

Chapter 4

Scattering Processes in Nanocarbon-Based Nanointerconnects

In order to overcome disadvantages of contemporary microtechnology, the miniaturization of electronic devices, the integration level expansion and the increase of the operation frequencies and power density are required, including the use of adequate materials and innovative chip interconnects. Due to their unique physical properties, especially due to a ballistic mechanism of conductivity, carbon nanotubes (CNTs) attract a permanently growing technological interest, for example, as promising candidates for nanointerconnects in high-speed electronics. New possibilities for modern nanoelectronics open with novel ‘marginal’ forms of graphene – nanoflakes (GNFs) and nanoribbons (GNRs), which are comparable with CNTs – demonstrate a wasteless ballistic mechanism of conductivity. Graphene nanointerconnects are also important for nanotechnology. Full integration of graphene into conventional device circuitry would require a reproducible large-scale graphene synthesis that is compatible with conventional thin film technology.

The main aim of the current research is to implement advanced simulation models for a proper description of the electrical resistance for *end* contacts between CNTs and GNRs of different morphologies and metallic substrates of different nature [1]. An adequate description of nanotube chirality [2] is one of the key points for the proper simulations on electric properties of CNT-based nanoelectronic devices.

The resistance of contact between arbitrary CNT and metallic catalytic substrate can considerably exceed that observed separately in a nanotube and a metal [3]. The conductance between real metals and CNTs still occurs, but it is mainly due to the scattering processes, which are estimated to be rather weak [4]. We draw attention to these scattering phenomena in detail (e.g. [1]).

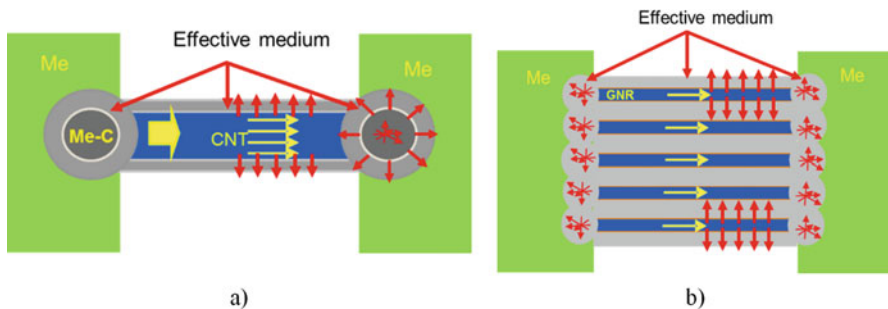


Fig. 4.1 Models of C-Me interconnects as prototypes of novel nanodevices: (a) CNT-Me interconnect; (b) multilayered GNR-Me interconnect

4.1 Non-regularities in Nanointerconnects

Now the main attention is focused on the junctions of carbon nanotubes (CNTs) and graphene nanoribbons (GNR) with contacting metallic elements of a nanocircuit. These contact spaces are essentially *non-regular*. Numerical simulations on the conductance and resistance of these contacts are performed using the multiple scattering theory and the effective media cluster approach. We have simulated both single-walled (SW) and multiwalled (MW) CNTs and single-layered (SL) and multilayered (ML) GNRs with different morphology. Figure 4.1 represents the contacts of metal substrates with CNTs and GNRs, respectively, as prototype nanodevices. The contact regions (CNT-Me and GNR-Me) are the objects of a microscopic approach responsible for the main contribution to the resistance. Meanwhile, the resistances of nanotubes, nanoribbons and the metallic substrate per se may be considered as macroscopic parameters.

There are some important applications of CNTs- and GNRs-based interfaces with other materials for novel nanosensor devices. Usually, these devices are considered as integrated devices around $10\text{--}50\ \mu\text{m}^2$ in size. The fundamental electron devices are field-effect transistors (FETs) (see Fig. 4.2a), which are very sensitive to various external influences of different nature such as mechanical, chemical, electrical, magnetic, etc.

A field-effect transistor (FET) is *nano* in size, whose on/off threshold depends on the tube dimensions, shape and temperature, among others. A local deformation of CNT (GNR) creates a change in the on/off threshold voltage of the transistor. The electrical properties of carbon-based interconnects change under the influence of external factors. The advantage of CNTs and GNRs in comparison with bulk materials is due to their small size, high strength, high electrical and thermal conductivity and a large surface area. Unique physical properties of CNTs and GNRs and their various interconnects allow considering them as sensing nanomaterials in different kinds of sensors – pressure, flow, thermal, gas, optical, mass, position, stress, strain, chemical and biological sensors.

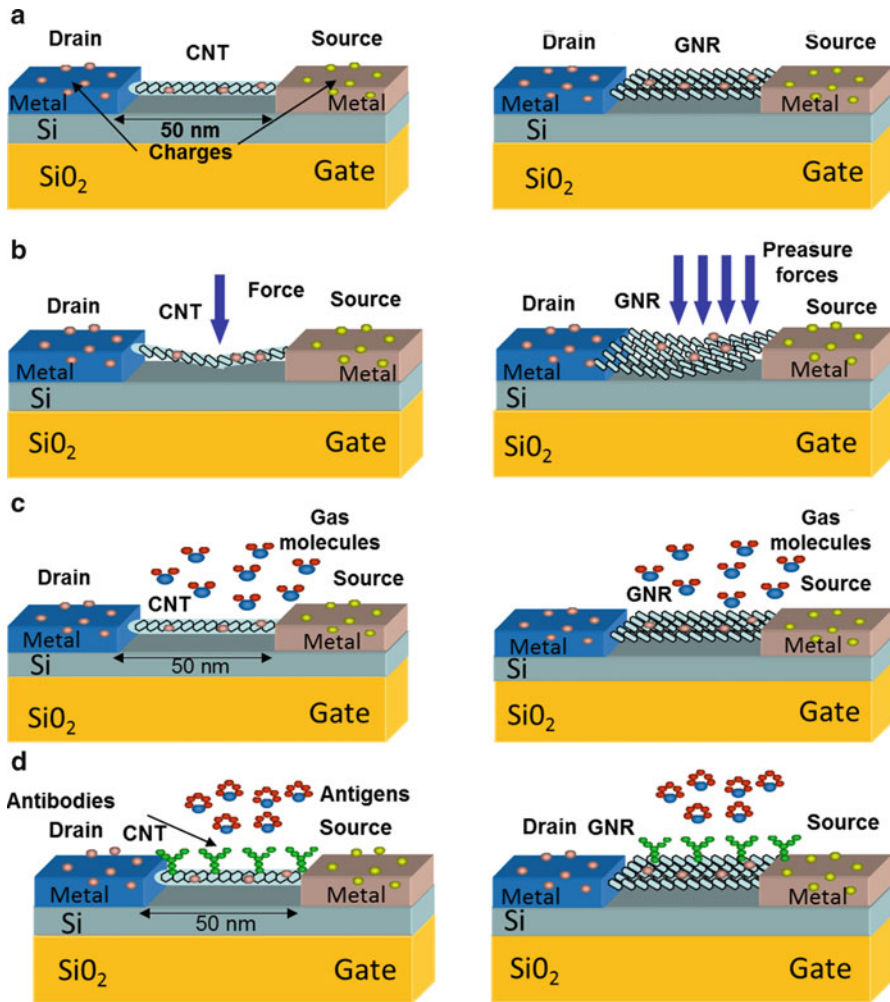


Fig. 4.2 (a) The unperturbed field-effect transistors based on a CNT and GNR. CNT- or GNR-based FET is mainly composed of a corresponding semiconducting carbon material suspended over two electrodes. (b) *Physical nanosensors*: a conducting threshold can be altered when the tube or graphene ribbon is bent. (c) *Chemical nanosensors*: a conducting threshold can be altered when the amount of free charges on the tube of graphene ribbon surface is increased or decreased by the presence of donor or acceptor molecules of specific gases or composites. (d) *Biological nanosensors*: monitoring of biomolecular processes such as antibody/antigen interactions, DNA interactions, enzymatic interactions or cellular communication processes, among others

Taking into account specific physical properties of CNTs and GNRs metal interconnects, which are explained by the presence of ‘dangling’ chemical bonds, we should point out the expressed sensitivity of electric properties of interconnect space to chemical, electric and magnetic influences. Moreover, we can treat

interconnects as spaces with morphological non-regularities. Therefore, we also consider interconnects as a perspective group of nanosensors. The recent classification of nanosensors based on CNTs and GNRs considers three main groups: physical, chemical and biological [1] (see Fig. 4.2).

Physical nanosensors are used to measure magnitudes such as mass, pressure, force or displacement. The working principle is usually based on the fact that the electronic properties of both nanotubes and nanoribbons change when these are bent or deformed (Fig. 4.2b).

Chemical nanosensors are used to measure magnitudes such as the concentration of a particular gas, the presence of a specific type of molecules or the molecular composition of a substance (Fig. 4.2c).

Biological nanosensors are used to monitor biomolecular processes such as antibody/antigen interactions, DNA interactions, enzymatic interactions or cellular communication processes, among others (Fig. 4.2d).

The central point of research is the interconnect space, where *non-regularity* effects are very essential. This space determines also the conductivity of interfaces of nanodevices and integrated nanosystems.

4.1.1 Scattering Processes in Nanocarbon-Based Nanointerconnects

The electronic structure for CNT–Me and GNR–Me interconnects can be evaluated through the electronic density of states (DOS) for carbon–metal contact considered as a ‘disordered alloy’, where clusters containing both C and Me atoms behave as scattering centres. The computational procedure that we have developed for these calculations is based on the construction of cluster potentials and the evaluation of both scattering (S) and transfer (T) matrices [5]. The general model of multiple scattering using the effective media approximation (EMA) combined with the coherent potential approach (CPA) for condensed matter is based on the atomic cluster formalism. When using the CPA as EMA approximation, the resistance of the interconnect is evaluated through Kubo–Greenwood formalism [6–8] or, in the simplest cases, through Ziman model [9].

A general model of multiple scattering with the effective media approximation (EMA) for condensed matter based on the atomic cluster approach is presented in Fig. 4.3. So far, the cluster formalism has been successfully applied for metal Cu metal [5], as well as for semiconductors, both elemental (Ge and Si) and binary ($\text{As}_x\text{Se}_{1-x}$ and $\text{Sb}_x\text{Se}_{1-x}$) [10, 11]. Special attention has been paid to the latter, since the concept of statistical weighing has been applied for the binary components in solid solutions.

We have developed structural models for CNT–Me and GNR–Me junctions, based on their precise atomistic structures, which take into account the CNT

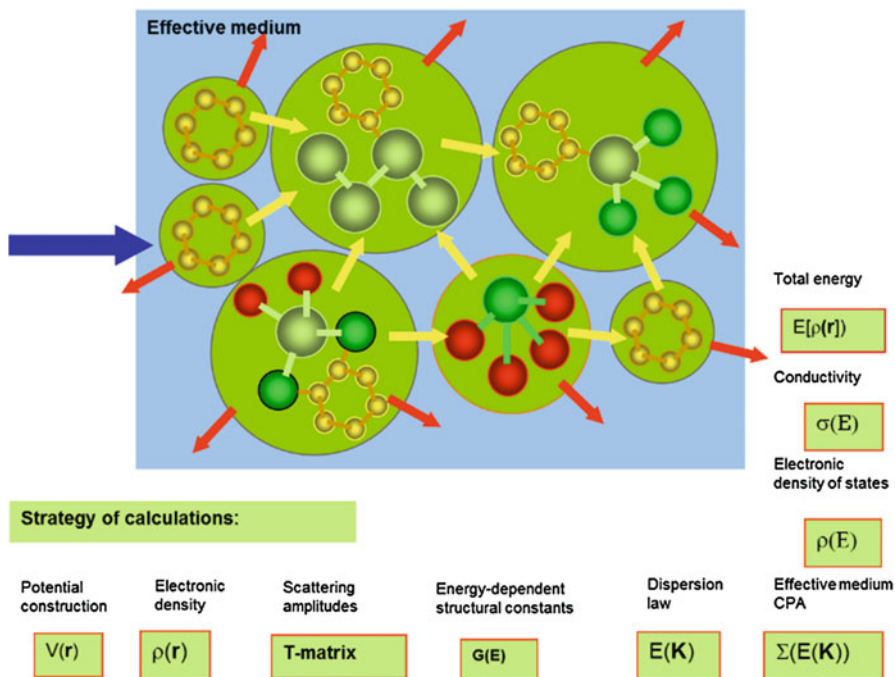


Fig. 4.3 Multiple scattering problem for the system of clusters as multiple scattering model of condensed matter: strategy of calculations on fundamental properties of condensed medium described within the effective media approximation

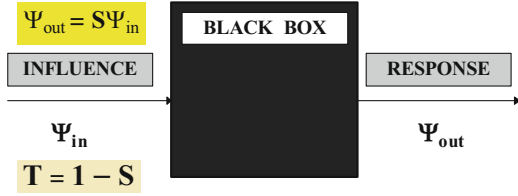
chirality effect and its influence on the interconnect resistance for Me (= Ni, Cu, Ag, Pd, Pt, Au) and predefined CNT (or GNR) geometry.

In the simplest cases, the electronic structure of CNT–Ni interconnects can be evaluated through the DOS for the C–Ni contact considered as a ‘disordered alloy’ [12]. In the current study, we have developed more complicated structural models of CNT–metal junctions based on a precise description of their atomistic structures. When estimating the resistance of a junction between a nanotube and a substrate, the main problem arises due to the influence of the nanotube chirality on the resistance of SW and MWCNT–Me interconnects (Me = Ni, Cu, Ag, Pd, Pt, Au) for a predefined CNT geometry.

4.2 Electronic Structure Calculations of Nanocarbon-Based Interfaces

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 centres (phonons, charge defects, structural defects, etc.), including a

Fig. 4.4 The scattering paradigm: influence (*in*) and response (*out*)



pure elastic way, called ballistic (Matissien rule). The developed computational procedure is based on the construction of cluster potentials and the evaluation of the S - and T -matrices for scattering and transfer, respectively, [8, 10]. It 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 $\Psi_{in}(\mathbf{r})$ and *response* $\Psi_{out}(\mathbf{r})$ gives a set of scattering amplitudes corresponding to possible scattering channels for any 'trial' energy. This allows us 'to decrypt' the electronic spectra of 'black box' [10, 12].

The scattering paradigm is presented in Fig. 4.4. This allows us to realize full-scale electronic structure calculations for condensed matter.

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

$$\psi_{in}(\mathbf{r}) = \varphi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\mathbf{r}). \quad (4.1)$$

The scattering of 'trial' waves, in the presence of a potential, yields new stationary solutions labelled as:

$$\psi_{out}(\mathbf{r}) = \psi_{\mathbf{k}}^{(\pm)}(\mathbf{r}) \quad (4.2)$$

for the modified Schrödinger equation $\hat{H}\psi_{\mathbf{k}}^{(\pm)}(\mathbf{r}) = E\psi_{\mathbf{k}}^{(\pm)}(\mathbf{r})$. An electronic structure calculation is considered here as a scattering problem, where the centres of scattering are identified with the atoms of clusters [1, 12].

The first step to modelling is the construction of potentials [12], both atomic and crystalline, which is based on analytical Gaspar's potential of screened atomic nucleus [13] and $X\alpha$ and $X\alpha\beta$ presentations for the electronic exchange and correlation, using the LDA (*local density approximation*).

Figure 4.5 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 an electronic structure, the calculations of scattering properties are necessary, generally, in the form of S - and T -matrices (Fig. 4.3). 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 the potential modelling and phase shifts in the framework of *MT*-approximation are presented elsewhere.

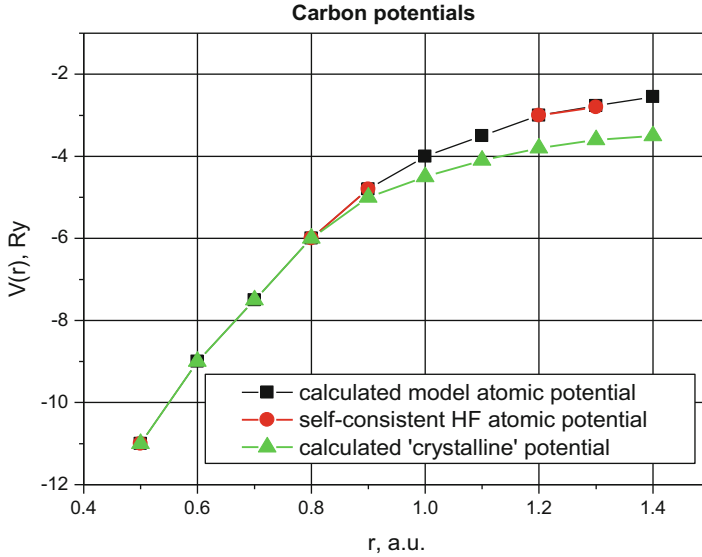


Fig. 4.5 Analytical carbon potentials based on a simulation procedure as compared to the results of Hartree–Fock calculations [1]

The formalism used here for calculations on the electronic structure is based on the CPA, the multiple scattering theory and 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 realistic analytical potential functions (e.g. [1, 8]).

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

$$\psi(\mathbf{r}) \rightarrow e^{ikz} + f(\theta) \frac{e^{ikr}}{r} \quad (\text{“liquid metal” model}) \quad (4.3)$$

and

$$\psi(\mathbf{r}) \rightarrow e^{ikz} + f(\theta, \varphi) \frac{e^{ikr}}{r} \quad (\text{spherical cluster model}). \quad (4.4)$$

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 $\delta_{lm}(E)$, and the T -matrix of the cluster is found as a whole. The indices l and m arise, as a result of expansions of such functions as Bessel’s functions j_l , Hankel’s functions h_l and spherical harmonics Y_{lm} .

In general, the modelling of disordered materials represents them as a set of atoms or clusters immersed in an effective medium, with the dispersion $E(\mathbf{K})$ and a

complex energy-dependent coherent potential $\Sigma(E)$ found self-consistently in the framework of the CPA. The basic equations of this approach are:

$$\Sigma(E) = V_{\text{eff}} + \langle T \rangle (1 + G_{\text{eff}} \langle T \rangle)^{-1}, \quad (4.5)$$

$$G(E) = G_{\text{eff}} + G_{\text{eff}} \langle T \rangle G_{\text{eff}} = \langle G \rangle, \quad (4.6)$$

$$\langle T(E, \mathbf{K}) \rangle = 0, \quad (4.7)$$

$$\Sigma(E) = V_{\text{eff}}, \quad (4.8)$$

$$\langle G \rangle = G(E) = G_{\text{eff}}, \quad (4.9)$$

$$N(E) = -(2/\pi) \ln \{ \det \| G(E) \| \}. \quad (4.10)$$

Here $\langle \dots \rangle$ denotes averaging; V_{eff} and G_{eff} are the potential and the Green's function of the effective medium, respectively; $T(E, \mathbf{K})$, the T -matrix of the cluster; and $N(E)$, the integral density of the electronic states. Equation (4.7) can be re-presented in the form:

$$\langle T(E, \mathbf{K}) \rangle = \mathbf{Sp} T(E, \mathbf{K}) = \int_{\Omega_{\mathbf{K}}} \langle \mathbf{K} | T(E, \mathbf{K}) | \mathbf{K} \rangle d\Omega_{\mathbf{K}} = 0, \quad (4.11)$$

where $|\mathbf{K}\rangle = 4\pi \sum_{l,m} (i)^l j_l(kr) Y_{lm}^*(\mathbf{K}) Y_{lm}(\mathbf{r})$ is the one-electron wave function, $\mathbf{Sp}$ means the calculation of the matrix trace while the integration is performed over all angles of $\mathbf{K}$ inside the volume $\Omega_{\mathbf{K}}$. Equation (4.7) enables obtaining the dispersion relation $E(\mathbf{K})$ of the effective medium. The DOS calculations have been performed using the relation:

$$\rho(E) = \frac{2}{\pi} \int \text{Im} \{ \mathbf{Sp} G(\mathbf{r}, \mathbf{r}', E) \} d\mathbf{r}, \quad (4.12)$$

where $G(\mathbf{r}, \mathbf{r}', E) = \sum_{l,m} Y_{lm}(\mathbf{r}) Y_{lm}(\mathbf{r}') G_l(\mathbf{r}, \mathbf{r}')$ is the angular expansion of Green's function.

The paradigm of the scattering theory and the developed strategy of simulation of CNTs electronic properties use the generalized scattering condition for the low-dimensional atomic structures of the condensed matter:

$$\psi_{\mathbf{k}}^{(\pm)}(\mathbf{r}) \underset{r \rightarrow \infty}{\propto} \phi_{\mathbf{k}}(\mathbf{r}) + f_{\mathbf{k}}^{(\pm)}(\Omega) \frac{\exp(\pm ikr)}{r^{(d-1)/2}}, \quad (4.13)$$

where Ω describes the integrated space in angular units while superscripts '+' and '-' label the asymptotic behaviour in terms of d -dimensional waves:

$$\frac{\partial \sigma_{a \rightarrow b}}{\partial \Omega} = \frac{2\pi}{\hbar v} |\langle \varphi_b | \hat{V} | \psi_a^+ \rangle|^2 \rho_d(E), \quad (4.14)$$

where d is the atomic structure dimension.

The calculations of conductivity are usually performed using Kubo–Greenwood formula [14]:

$$\sigma_E(\omega) = \frac{\pi\Omega}{4\omega} \int [f(E) - f(E + \hbar\omega)] |D_E|^2 \rho(E) \rho(E + \hbar\omega) dE, \quad (4.15)$$

where ω is a real frequency parameter of Fourier transform for the time-dependent functions, $f(E)$ is Fermi–Dirac distribution function, $D_{E,E'} = \int_{\Omega} \Psi_{E'}^* \nabla \Psi_E d\mathbf{r}$, $\Psi_E(\mathbf{K}) = A \exp(i\mathbf{K}\mathbf{r})$ and $\mathbf{K}$ is the complex wave vector of effective medium.

The dispersion function $E(\mathbf{K})$ determines the properties of the wave function $\Psi_E(\mathbf{K})$ upon the isoenergy surface in $\mathbf{K}$ -space.

For static conductivity ($\omega = 0$ and $T = 0$ K), Eq. (4.16) gives the Drude-like formula:

$$\sigma_{E(\mathbf{K})} = \frac{e^2 n^*}{m^*} \tau, \quad (4.16)$$

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

$$m^* = \left(\partial^2 E / \partial K_R^2 \right)^{-1}, \quad (4.17)$$

where K_R is a modulus of the real part of the vector $\mathbf{K}$.

There are some ideas to estimate the conductivity in static and frequency regimes taking into account the temperature effects. However, in the case of CNT (of GNR), 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, GNRs and the related systems.

Usually two basic electron conductivity mechanisms in CNT-based structures are considered. The ballistic mechanism is engaged in electron transport within CNTs, while the collisional mechanism is characteristic of CNT-substrate interconnects. Hence the general conductivity σ_{gen} is evaluated as follows: $\sigma_{\text{gen}}^{-1} = \sigma_{\text{coll}}^{-1} + \sigma_{\text{ball}}^{-1}$. For pure CNTs, we clearly observe that $\sigma_{\text{ball}} \gg \sigma_{\text{coll}}$. The collisional contribution is basically connected with the specific morphology of interconnects space [14]. In the framework of multiple scattering theory formalism and effective medium approximation, we can evaluate both factors of conductivity.

4.3 Electromagnetics of CNT and Graphene-Based Systems

4.3.1 ‘Liquid Metal’ Model for CNT–Metal Junction: CNT–Ni case

The term ‘liquid metal’ means the structural disorder of the substance involved; more precisely, only the nearest order (short-range order – SRO) is considered as it usually occurs in a liquid. It also means that the interatomic distance between the nearest neighbours (first coordination sphere) is fixed, whereas the angular coordinates are random. In the context of this model, the interconnect space C–Ni is considered as ‘liquid’ alloy C_xNi_{1-x} .

Both Figs. 4.6 and 4.7 depict the idealized images of contacts between CNTs and the Ni substrate.

The model in CPA approach (4.11) gives the dispersion law for the effective medium and the electronic density of states (EDOS, see Eq. (4.12)), where the argument $\mathbf{K}$ of dispersion function $E(\mathbf{K})$ is a complex: $\mathbf{K}_R + i\mathbf{K}_I$. The ‘mixed’ dispersion law [12]:

$$E_{C-Ni}(\mathbf{K}_R) = xE_C(\mathbf{K}_R) + (1-x)E_{Ni}(\mathbf{K}_R) \quad (4.18)$$

means configurationally averaged state of the electronic structure within the interconnect space with a variable extent of disorder. The ‘liquid metal’ alloy model can be used for evaluating mixed effective mass $m^*_{C-Ni}(E)$ (see Eq. (4.17)). Taking into account the spectral dependence of the effective mass $m^*(E)$ and estimating the spectral resistivity $\rho_x(E) = 1/\sigma_x(E)$, and following Eq. (4.16), we can estimate the average layer resistivity $\rho_{x,av}$ as follows:

Fig. 4.6 Fragment of interconnects between the Ni substrate and C nanotubes

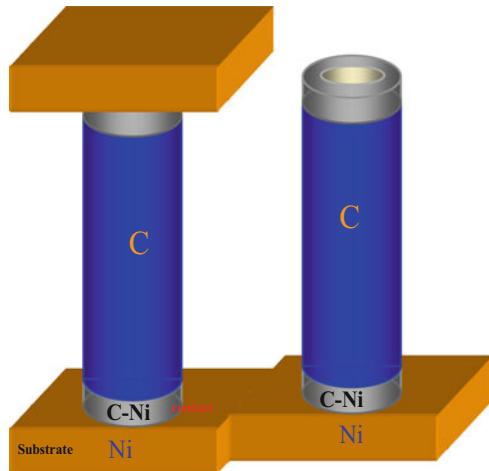


Fig. 4.7 Model of CNT–Ni interconnect as a disordered alloy

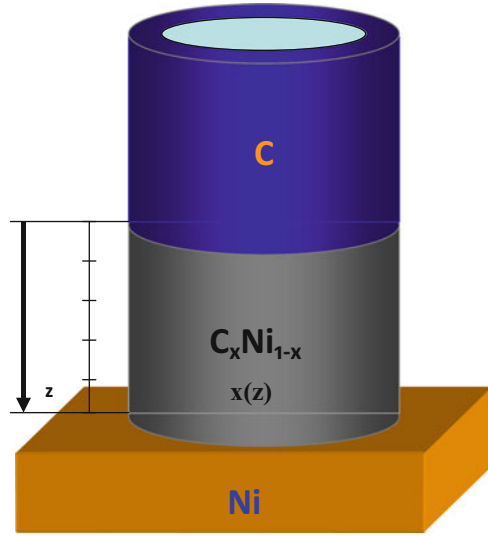


Table 4.1 Dependence of specific resistivity $\rho(x)$ on alloy composition (x)

No.	x	Layer resistivity C_xNi_{1-x} , $\rho(x)$, 10^2 Ohm·nm
1	0.00	0.807
2	0.10	0.813
3	0.20	0.821
4	0.30	0.833
5	0.40	0.849
6	0.50	0.871
7	0.60	0.905
8	0.70	0.962
9	0.80	1.081
10	0.90	1.458
11	1.00	8.231

$$\rho_{x,av} = \frac{\int_0^{E_{fin}} \rho_x(E) dE}{E_{fin}}, \quad (4.19)$$

where E_{fin} is the width of the conduction band and $x(z)$ is the stoichiometry coefficient depending on the coordinate z of the ring layer (Fig. 4.7). The dependence of specific resistivity on alloy composition is presented in Table 4.1.

The evaluation of resistance for the CNT–Ni contact gives ~ 105 kOhm for the nanotube with the internal and external radii – $R_1 = 1.0$ nm and $R_2 = 2.0$ nm, respectively.

Evidently, the results of the resistance evaluation for interconnect depend essentially on both the layer height l_0 and the spectral integration parameter E_{fin} , which is responsible for the electron transport of really activated *hot electrons*.

The ‘liquid metal’ model [12] does not operate with CNT chirality in the interconnect space. Limitations of chirality effects (e.g. chirality angle) in the CNT–Me junctions forced to develop a semiempirical model that considers the local atomic structure of the interconnect. For this aim, we have constructed a model of ‘effective bonds’ for the interconnect with a realistic atomic structure.

4.3.2 Model of ‘Effective Bonds’ for Simulations of CNT–Me and GNR–Me Junctions

The model of CNT–Me and GNR–Me nanointerconnects (Fig. 4.1) has been developed in the present research. Within the electronic transport formalism, it consists of two regions supporting two different electron transport mechanisms: *ballistic* (elastic) and *collisional* (non-elastic). These electron transport processes are simulated using the corresponding boundary conditions in the form of the effective medium. The CNT and GNR chiralities (n,m) are simulated by the corresponding orientation of the chirality vectors within the scattering medium. The most problematic areas for the proper simulation are CNT–Me and GNR–Me *end-type* junctions, where the atomic structural disorder (non-regularity) is observed and the conductivity mechanism is changed.

The influence of chirality on resistance in the vicinity of interconnect depends on the number of statistically realized bonds between the CNT (GNR) and the metal contact (e.g. Ni, Cu, Au, Ag, Pd, Pt).

Using the simulation models, presented earlier [1], we have determined the resistance for both (SW and MW) CNT–Me and (SL and ML) GNR–Me interconnects, based on the evaluation of the interface potential barriers and implementation of Landauer formula [14], which defines the integrated conductance:

$$I_G = \frac{2e^2}{h} \sum_{i=1}^N T_i = \left(\frac{1}{12.92(\text{kOhm})} \right) \sum_{i=1}^N T_i = 0.0774 \sum_{i=1}^N T_i. \quad (4.20)$$

The chirality (m,n) is simulated by the corresponding orientation of carbon rings within the scattering medium (Fig. 4.8).

CNT interconnect configuration models for zigzag and armchair morphologies and active bond formation for computer simulations are presented in Figs. 4.9 and 4.10.

Figures 4.11, 4.12 and 4.13 demonstrate *end-type* contact formation.

In the case of *side-type* contact for GNR–Me interconnects, the number of effective bonds per contact square is quite high (see Fig. 4.14).

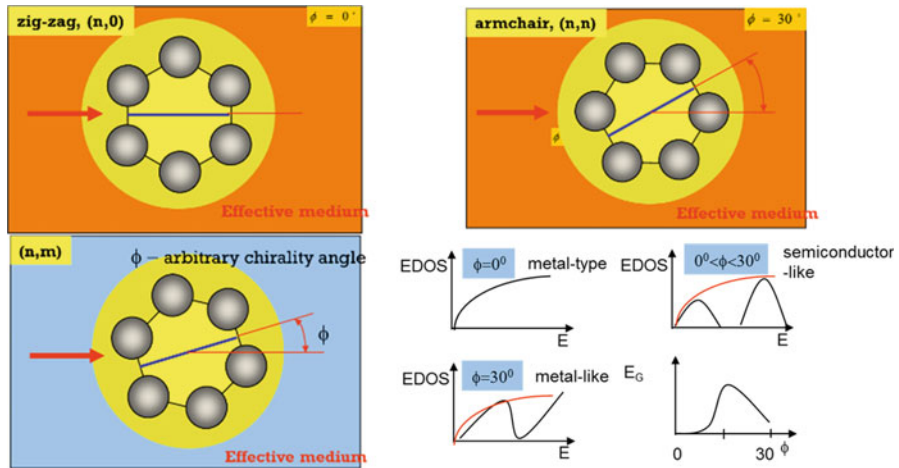


Fig. 4.8 Modelling of chirality: carbon ring rotation within CNT and GNR and the expected results

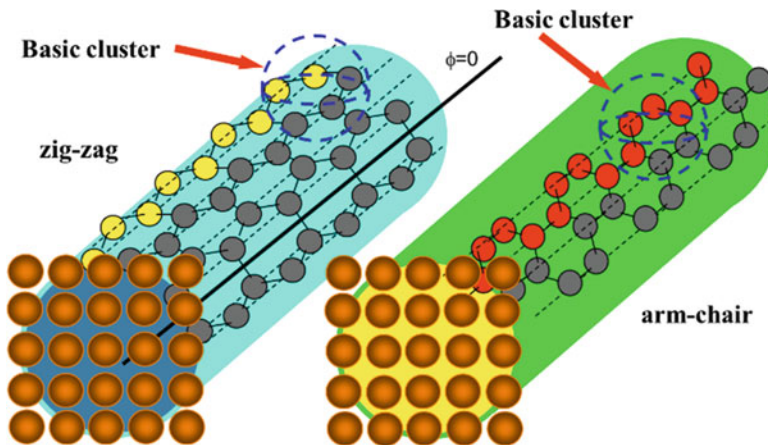


Fig. 4.9 CNT interconnect configuration model

4.3.3 SWCNT and SL and ML GNR Simulations

Figures 4.11, 4.12 and 4.13 present a creation of C–Me ‘effective bonds’. Substrates of *fcc*-metals are considered here [100]. It should also be emphasized that this is a probabilistic process when only more-or-less equilibrium bonds (‘effective bonds’) are formed at interatomic distances corresponding to the minimum total energies. The evaluation of a number of ‘effective bonds’ using Eq. (4.20) 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.

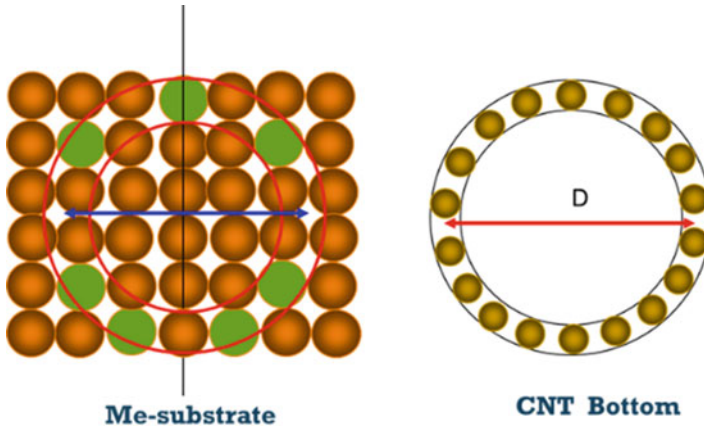


Fig. 4.10 Active bonds formation in the simulation of catalytic growth of CNT on the Me-substrate

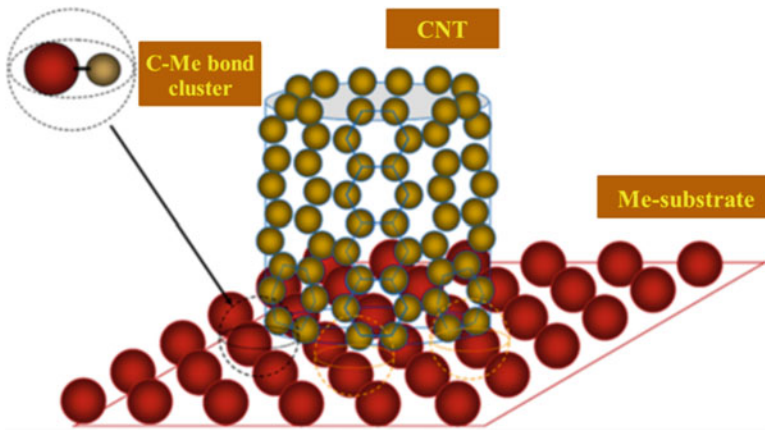


Fig. 4.11 CNT–Me interconnect formation model

The calculations of the ‘effective bonds’ capabilities lead to an estimate of the energy-dependent transparency coefficient of the potential barrier C–Me (Figs. 4.15 and 4.16). 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. 4.16) is defined as:

$$T = \sqrt{\frac{E_2}{E_1}} \left(\frac{2\sqrt{E_1}}{\sqrt{E_1} + \sqrt{E_2}} \right)^2, \quad (4.21)$$

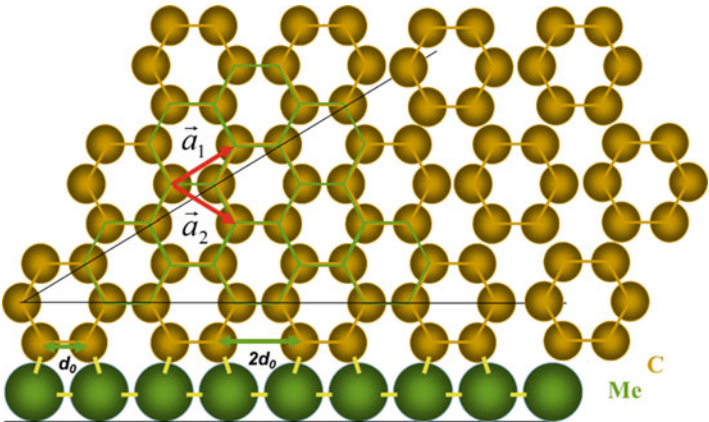


Fig. 4.12 Zigzag CNT–Ni interconnect formation

Fig. 4.13 Armchair GNR–Me end-type interconnect formation model

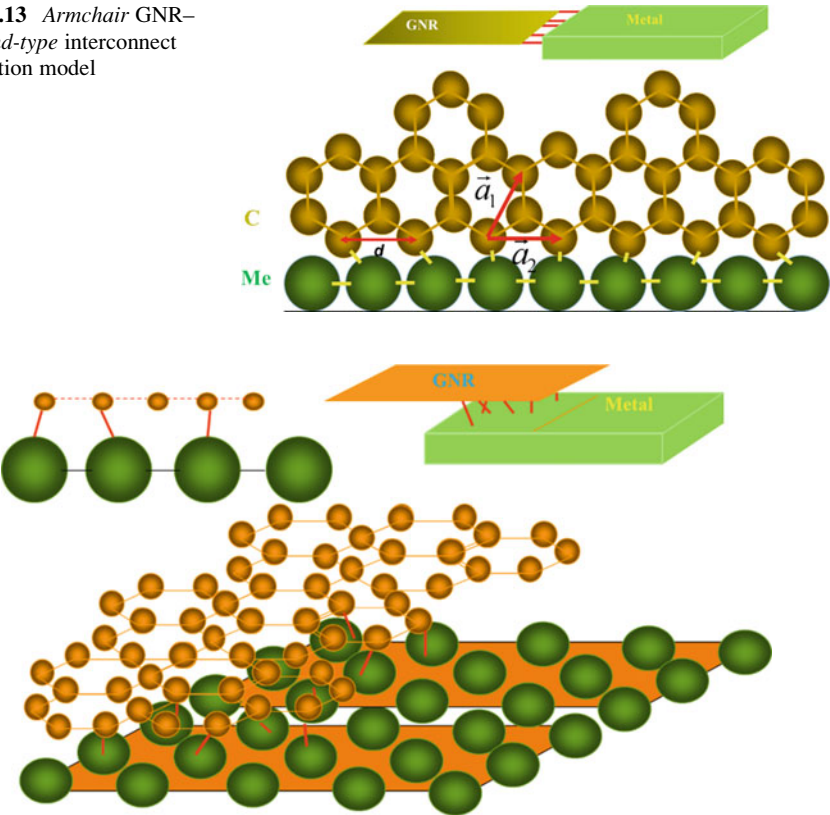


Fig. 4.14 GNR–Me side-type interconnect formation model

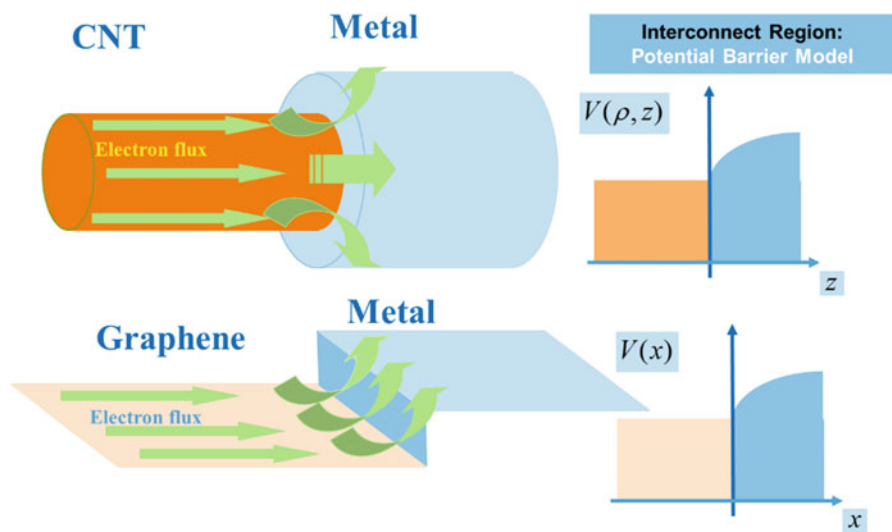


Fig. 4.15 Interconnect potential model for the scattering problem: CNT-Me, GNR-Me

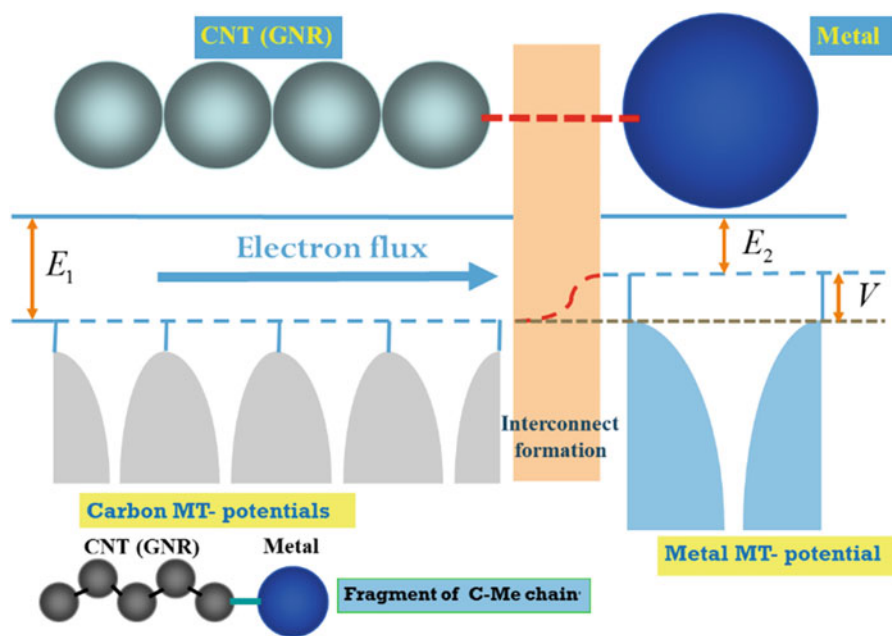


Fig. 4.16 Formation of a potential barrier for SWCNT-Me (SL GNR-Me) junction

Table 4.2 Resistances for SWCNT–Ni interconnects

Diameter (nm)	Chirality indices	Number of bonds in contact	Modulus of chirality vector (nm)	Interconnect resistance (kOhm)
<i>zigzag</i> , $\phi = 0^\circ$				
1.010	C(13,0)	12	2.952	665,19
2.036	C(26,0)	24	6.394	333,33
5.092	C(65,0)	64	15.990	124,72
10.100	C(130,0)	129	32.002	61,87
20.360	C(260,0)	259	63.940	30,82
<i>armchair</i> , $\phi = 30^\circ$				
0.949	C(7,7)	12	2.982	665,19
2.035	C(15,15)	28	6.391	205,71
5.021	C(37,37)	72	15.765	111,11
10.041	C(74,74)	146	31.531	54,79
20.084	C(128,128)	294	63.062	27,21
<i>C(3<i>m</i>,<i>m</i>)</i> , $\phi = 14^\circ$				
0.847	C(9,3)	3	2.66	2666,66
1.694	C(18,6)	5	5.32	1600,00
5.082	C(54,18)	16	15,96	500,00
10.16	C(108,36)	36	32.05	222,22
20.32	C(216,72)	80	64.10	100,00
<i>C(2<i>m</i>,<i>m</i>)</i> , $\phi = 19^\circ$				
1.036	C(10,5)	5	3.254	1600,00
2.072	C(20,10)	9	6.508	888,88
4.973	C(48,24)	17	15.614	470,50
10.1528	C(98,49)	47	31.880	170,21
20.5128	C(198,99)	97	64.410	82,47

where E_1 and E_2 are the corresponding electron energies. Evaluation of resistances of CNT–Ni junctions for various NT diameters and chiralities is presented in Table 4.2 (see also Figs. 4.17 and 4.18).

These resistances have been evaluated taking into account that only thermally activated electrons, i.e. a small part Δn of all quasi-free electrons n , participate in the conductance process with Fermi velocity v_F . This ratio can be evaluated as follows (see also Fig. 4.19):

$$\frac{\Delta n}{n} \approx \frac{\frac{1}{2}\rho(E_F(0))kT}{\frac{2}{3}\rho(E_F(0))E_F(0)} = \frac{3}{4} \frac{kT}{E_F(0)}, \quad (4.22)$$

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

Evaluations of thermalization effect for Ni, Pd and Au substrates are presented in Fig. 4.20.

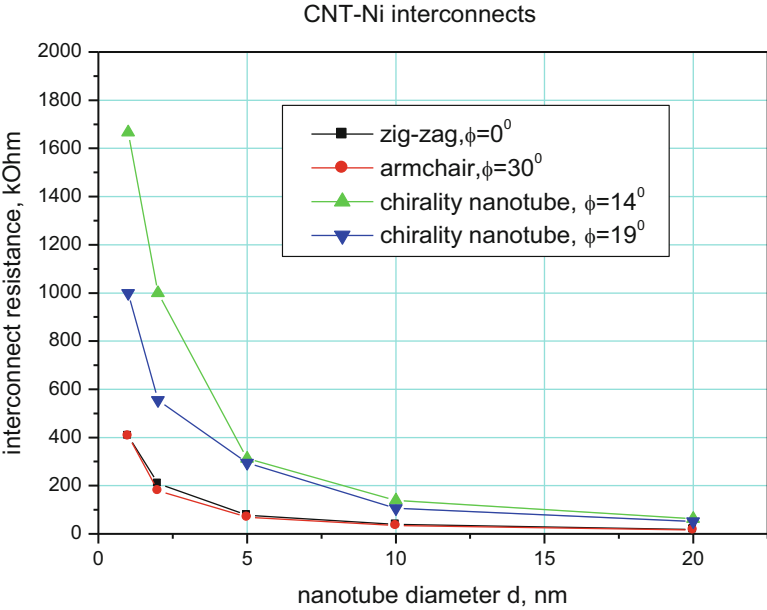


Fig. 4.17 CNT–Ni interconnect resistances via NT diameter

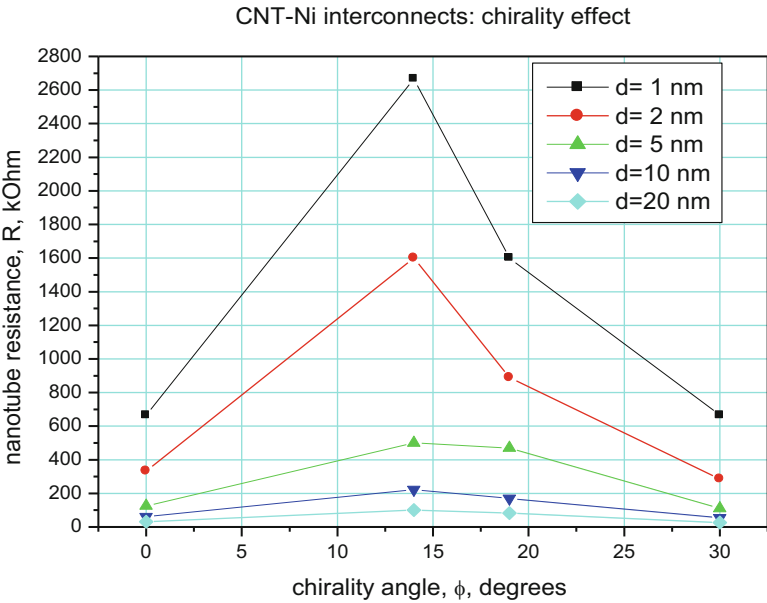


Fig. 4.18 CNT–Ni interconnect simulation: *chirality effects*

Fig. 4.19 Hot electrons of conductivity: evaluation of thermalization factor

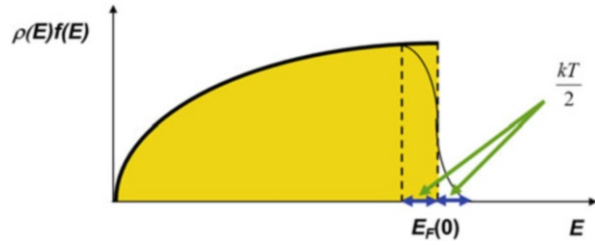
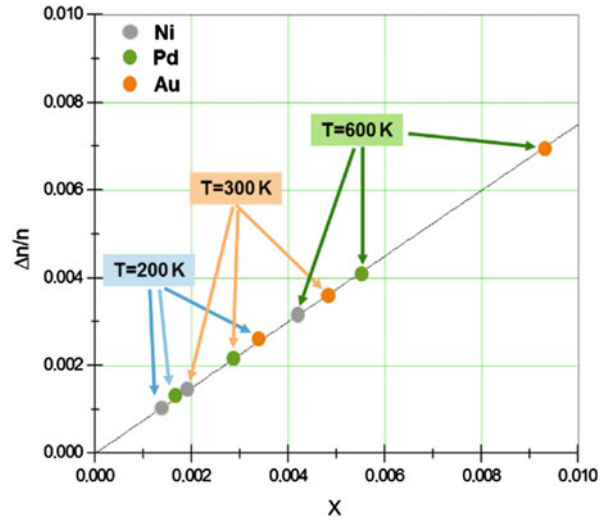


Fig. 4.20 Thermalization effect in CNT–Ni, CNT–Pd and CNT–Au



$$\frac{\Delta n}{n} = \frac{3}{4} \frac{kT}{E_F(T)} \approx \frac{3}{4} \frac{kT}{E_F(0)} \frac{1}{1 - \left(\frac{\pi kT}{2\sqrt{3}E_F(0)} \right)^2},$$

$$x = \frac{kT}{E_F(0)}, \quad \frac{\Delta n}{n} \approx 0,75 \frac{x}{1 - 0,82x^2}.$$

The role of thermally activated electrons is described by the scattering mechanism changing in the space of CNT–Me interconnect. The mean free path L in the CNT is of order 10^2 – $10^4 a_C$, 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 – $2 a_C$. From the uncertainty condition $\kappa L \approx 1$ (where $L \sim a_C \sim 2 \text{ a.u.}$ is a free path), it is possible to evaluate 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 ϕ within the interconnect space leads to the 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 the decrease of interconnect conductance, which is well observed when performing variation of nanotube diameter (Fig. 4.17).

Specific results for chirality effect simulations are shown in Fig. 4.18, with the evident maximum of the resistance for $\phi \approx 15^\circ$, where a large number of non-equilibrium bonds is formed, with higher potential barriers and lower transparency.

4.3.4 Parametric Calculations of CNT–Me Interconnect Resistances

In the course of the study, parametric calculations of the effective numbers of bonds and resistances for Ni, Pd and Au CNT interconnects were performed, where CNT diameters varied from 1 to 22 nm and chirality angle from 0° to 30° (with the step of 5°) for two basic metal substrate orientations ([100] and [111]). The aim of these detailed simulations is to create approximation dependences and data base of interconnect compositions for various technological applications [15, 16]. Technologically, reasonable results of these simulations (Au–Me interconnect [100], [111]) are shown in Fig. 4.21.

The dependence of the interconnect resistance on the number of effective bonds ($R_{\text{interconnect}} \times N_{\text{eff. bonds}}$) is a constant value. In the case of CNT–Au interconnect ([100]), it equals approximately 4000 kOhm (Figs. 4.22 and 4.23).

Figure 4.24 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 appears much less appropriate 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 SWCNT growth (e.g. Fe, Co and Ni), have stronger bonds to the ends of SWCNTs than noble metals [16]; therefore, some compromise exists between electrical parameters and strengths of the interconnect bonding.

4.3.5 Resistance MWCNT–Me Junctions

We have constructed atomistic model of MWCNTs which could fit into a porous alumina with the diameters of holes ~ 20 nm. In particular, a model of MWCNT with a predefined combination of *armchair* (ac) and *zigzag* (zz) shells is presented in Table 4.3 and Fig. 4.25.

Using the simulation models presented earlier, we have developed an ‘effective bonds’ model for MWCNT–Me junction resistance [12]. The results of these simulations are presented in Fig. 4.26. For MWCNT–Me junction, the integral

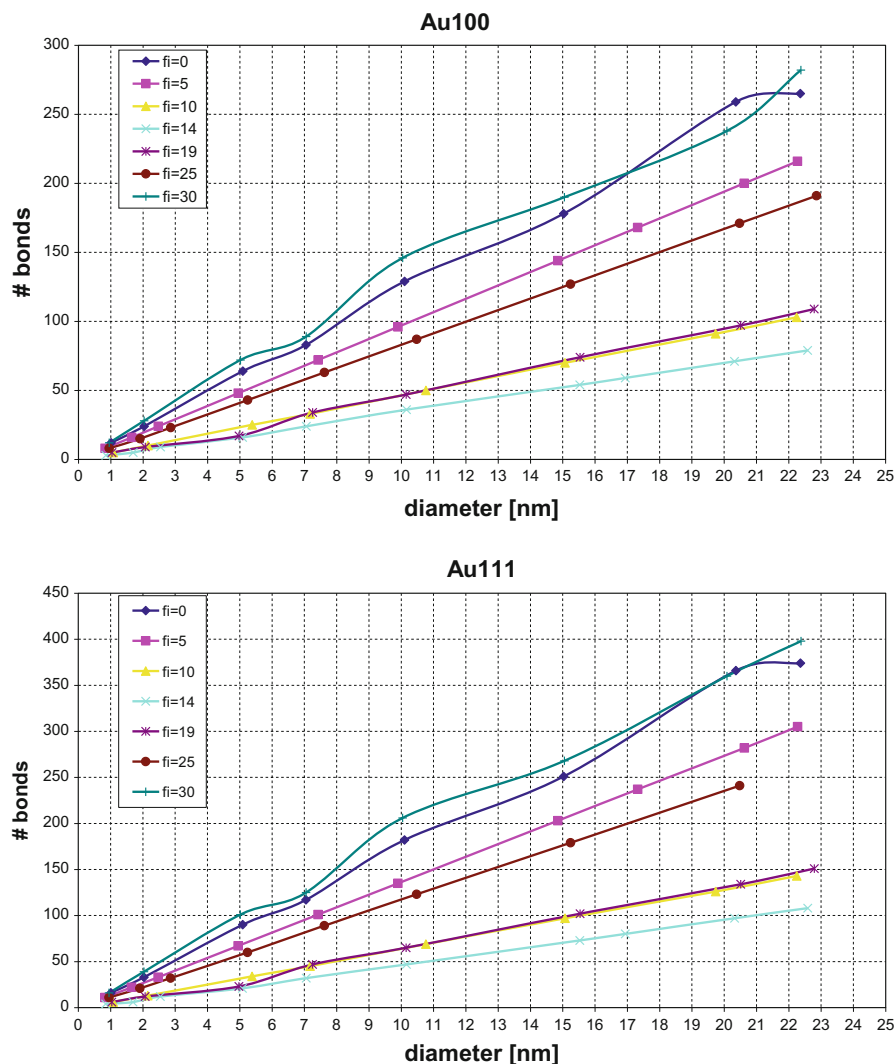


Fig. 4.21 Results of parametric calculations of effective bonds via CNT diameter for CNT–Me interconnects: (a) Au[100]–CNT; (b) Au[111]–CNT; (c) Pd[100]–CNT; (d) Pd[111]–CNT; (e) Ni [100]–CNT; (f) Ni[111]–CNT

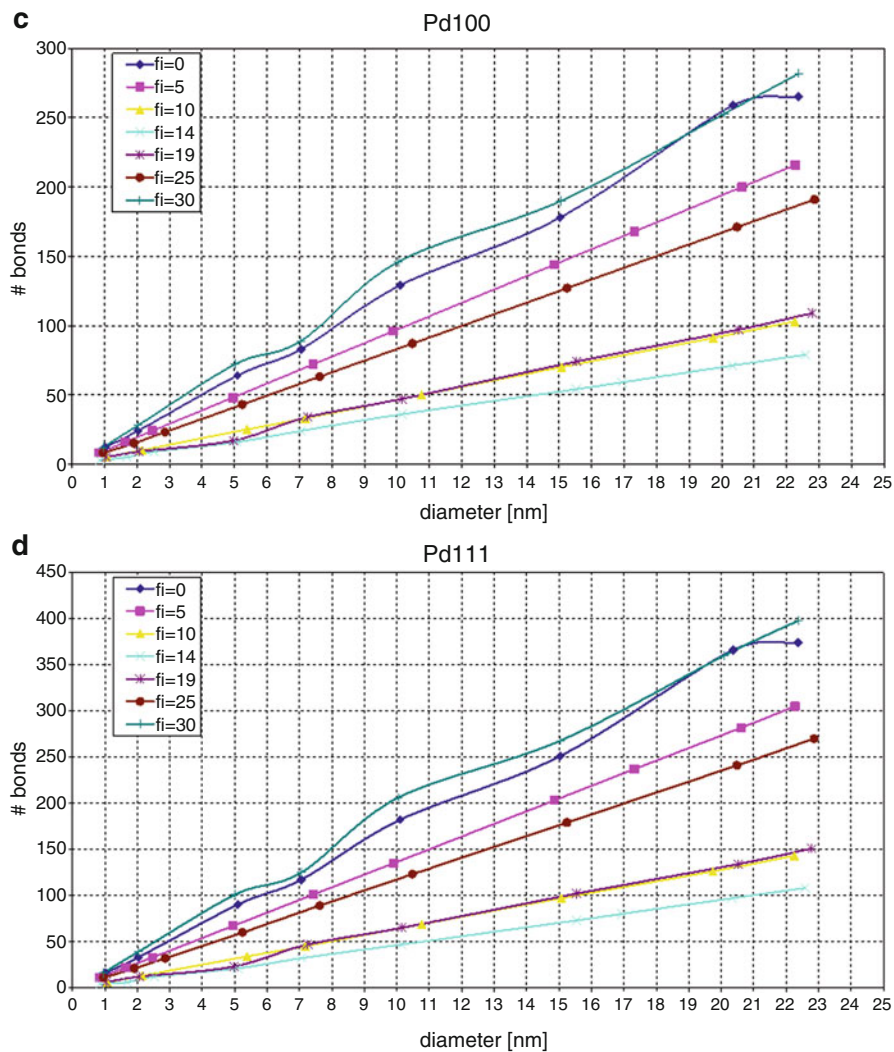


Fig. 4.21 (continued)

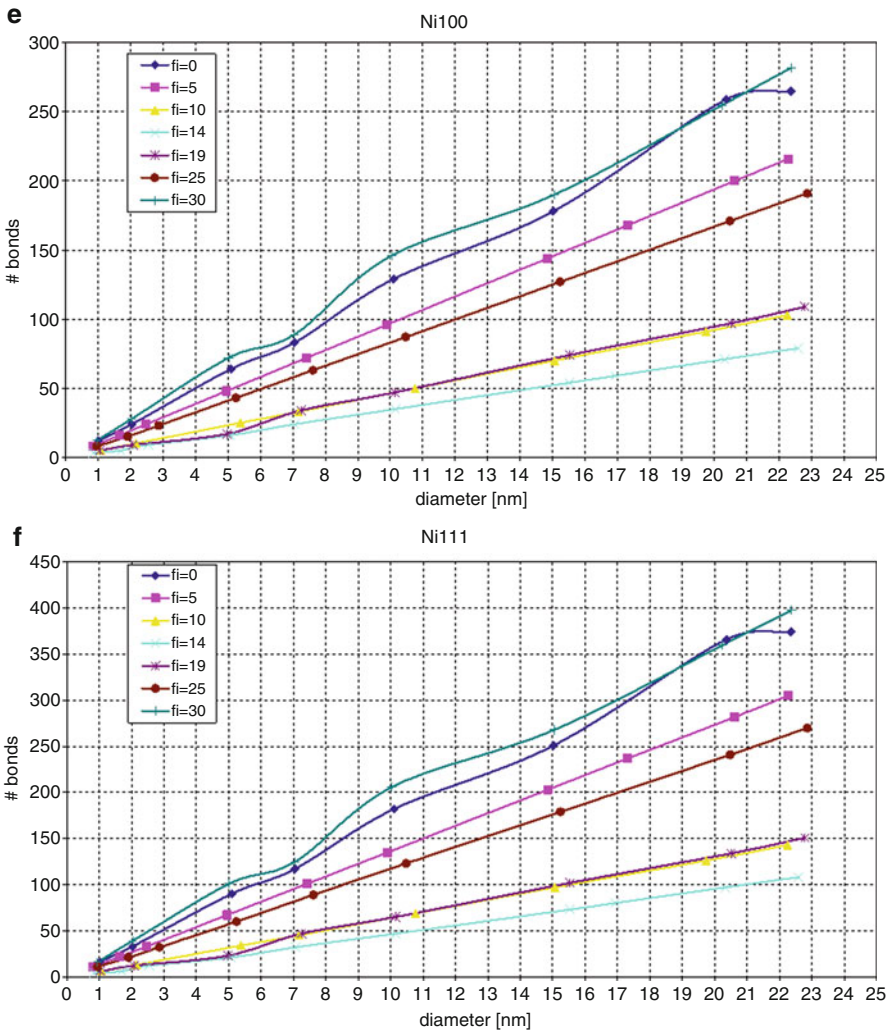


Fig. 4.21 (continued)

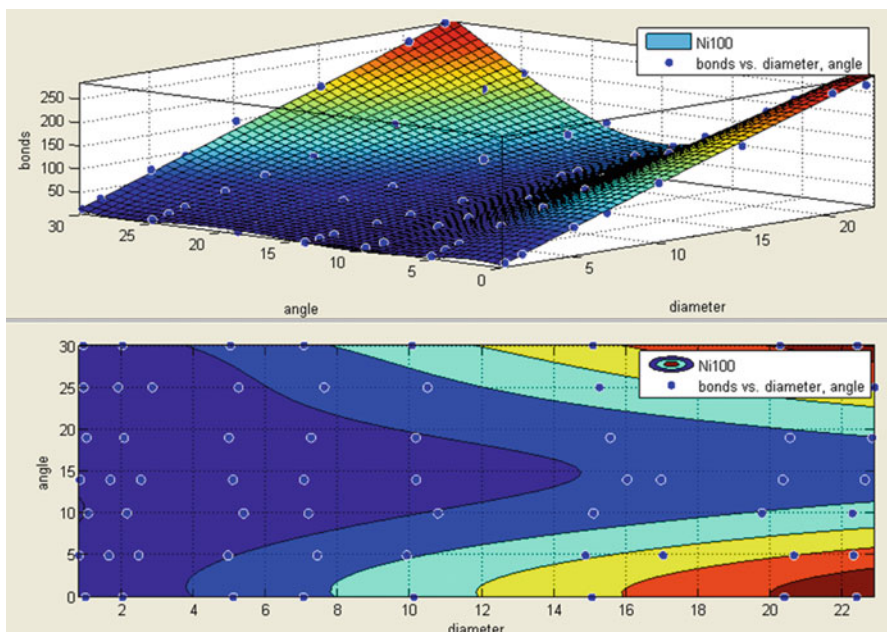


Fig. 4.22 3D-diagram of parametric calculations of effective bonds via CNT diameter for CNT–Ni interconnects

bonding with a corresponding substrate may be not as significant as in the case of SWCNTs, where a weak bonding can be fundamental. Figure 4.26 shows similar ratios of electric resistances for SWCNTs (Fig. 4.24), in favour of Au, Ag and Pt. It should be noted, that technological qualities of CNT–Me interfaces predefine the resulting resistance. In particular, experimental evaluations of CNT–Pt interconnect resistances for *side-type* and *end-type* contacts are 50 k Ω and 50–300 k Ω , correspondingly (see [17]).

4.3.6 Current Loss Between the Adjacent Shells Inside the MWCNT

Using the model of inter-shell potential within the MWCNT, the transparency coefficient has also been evaluated, which determines the possible ‘radial current’ losses. Figure 4.27 shows the inter-shell potential which is calculated using the developed realistic analytical potentials (see comments on the procedure of the potential construction, e.g. in [5]).

In Fig. 4.27, A is the electron emission energy, E is the electron energy and V is the height of the potential barrier between the nearest atoms in neighbouring

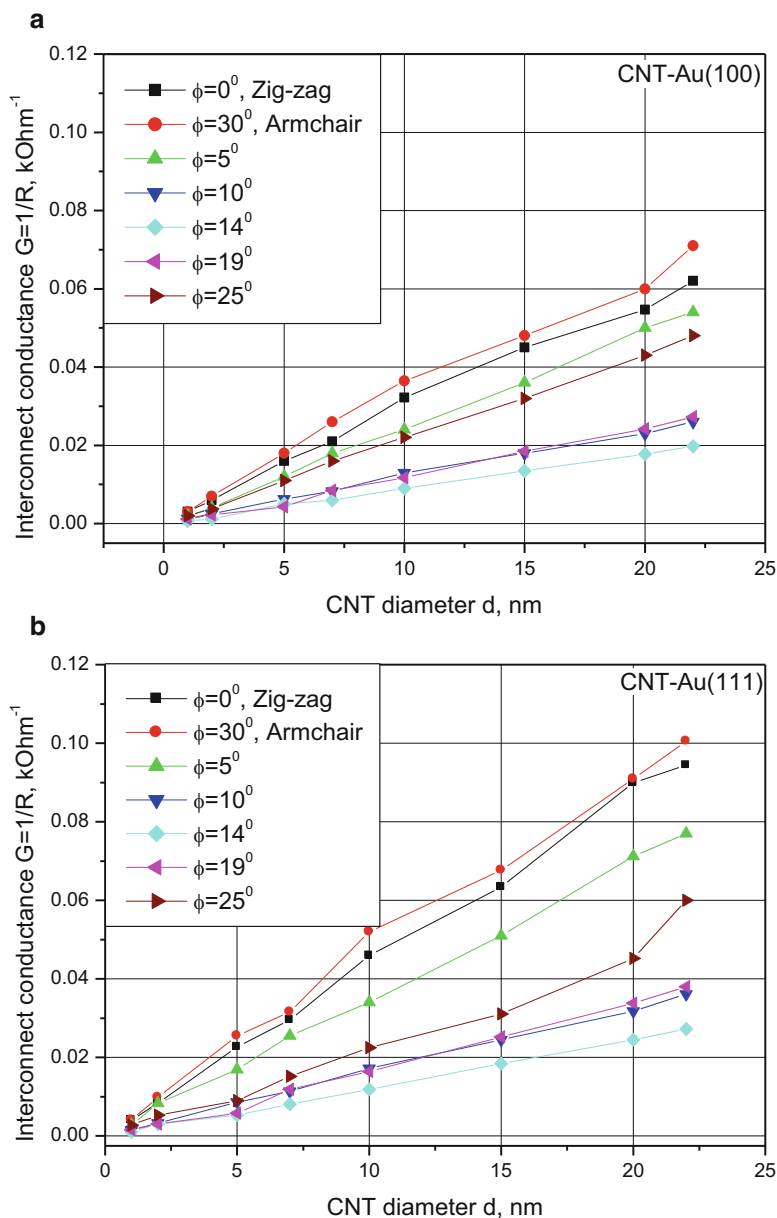


Fig. 4.23 Results of parametric calculations of resistances via CNT diameter for CNT-Me interconnects: (a) Au[100]-CNT; (b) Au[111]-CNT; (c) Pd[100]-CNT; (d) Pd[111]-CNT; (e) Ni[100]-CNT; (f) Ni[111]-CNT

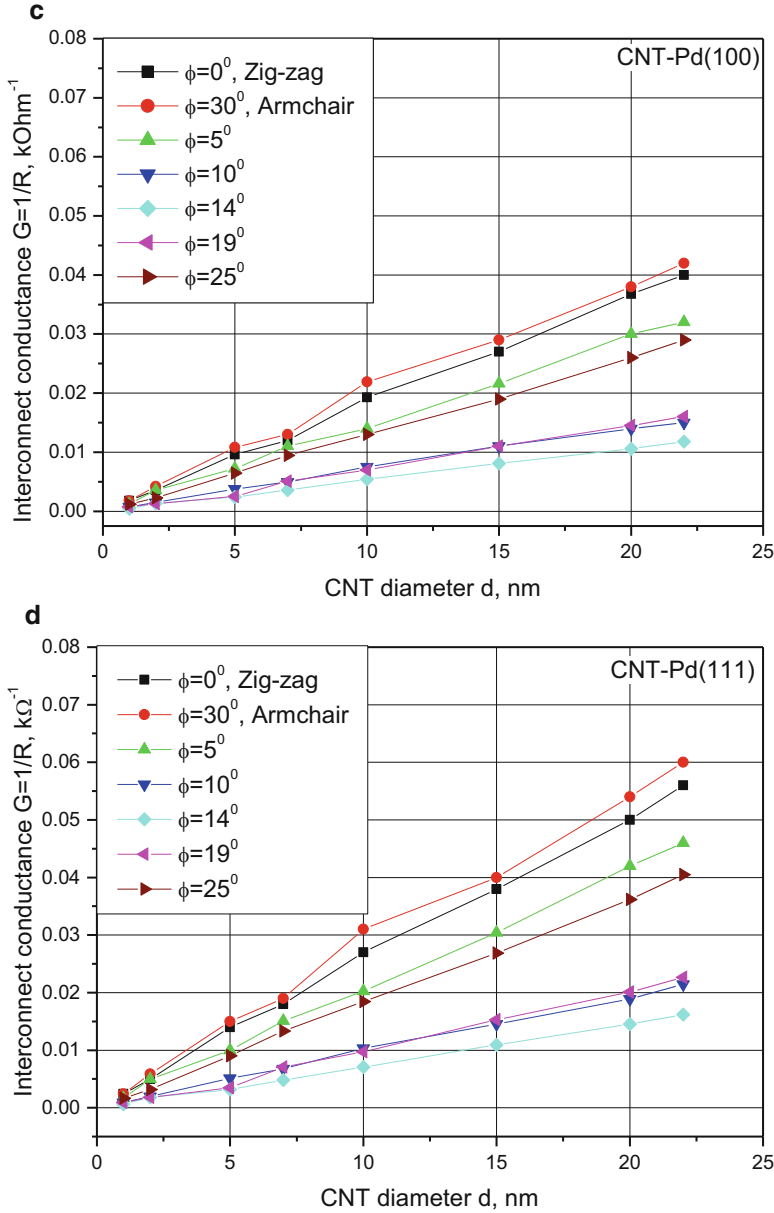


Fig. 4.23 (continued)

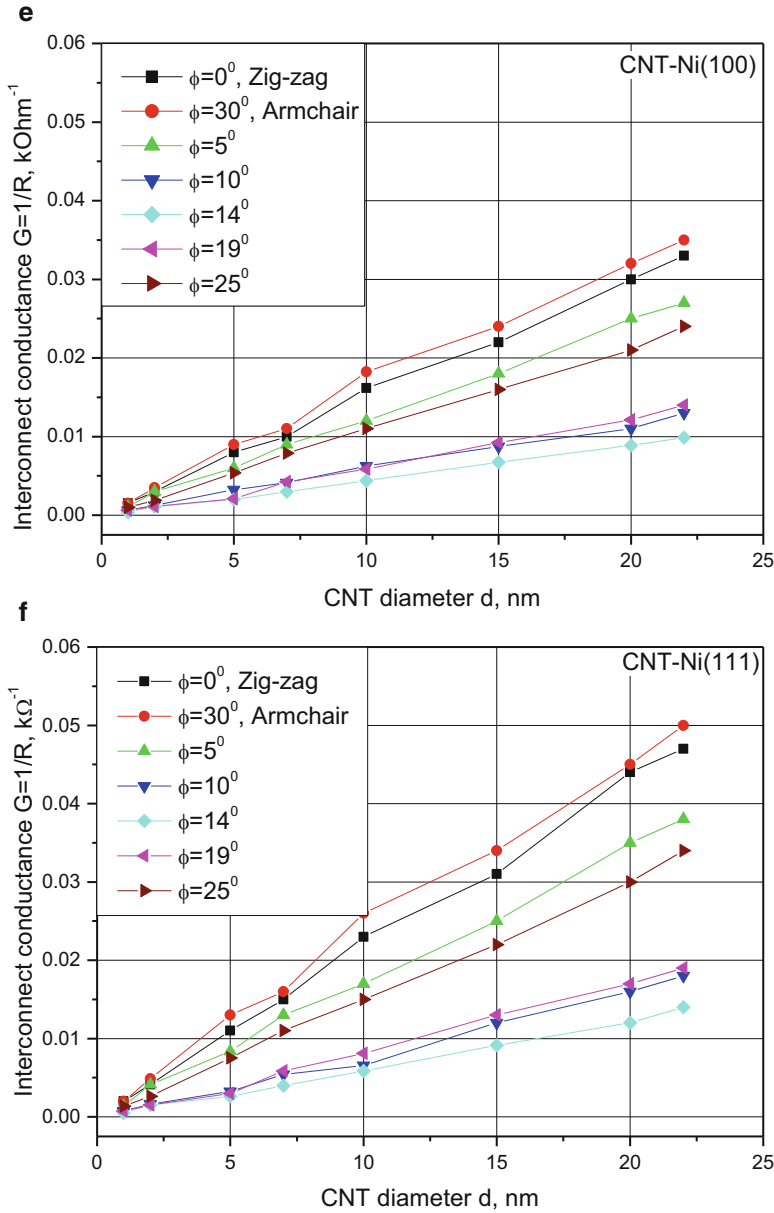


Fig. 4.23 (continued)

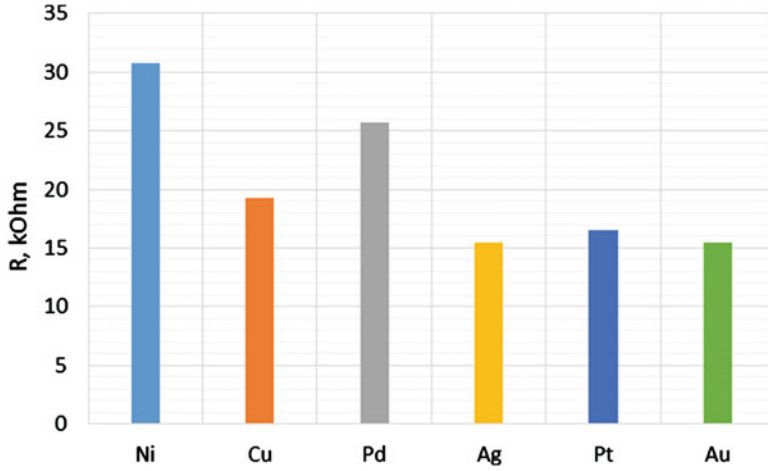


Fig. 4.24 Resistances of the zigzag-type SWCNT-Me interconnects for the CNT diameter ~ 1 nm

Table 4.3 Details of the model for MWCNT-Me interconnects

Diameter of CNT shell (nm)	Chirality
12.88	(95,95) <i>ac</i>
13.54	(173,0) <i>zz</i>
14.24	(105,105) <i>ac</i>
14.87	(190,0) <i>zz</i>
15.58	(199,0) <i>zz</i>
16.27	(120,120) <i>ac</i>
16.99	(217,0) <i>zz</i>
17.69	(226,0) <i>zz</i>
18.44	(136,136) <i>ac</i>
19.18	(245,0) <i>zz</i>
19.88	(254,0) <i>zz</i>

nanotube shells. Thus, a radial transparency coefficient T for the two different energy ratios can be defined as follows:

$$E > V, T = \frac{4Ek_2^2}{(E - k_2^2) \sin^2 k_2 a + 4Ek_2^2}, k_2^2 = E - V, \quad (4.23)$$

$$E < V, T = \frac{4E\kappa_2^2}{(E - \kappa_2^2) \sinh^2 \kappa_2 a + 4E\kappa_2^2}, k_2^2 = V - E, \quad (4.24)$$

where k_2 is the electron wave number in the case of above-barrier motion and κ_2 is the same for under-barrier motion. For example, between the second and first shells (*zz-ac* case, Fig. 4.19) $a = 13.54 - 12.88 = 0.66$ nm = 12.47 a.u. and $T = 3.469 \cdot 10^{-6}$ per 1 bond.

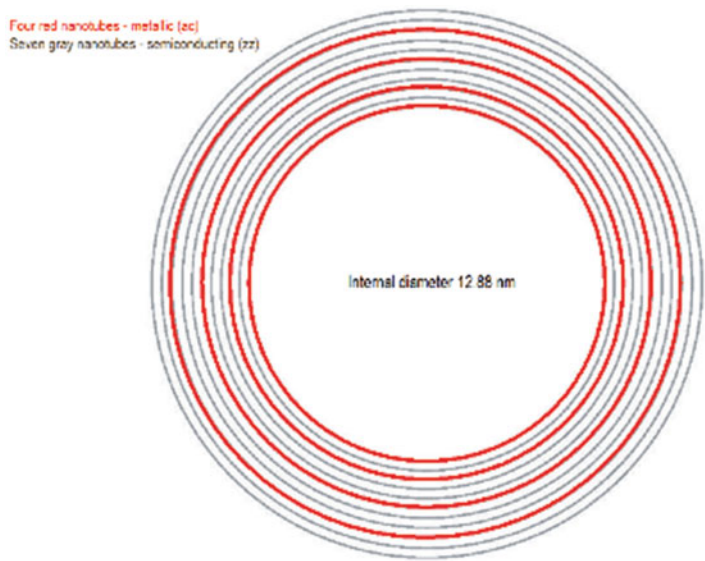


Fig. 4.25 Model of MWCNT with a predefined combination of *armchair* (ac) and *zigzag* (zz) shells

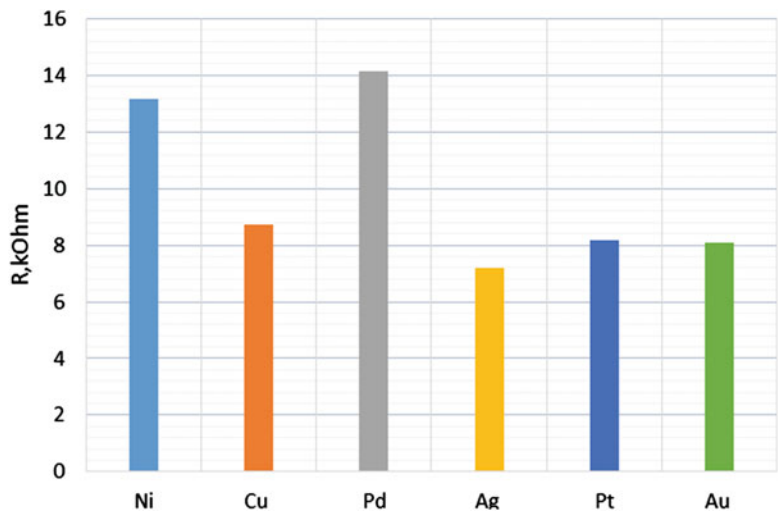
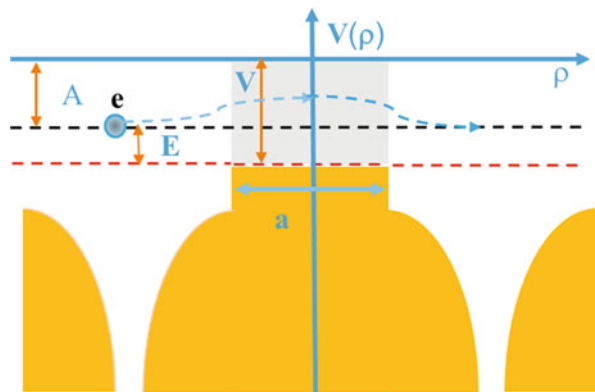


Fig. 4.26 Resistances of various MWCNT–Me interconnects

Fig. 4.27 Inter-shell transparency and inter-shell MT-potential model (MT-muffin tin)



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 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 shortest effective barriers is varied in a probabilistic way. This also means that current–voltage parameters of MWCNTs can be less stable than in the case of SWCNTs. It has been found that inter-shell interactions, such as inter-shell tunnelling of electrons and Coulomb interactions, cause a reduction of the total MWCNT conductance [18–20].

4.3.7 Resistances and Capacitances of SL GNR–Me, ML GNR–Me Interconnects

Similar calculations of resistances and capacitances have been carried out for special configurations of SL GNR(zigzag)–Me interconnect and for ML GNR(zigzag)–Me interconnect (*end-type* contacts) (Figs. 4.28, 4.29, 4.30 and 4.31), which is essential, e.g. in case of planar technology in nanodevices design [15, 16, 23].

For cases of *side-type* contact, the number of effective bonds per contact square is essential. Figure 4.32 shows the conductance of GNR–Au interconnect via the depth ‘ y ’ of contact overlapping.

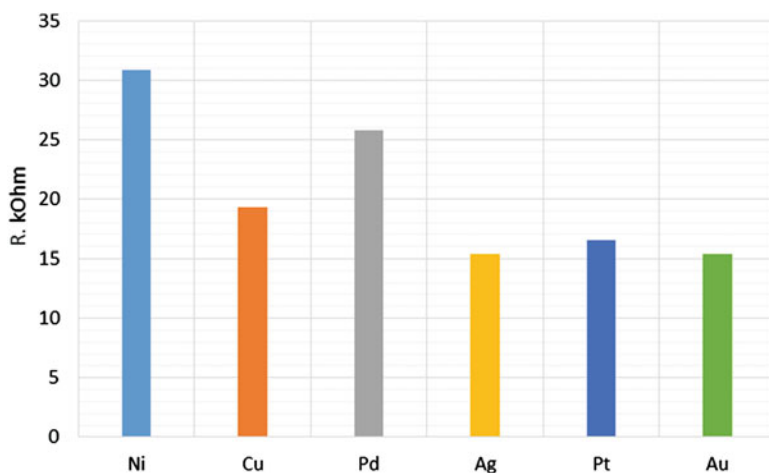


Fig. 4.28 Resistances of SL GNR(zigzag)–Me *end-type* interconnects. SL GNR–metal interconnect, width – 125 nm

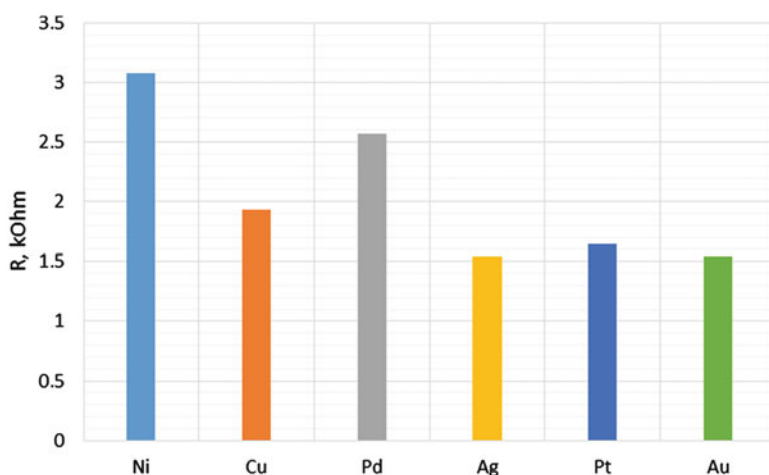


Fig. 4.29 Resistances of ML GNR(zigzag)–Me *end-type* interconnects. ML GNR–metal interconnect, width – 125 nm, 10 layers

4.3.8 Frequency Properties of CNT–Me and GNR–Me Interconnects

Figures 4.33 and 4.34 show parametric simulations of SWCNT (zigzag)–Au interconnect impedances Z via chiralities and curvatures. These results correlate with calculations in the framework of semiclassical approach of Maksimenko et al.

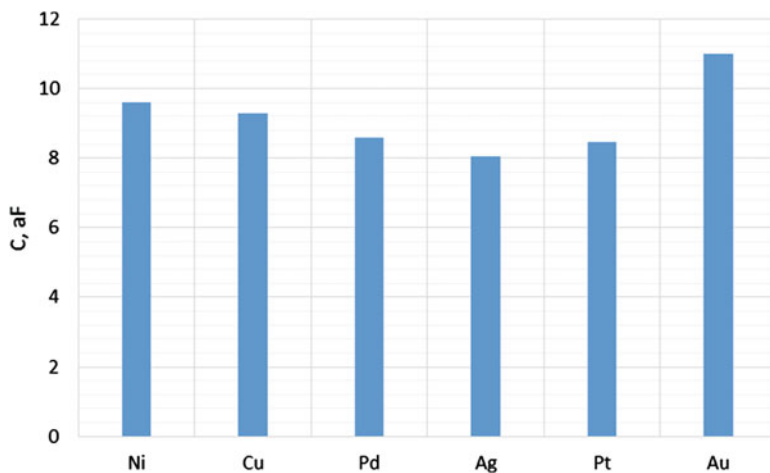


Fig. 4.30 Capacitances of SL GNR (*zigzag*)–Me *end-type* interconnects. SL GNR–metal interconnect, width – 125 nm

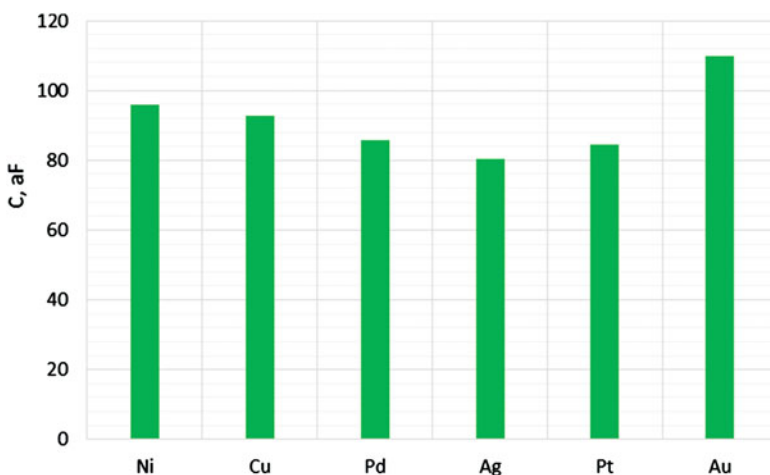


Fig. 4.31 Capacitances of ML GNR (*zigzag*)–Me *end-type* interconnects. ML GNR–metal interconnect, width – 125 nm, 10 layers

[21, 22], where the GHz–THz range has demonstrated essential changes of interconnect resistances.

Our calculations (see Fig. 4.35) have been also carried out for Au(100) and MWCNT(*zigzag*) with external diameter $d = 20$ nm and are presented in Fig. 4.25. Evaluations of C–Au potential barrier gave for *zigzag* SWCNT–Au $V = 10.2297$ eV and the corresponding capacitance $C_b \approx 11.45$ aF. Using the evaluation of local single bond resistance (see Sect. 4.3.4):

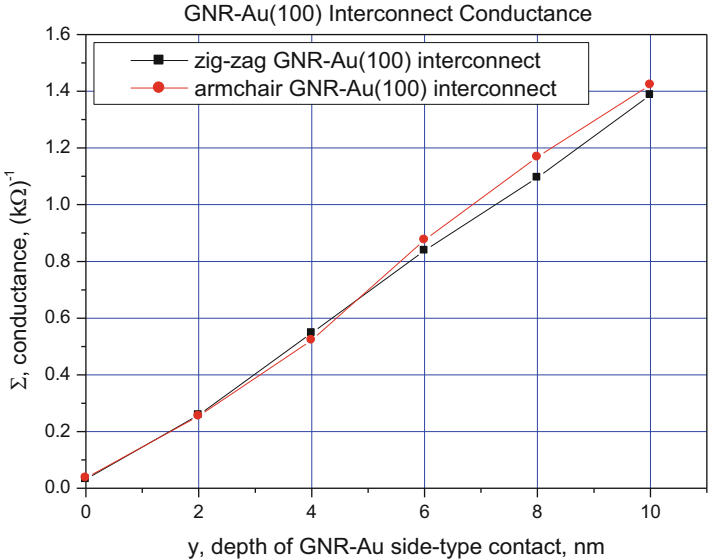


Fig. 4.32 Conductance of GNR–Au interconnect (*side-type* contact) via the depth ‘y’-parameter of contact overlapping

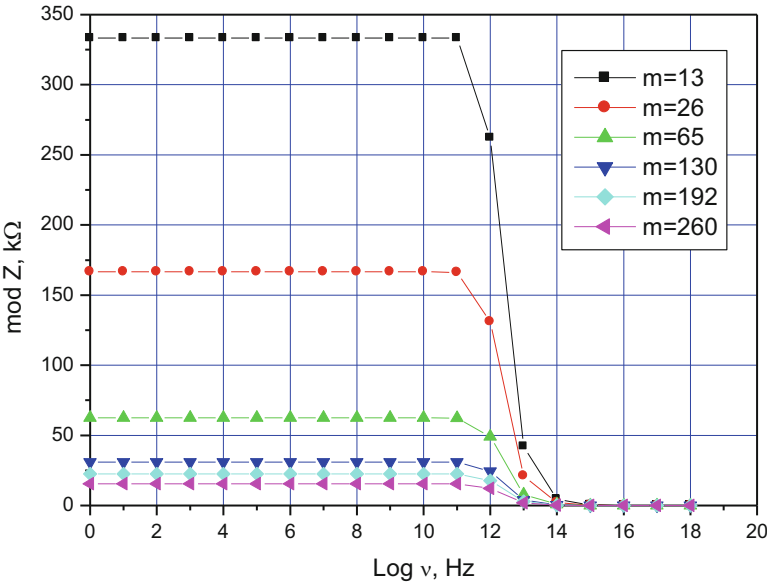


Fig. 4.33 SWCNT (*zigzag*)–Au(100) interconnect impedances via the frequency for various chiralities

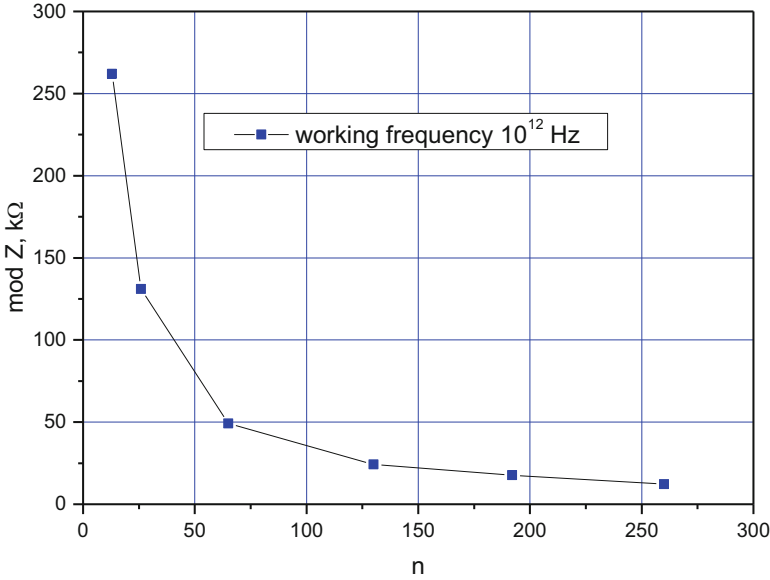


Fig. 4.34 SWCNT (zigzag)–Au(100) interconnect impedance via the curvature parameter (chirality index) n

$$R_b \approx 4000 \text{ k}\Omega, \quad \frac{1}{Z_{\text{SINGLE}}} = \frac{N_b}{R_b} + i\omega N_b C_b, \quad \frac{1}{Z_{\text{MULT}}} = \sum_{i=1}^N \left(\frac{N_{b,i}}{R_{b,i}} + i\omega N_{b,i} C_{b,i} \right),$$

$$|Z_{\text{SINGLE}}| = \frac{1}{\sqrt{\left(\frac{N_b}{R_b}\right)^2 + (N_b C_b)^2 \omega^2}} = \frac{1}{\sqrt{\left(\frac{N_b}{R_b}\right)^2 + (2\pi N_b C_b)^2 \nu^2}},$$

where ω is the cyclic frequency, N_b is the number of effective bonds, $N_{b,i}$ is the number of effective bonds in particular CNT in the MWCNT tested morphology and N is the number of CNTs in MWCNT.

4.3.9 Concluding Remarks

Using the *effective bonds* model, we have predicted the resistivity of interconnects between a metal substrate and SW or MWCNTs (SL GNR or ML GNR). There also exists a qualitative compatibility of results obtained for CNT–Me junctions using both approaches considered in this research: (1) Ab initio *liquid metal* model and (2) semiempirical *effective bonds* model based on the Landauer relationship. At the same time, the latter results are quantitatively comparable with those measured experimentally, i.e. within the range of several up to 50 kΩm.

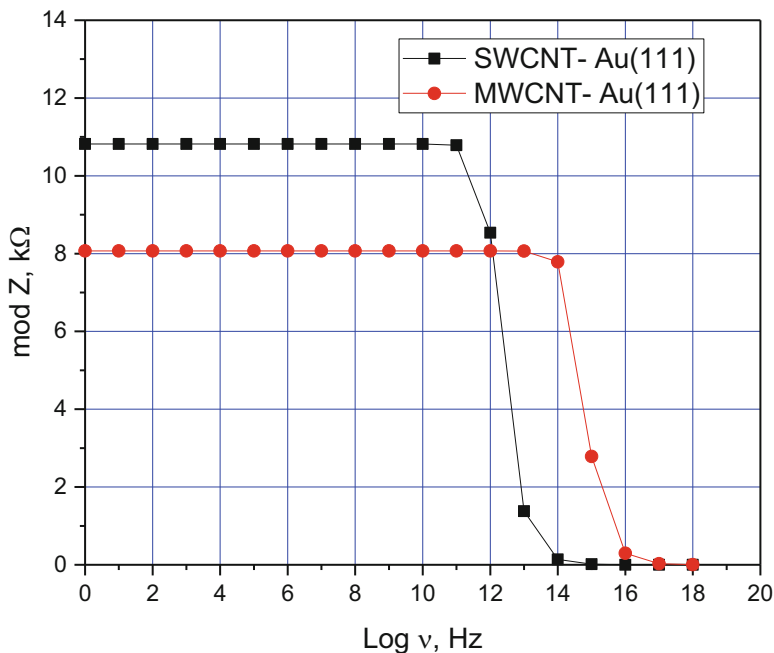


Fig. 4.35 Interconnect impedances via the frequency for various for SWCNT–Au and MWCNT–Au: comparison connected with critical impedance changes

We have also developed the model of inter-shell interaction for MWCNTs, which allows estimating the transparency coefficient as an indicator of possible ‘radial current’ losses.

We have emphasized that conductance and other current-voltaic parameters depend on the morphology of the nearest shells in MWCNTs and ML GNRs, which leads to complications for technology and production of nanodevices with stable electric characteristics.

We are able now to create a database of CNT–metal and GNR–metal junction combinations taking into account a set of parameters, namely, the angle of chirality, the CNT diameter, the number of walls or layers, the type of metal substrate (Me) and the orientation of metal substrate (e.g. (100), (111) or (110)). Thus, we are able to forecast interconnect properties for various SW, MWCNT and SL and ML GNR configurations.

Potential nanosensor devices based on CNTs, GNRs and their interconnects are absolutely feasible and can be very effective for external influences of different nature. They can change the electron transport regime and promote the current losses. At the same time, the interconnect interfaces can also be sensitive to chemical adsorbents, electrical and magnetic fields, changing the properties of interconnect potential barrier and efficiency of conducting channels. All these mechanisms of nanosensing are possible to simulate in the framework of the proposed models.

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