.

Due to the evident limitations for the simulations of a chirality effect within the “liquid metal” model of the CNT-Me junction (e.g., an absence of a proper chirality
resonance), we have developed the semi-empirical model with a precise description of the local atomic structure of this junction. For this purpose, we have constructed a model of ‘effective bonds’ for the interconnects with the realistic atomic structure.

3. MODEL OF ‘EFFECTIVE BONDS’ FOR SIMULATIONS OF SW CNT-Me JUNCTIONS

Within the electronic transport formalism, a model of “effective bonds” consists of two regions supporting the two different electron transport mechanisms: ballistic (elastic) and collisional (non-elastic). These electron transport processes are simulated by the corresponding boundary conditions in the form of the effective medium. The CNT chirality \((m, n)\) is simulated by the corresponding orientation of carbon rings within the scattering medium (Fig. 5).

The most problematic areas for proper simulation are the CNT-Me junctions, where the atomic structural disorder is observed and the conductivity mechanism is changed. The influence of chirality on the resistance in the vicinity of interconnect depends on the number of statistically realized bonds between the CNT and the catalytic substrate (e.g., Ni, Cu, Au, Ag, Pd, Pt) formed during the CNT growth above the metallic catalyst surface (Fig. 6).

3.1. A Mechanism of the Ballistic Conductivity as a Result of the Multiple Scattering

We assume that (i) the conducting nanotubes are not too long and (ii) the electrons are not drastically scattered by any defect (imperfection) of this nanomaterial. The effect of the charge accumulation is neglected as well. We are dealing with the so-called ‘ballistic’ mechanism of the electronic transport. Such a model is similar to an ideal billiard with moving the elastic balls-electrons. This means that we consider that the length of CNT provides the ideal ballistic conductivity in conditions standing waves of open resonator. According to the Landauer model, \(g_{\text{res}} = (e^2/h)Sp(T_{mn}T_{nm}), \ m \neq n\), where \(g_{\text{res}}\) are the conductance coefficients, \(Sp\) means the calculation of the matrix trace while \((e^2/h)T_{12}\Delta \mu\) is the current flow between the two reservoirs with a difference between the chemical potentials \(\Delta \mu = \mu_1 - \mu_2\) \((T_{12}\) is the transmission coefficient found to be between 1 to 2 in the one-channel case) based on the conception of the quantum conductance \(2e^2/h = 0.777\ \Omega\) (or, the resistance is about 12.92 kOhm).

Using the simulation models, presented earlier, we have developed resistance models for both SW and MW CNT-Me interconnects, based on the interface potential barriers evaluation and Landauer formula, which defines the integrated conductance:

\[
I_0 = \frac{2e^2}{h} \sum_{i=1}^{N} T_i = \left( \frac{1}{12.92\ \Omega} \right) \sum_{i=1}^{N} T_i = 0.0774 \sum_{i=1}^{N} T_i
\]

(10)

where \(N\) is the number of conducting channels and \(T_i\) the corresponding transmission coefficient.

3.2. Chirality and Thickness Simulations

Figure 6 presents a creation of C-Me ‘effective bonds.’ We consider here the (001) substrates of fcc-metals. We should also underscore that this is a probabilistic process when only more-or-less equilibrium bonds (“effective bonds”) are formed at inter-atomic distances corresponding to the minimum total energies. The evaluation of a number of “effective bonds” using Eq. (10) is principal for the number of “conducting channels,” since the conductance is
proportional to the number of appeared “effective bonds” within the CNT-Me interconnect.

The calculation of conducting abilities of “effective bond” leads us to estimate the energy-dependent transparency coefficient of a potential barrier C-Me (Fig. 7). The scattering process for this potential barrier is regulated by the effect of “thin film” for conductivity electrons, which leads to quantization in voltaic parameters (in the case of full transparency). The transmission (transparency) coefficient \( T \) for the barrier scattering problem (Fig. 7) is defined as:

\[
T = \frac{E_2}{E_1} \left( \frac{2\sqrt{E_1}}{\sqrt{E_1} + \sqrt{E_2}} \right)^2
\]

(11)

where \( E_1 \) and \( E_2 \) are the corresponding electron energies. Evaluation on resistances of CNT-Ni junctions for various NT diameters and chiralities are present in Table I (see also Figs. 6 and 7).

These resistances have been evaluated taking into account that only thermally activated electrons (Fig. 8), i.e., a small part \( \Delta n \) of all quasi-free electrons \( n \), participates in the conduction process with Fermi velocity \( v_F \). This ratio can be evaluated as follows:

\[
n = \int_0^{E_F(0)} \rho(E) dE = \frac{2}{3} AE_F^{1/2}(0)
\]

\[
\Delta n \approx \int_{E_F(0) - 1/2kT}^{E_F(0) + 1/2kT} \rho(E) f(E) dE = \frac{1}{2} \rho(E_F(0)) kT
\]

\[
\frac{\Delta n}{n} \approx \frac{3}{2} \rho(E_F(0)) kT = \frac{3}{4} \frac{kT}{E_F(0)}
\]

(12)

where \( f(E) \) is a Fermi-Dirac distribution function and \( \rho(E) \) is a DOS while \( kT = 0.0258 \text{ eV} \) for \( T = 300 \text{ K} \).

The role of thermally activated electrons (Fig. 8) is described by the scattering mechanism changing in the space of CNT-Me interconnect (Fig. 6). The mean free path \( L \) in the CNT is of order \( 10^2 - 10^3 a_c \), where \( a_c \) is a carbon covalent radius, which can be explained by the ballistic mechanism of electron transport within the energy channel of the CNT. At the vicinity of interconnect, we observe a drastic decrease of the electron mean free path down to \( 1 - 2a_c \). From the uncertainty condition \( \kappa L \approx 1 \) (where \( L \sim a_c \sim 2 \text{ a.u.} \) is a free path), we can evaluate the Fermi electron wave number \( \kappa \propto \kappa_F \approx 1/a_c \approx 0.5 \text{ a.u.}^{-1} \). It means that \( E_F \sim 0.25 \text{ Ry} \), i.e., a large increase of resistance occurs in the interconnect space. In particular, the variation of the chirality angle \( \phi \) within the interconnect space leads to a fluctuation of the number of C-Me atomic bonds. In the case of \( 0^\circ < \phi < 30^\circ \), a certain number of non-stable and non-equilibrium bonds can
be created. Evidently, this leads to a decrease of interconnect conductance, which is well-observed when performing variation of nanotube diameter (Fig. 9).

Specific results for chirality effect simulations are shown in Figure 10, with an evident maximum of the resistance for $\phi \approx 15^\circ$, where the large number of non-equilibrium bonds is formed, with higher potential barriers and lower transparency.

Figure 11 shows the generalized results of simulations on resistance of junctions obtained for various metallic substrates. It is clear that Ag and Au substrates are more effective electrically while Ni is rather a ‘worse’ substrate for interconnect, although it yields the most effective catalyst for CNT growth.

On the other hand, the catalysts which are usually used for the SW CNT growth (e.g., Fe, Co and Ni), have a stronger bound to the ends of SW CNTs than the noble metals,15 i.e., some compromise exists between the electrical parameters and strengths of the interconnect bonding.

4. MW CNT-Me JUNCTIONS: CONDUCTANCE AND RESISTANCE

Our current study focuses on the development of models describing the growth mechanism of carbon nanotubes upon nanostructured Ni catalyst inside the pores of $\text{Al}_2\text{O}_3$ membranes. The scope of these simulations allows us to predict that a specific morphology of CNTs could be formed inside the specific membranes having a defined periodicity and the hole dimensions. These simulations are necessary, in order to understand the basic mechanism of CNT growth and to achieve the tight control on the fabrication process. We have constructed atomistic models of both SW CNT bundles and MW CNTs which could fit into a porous alumina with diameters of holes $\sim 20$ nm. In particular, a model of MW CNT is presented in Figure 12, with a pre-defined combination of armchair (ac) and zigzag (zz) shells (Table II).

![Fig. 12. A cross-section of the supercell model for MW CNT with a height of 6.39 nm and an external diameter 19.89 nm.](image1)

![Fig. 11. Resistances of the zigzag-type SW CNT-Me interconnects for the CNT diameter $\sim 1$ nm.](image2)

Table II. Details of the model for MW CNT-Me interconnect.

<table>
<thead>
<tr>
<th>Diameter of CNT shell, nm</th>
<th>Chirality</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.88</td>
<td>(95,95) ac</td>
</tr>
<tr>
<td>13.54</td>
<td>(173,01) zz</td>
</tr>
<tr>
<td>14.24</td>
<td>(105,105) ac</td>
</tr>
<tr>
<td>14.87</td>
<td>(190,01) zz</td>
</tr>
<tr>
<td>15.58</td>
<td>(120,120) ac</td>
</tr>
<tr>
<td>16.27</td>
<td>(217,01) zz</td>
</tr>
<tr>
<td>16.99</td>
<td>(226,01) zz</td>
</tr>
<tr>
<td>17.69</td>
<td>(136,136) ac</td>
</tr>
<tr>
<td>18.44</td>
<td>(245,01) zz</td>
</tr>
<tr>
<td>19.18</td>
<td>(254,01) zz</td>
</tr>
</tbody>
</table>

Table III. Resistances for the MW CNT-Me interconnects.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Z</th>
<th>Interconnect resistivity, kOhm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>79</td>
<td>2.313</td>
</tr>
<tr>
<td>Pt</td>
<td>78</td>
<td>2.345</td>
</tr>
<tr>
<td>Pd</td>
<td>47</td>
<td>4.050</td>
</tr>
<tr>
<td>Ag</td>
<td>46</td>
<td>2.062</td>
</tr>
<tr>
<td>Cu</td>
<td>29</td>
<td>2.509</td>
</tr>
<tr>
<td>Ni</td>
<td>28</td>
<td>3.772</td>
</tr>
</tbody>
</table>

Fig. 13. Resistances of various MWCNT-Me interconnects.

Figure 13 shows similar ratios of electric resistances as for SW CNTs (Fig. 13), in favor of Au, Ag and Pd.

Using the simulation models presented earlier, we have developed an “effective bonds” model for the MWCNT-Me junction resistance,16 based on the interface potential barriers evaluation and Landauer formula, Eq. (10). Results of these simulations are presented in Figure 13 and Table III. For MWCNT-Me junction, the integral bonding with a corresponding substrate may be not so significant as in the case of SW CNTs, where the weak bonding can be principal.

5. A CURRENT LOSS BETWEEN THE ADJACENT SHELLS INSIDE THE MW CNT

Using the model of inter-shell potential within the MW CNT we also have evaluated the transparency coefficient, which determines the possible ‘radial current’ losses.

Figure 14 shows the inter-shell potential which is calculated using the developed realistic analytical potentials (see comments of Part 2 and the procedure of the potential construction, e.g., in Ref. [3]).

In Figure 14, \( A \) is the electron emission energy, \( E \) the electron energy, \( V \) the height of the potential barrier between the nearest atoms in neighboring nanotube shells. Thus, a radial transparency coefficient \( T \) for the two different energy ratios can be defined as:

\[
E > V, T = \frac{4E_k^2 \sin^2 k_2 a + 4E_k^2}{(E - k_2^2) \sin^2 k_2 a + 4E_k^2} \cdot k_2^2 = E - V
\]

(13)

\[
E < V, T = \frac{4E_k^2 \sin^2 k_2 a + 4E_k^2}{(E - k_2^2) \sin^2 k_2 a + 4E_k^2} \cdot k_2^2 = V - E
\]

where \( k_2 \) is the electron wave number in the case of above-barrier motion and \( k_2 \) is the same for the under-barrier motion. For example, between the 2nd and 1st shells (zz-case, Fig. 14) \( a = 13.54 - 12.88 = 0.66 \text{ nm} = 12.47 \text{ a.u.} \) and \( T = 3.469 \times 10^{-6} \) per 1 bond.

Clearly the total radial conductance is proportional to \( T \) and the number of effective potential barriers. It is also clear that the “radial current” losses (or, simply a radial current) are similar to the Hall current due to the induced magnetic field of the basic axial current. A pure scattering mechanism is also possible. However, the radial conductance per CNT length depends on the morphology (chirality) of the nearest nanotubes, when the number of the shortest effective barriers is varied in a probabilistic way. This also means that the current–voltage parameters of MW CNTs can be less stable, than in the case of SW CNTs. It was found that the inter-shell interactions, such as the inter-shell tunneling of electrons and Coulomb interactions\(^{17-19}\) cause a reduction of the total MW CNT conductance.

6. CONCLUSIONS

Using the ‘effective bonds’ model based on the Landauer relationship, we have developed the corresponding
semi-empirical formalism and predict the resistivity of interconnects between the metal substrate (e.g., Ni) as well as both the SW and MW CNTs. The calculated results are quantitatively comparable with those measured experimentally, i.e., within the range from several up to 50 kOhm.\textsuperscript{20}

We have also described the model of inter-shell interaction in the case of MW CNTs which allows us to estimate the transparency coefficient as an indicator of possible 'radial current' losses. We underscore that a conductance and other current–voltaic parameters depend on the morphology of the nearest shells in the MW CNTs, which leads to complications for technology and production of nanodevices with the stable electric characteristics.

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References and Notes


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