Ab initio model of carbon nanotubes growth on nano-structured Ni catalyst in a nanoporous Al_2O_3 membrane and resistance calculations for their junctions with various metal substrates

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***Abstract*— We consider the carbon nanotube growth in nanoporous alumina membranes comparing the results of ab initio simulations performed on 2D periodic models of C/Ni(111) and C/θ-Al2O3(010) nanostructures. Our results predict a quite effective and reproducible growth of carbon nanotubes upon the nickel nanostructured substrate. In absence of catalyst nanoparticles upon the bottom of the nanopores inside alumina membrane, the carbon structures could grow from the walls towards the centers of nanopores, yielding either carbon nanoscrolls or rather thick amorphous (soot-like) microtubes. We also consider the junctions of carbon nanotubes with contacting metallic elements of a nanocircuit, carrying out numerical simulations on the contacts resistance, using multiple scattering theory and the effective media cluster approach. Calculations for different multiwalled nanotube-metal contacts yield quantitatively realistic results, from several to hundreds kOhm, depending on nanotube chirality, diameter and thickness. As an indicator of possible 'radial current' losses we also report on the simulation of the multiwalled nanotube inter-wall transparency coefficient.**

I. CNT GROWTH IN NANOPOROUS ALUMINA MODEL

Due to their unique properties, carbon nanotubes (CNTs) have become an important constituent of future generation nanoelectronics. Progress in this field is still hindered by the inability to reproduce a growth of carbon CNTs with predetermined chirality indices (and thus electronic properties) since contemporary methods of nanotube synthesis yield a mixture of metallic and semiconducting nanotubes with varying band gaps. The chemical vapor deposition (CVD) growth of CNTs above metallic catalyst particles positioned inside an alumina membrane (at the bottom of its semi-closed nanopores) is believed to be the most promising approach for gaining a control over the geometry and the electronic properties of nanotubes [1]. Moreover, the CVD growth of nanotubes can be achieved at low temperature, another important requirement for application of CNTs in nanoelectronics. The structure of interconnect between the nanoparticle of metallic catalyst and the CNT is important for understanding both the electronic transport through nanotube and the mechanism of its growth. Decomposition of gas-phase carbon-hydrogen precursors (C_nH_m) on the catalyst surface is the first step for the CVD growth of CNTs. This initial step is followed by two important processes: (*i*) the diffusion of carbon on the particle surface or across its interior (a rate-determining step) and (*ii*) the nucleation of the graphitic fragment as followed by further incorporation of carbon into the growing nanotube which determines a CNT chirality [3]. Depending on the size and the structure of such a metallic particle, either well separated SW nanotubes and their bundles (containing up to several hundreds of the closely-packed nanotubes of different chiralities) or MW NTs, which shells also present various chiralities, could be synthesized. The microscopic images of CNTs growing from the catalytic nanoparticles [4] help to clarify how the atomistic models of interconnects can be drawn. There were performed so far a few theoretical (mainly, first principles) simulations, only of a single SW CNT growth upon metal nanocluster (Me = Ag, Au, Co, Cu, Fe, Ni, Pd, Pt) where the most likely armchair- (*m*,*m*) and zigzag-type (*n*,0) chiralities were considered [5-8].

Another form of 1D-periodic nanostructure named by carbon nanoscroll (CNS) can be formed from a graphene sheet by its twisting, thus leading to a spiral configuration. CNSs were synthesized after sonication, to assist exfoliation and spiral wrapping of the graphite sheets [9]. Visually, CNSs are similar to MW CNTs showing similar interlayer distance of 3.4-3.6 Å. It is impossible to distinguish between the two structures based on the electron micrographs alone [10]. Unlike MW CNT, nanoscroll keeps the same chirality along the whole wrapped surface. However, the HRTEM study indicates the coexistence of NS and MW segments within the same C-tubular structure [11]. In this study, we have compared the results of *ab initio* simulations performed on 2D periodic models of C/Ni(111) and C/θ-Al_2O_3(010) nanostructures, which can describe peculiarities of the initial stage of growth for the SW CNT bundle upon the catalyst particle. The only limitation in this model is that the chiralities of nanotubes in the bundle are equivalent. Models of 2D supercells of the corresponding substrate are discussed. Appearance of the adsorbed carbon atoms follows from the dissociation of CVD hydrocarbon molecules, *e.g.*, CH_4: $(CH_4)_{ads} \rightarrow (CH)_{ads} + 3H_{ads}$ and $(CH)_{ads} \rightarrow C_{ads} + H_{ads.}$ Association of the adsorbed carbon atoms upon the catalyst surface precedes further swelling of the $(C_n)_{ads}$ islands after appearance of pentagonal defects within a honeycomb sheet [12] which is a more probable upon the catalyst surface containing either defects or nanoclusters (as in the case of the nanostructured substrate). The consequent growth of the capped CNTs is more effective upon the nanostructured Ni than a flat substrate (*cfr.* values of CNT adhesion energy *per* boundary C atom for chiralities of armchair-type, 4.01 *vs*. 2.51 eV, and zigzag-type, 4.61 *vs*. 2.14 eV, respectively). The electronic charge transfer from the Ni catalyst towards the CNTs has been calculated for both chiralities (>1 *e per* C atom).

Our calculations have been performed using the gradient corrected (GGA) exchange-correlation functional of Perdew, Burke and Ernzerhof (PBE) [13] with spin-polarization as implemented into the *CRYSTAL* computer code [14]. Previously, we successfully applied a similar computational formalism for simulation of: (*i*) oxygen interaction with the Al(111), Al(001) and stepped Al(111) substrates [15], (*ii*) silver adhesion upon the α-Al_2O_3(0001) surface [16] as well as (*iii*) SW nanotubes of AlN [17] and BN [18]. Our results predict a quite effective and reproducible growth of carbon nanotubes upon the nickel nanostructured substrate. In absence of catalyst nanoparticles upon the bottom of the nanopores inside alumina membrane the carbon structures could grow from the walls towards the centers of nanopores: either carbon nanoscrolls or rather thick amorphous (soot-like) microtubes. At the bottom level of the multiscale modeling, *ab initio* methods can be used for determining the electronic structure of the assumed carbon-metal nanocomposites. Moreover, the obtained results can be employed in the construction of single-particle Hamiltonian used in the analytical tight-binding calculations of the conducting channels in the Me/MW-CNT interconnects, as well as in further MD and KMC simulations.

II. CNT-METAL JUNCTION RESISTANCE RESULTS

Next, basic attention is paid to the CNTs contacts with other conducting elements of a nanocircuit. In this part of our study, simulations of conductivity and resistivity are performed using the multiple scattering theory and effective media cluster approach. The main problems at the current stage of researches on CNT interconnect resistance appear due to the influence of chirality effects in interconnects of SW and MW CNT with the fitting metals (Me = Ni, Cu, Ag, Pd, Pt, Au) for predefined CNT geometry. The main task of this study is the implementation of advanced ab initio simulation models for construction of nanocircuits containing CNTs and their junctions with metallic contacts. Both the local and integral CNT properties have been simulated using prototype NT models such as a dispersion law, the electronic density of states (EDOS), the conductivity, resistivity, effective masses, etc.

The scattering theory approach allows us to calculate both the electronic structure and elastic properties of condensed matter considered as the static phenomena simultaneously with the dynamical phenomena of the electron transport. A computational procedure developed for these calculations [19] is based on construction of the cluster potentials and evaluation of the S-and T-matrices for scattering and transfer, respectively. Certain approximations are necessary to obtain reliable results. For instance, the CPA (coherent-potential approach [20]) is considered as an effective-medium-approximation (EMA). The specific conductivity (σ) could be evaluated through the Kubo-Greenwood formalism [19,20] or, in simple cases, using the Drude-type formula. The specific resistivity (ρ) could be described through participations of charge carriers in transport according to various mechanisms based on the scattering centers, namely, atoms of clusters, phonons, charge defects, structural defects, *etc.*, including the pure elastic way, called as ballistic. The temperature and frequency properties can be also described and estimated using the formalism of scattering theory.

The first step of CPA-EMA modeling is the construction of potentials, both atomic and crystalline which uses the special well-tested analytical procedures based the Gaspar-like potentials and X_α and $X_{\alpha\beta}$ presentations for the electronic exchange and correlation in form of the electronic density expansions [19]. Then, to obtain the electronic structure, the calculations on scattering properties are necessary, generally, in the form of S- and T-matrices. The electronic structure calculations begin with the definition of the initial atomic structure to produce a medium for solution of the scattering problem for a trial electronic wave [19]. As the zero approach in the modeling procedure, one postulates the atomic structure on the level of short- and medium-range orders. Further calculations on the density of the corresponding electronic states (DOS) can be done using the variation principles.

There exist a few algorithms both to estimate the conductivity in static and frequency regimes as well as to take

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 for the interpretation of electrical properties of CNT and their systems.

CPA-EMA model of the CNT-Ni nanointerconnect [21] is developed in the current study. Within the formalism of electronic transport it consists of two regions supporting two different electron transport mechanisms: ballistic (elastic) and collisional (non-elastic):

Mechanism of the ballistic conductivity as a result of the multiple scattering (valid for CNT and metal substrate). We assume that the conducting nanotubes are not so long and the electrons are not scattered too much by any defect (imperfection) of this nanomaterial. The effect of the charge accumulation is neglected here as well. This situation is similar to an ideal billiard with moving elastic balls-electrons, according to the Landauer model [22].

(b) Non-elastic mechanism. Using the simulation models, presented earlier [19,21], we consider a resistance model for the metal interconnect with single- and multi-wall (SW and MW) CNTs based on evaluation of the interface potential barriers and implementation of Landauer's formula. All resistance calculations have been performed taking into account that not all the electrons participate in a conduction process with the Fermi velocity v_F. For this aim, we must take into account the *thermally activated electrons*. The reason for determination of *thermally activated electrons* is caused by the scattering mechanism, which is changing in the space of CNT-Metal interconnect.

I. SW NT simulations The 'effective bonds' model means that the conductivity of CNT-metal interconnect is proportional to the number of *direct* chemical bonds between CNT and metal, which depend on the CNT chirality and metal substrate atomic configuration. Thus, we can evaluate the Landauer's multiplier for conductance calculations. We have also proposed a parameter φ (chirality angle) for the identification of nanotube chirality. Our results show the effect of the nanotube diameter and chirality on CNT-Ni interconnect resistivity. It is clear that the larger is the CNT diameter, the larger the number of direct junction bonds and the total conductance (*i.e.*, the resistance is smaller). A similar effect is observed for varying chirality: the number of direct bonds is higher for armchair and zigzag CNT chiralities.

We also compared the resistance for the interconnects of the same SW CNT with various metal substrates (Ag, Au, Cu, Ni, Pd and Pt). Although nickel is a good catalyst for CNT growth, resistance of its interconnect with nanotube has been found to be noticeably higher as compared to that for silver, gold and platinum substrates.

II. MW NT simulations Using the simulation models presented earlier [19,21] we have developed a model of multi-wall CNT-Me junction resistance based on the interface potential barriers evaluation and Landauer's formalism described above. Using the Landauer's formula for the conductivity , we have estimated the effective resistance of MW CNT-Me junctions, taking into account only thermally activated electrons. Our calculations allow for a comparison of resistance values of junctions between the considered MW CNT and the same metal substrates as presented above in the case of SW CNTs. We can conclude that for the interconnects of metals with both SW and MW CNTs, the smaller resistance is again observed for Ag, Au and Pt. Obviously, resistance of the metal interconnect with MW CNT is several times smaller than that with SW CNT since the number of direct junction bonds is substantially larger in the former case.

III. Evaluation of current losses between the adjacent shells in MW CNT Using the model of interwall potential in MW CNT we also evaluate the coefficient of transparency which determines the possible 'radial current' losses. Transparency *T per* one C-C bond along the interwall distance determines the radial current losses. For example, if the larger shell possesses the zigzag chirality whereas chirality of the smaller one is armchair while distance between them is a = 13.54-12.88 = 0.66 nm, the radial current loss factor can be estimated as $T = 3.469*10^{-6}$ *per* one C-C bond. Using the model of *'effective bonds'* developed in current study in the framework of CPA-EMA formalism based on scattering theory and Landauer's approach, we can predict the resistivity properties for both SW and MW CNT-Me interconnects. Resistance of the latter for the same external nanotube diameter and metal substrate is substantially smaller, *i.e.*, the effectiveness of the multiwall nanotubes for the CNT interconnects is noticeably higher. We have also developed the model of interwall interaction in MW CNT as well as estimated the transparency coefficient as indicator of possible 'radial current' losses.

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