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Interaction between carbon nanotubes and metals: Electronic properties, stability, and sensing

F. Fuchs [a,*], A. Zienert [a], C. Wagner [a], J. Schuster [b], S.E. Schulz [a,b]

[a] Center for Microtechnologies, Reichenhainer Str. 70, Chemnitz D-09126, Germany
[b] Fraunhofer Institute for Electronic Nano Systems, Technologie-Campus 3, Chemnitz D-09126, Germany

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ABSTRACT

The interactions between carbon nanotubes (CNTs) and metal adatoms as well as metal contacts are studied by means of ab initio electronic structure calculations. We show that the electronic properties of a semiconducting (8,4) CNT can be modified by small amounts of Pd adatoms. Such a decoration conserves the piezoelectric properties of the CNT. Besides the electronic influence, the stability of a single adatom, which is of big importance for future technology applications, is investigated as well. We find only small energy barriers for the diffusion of a Pd adatom on the CNT surface. Thus, single Pd adatoms will be mobile at room temperature. Finally we present results for the interaction between a metallic (6,0) CNT and metal surfaces. Binding energies and distances for Al, Cu, Pd, Ag, Pt, and Au are discussed and compared, showing remarkable agreement between the interaction of single metal atoms and metal surfaces with CNTs.

1. Introduction

The ongoing miniaturization of electronic devices poses increasing challenges in the field of material science. Some of these demands can be only fulfilled by the introduction of new materials or nanostructures.

Very promising candidates for various applications in micro- and nanoelectronics are carbon nanotubes (CNTs), which offer outstanding electrical [1] and mechanical [2,3] properties. Depending on their atomistic structure (chirality), there exists a large variety of CNTs with different electronic properties. They can have semiconducting properties, showing a band gap, which is for example useful to produce CNT-based transistors. Metallic CNTs without a band gap can be used in interconnect systems. There are also CNTs with a very tiny band gap, typically below 0.1 eV [4,5]. They have almost metallic properties and are called semimetallic CNTs. While metallic CNTs do not show any change of the band gap due to uniaxial deformation, the band gap of semiconducting and semimetallic CNTs is sensitive to such a deformation [3,6–8]. These types of CNTs are therefore candidates for mechanical sensor devices such as acceleration sensors.

Even though the general physics of CNTs is widely understood, there are still many open questions which are important for technology and which need to be solved on the way towards interconnect and sensor applications of CNTs. One of them is the interaction of the CNTs with metals. Contacts between CNTs and metals are of great importance because metals are used as electrodes in CNT-based circuits. Hereby, a variety of metals with different properties can be used. Finding the most suitable material and understanding the interactions is very important for future devices. In this work, we will present a comparative study of the binding energies between CNTs and the metals Al, Cu, Pd, Pt, Ag, and, Au.

Another important aspect of the interaction between CNTs and metals is the fact, that the decoration of CNTs with metals can be used to adjust the CNT properties [9,10]. This is interesting as for many applications CNTs with similar properties are required, but the separation of CNTs with desired properties is challenging and expensive. A metal decoration of CNTs can simply be done using e.g. electron beam physical vapor deposition [11]. Thus, a promising idea is to take CNTs which are easy to separate (e.g. a mixture of different types of semiconducting CNTs) and to adjust their properties depending on the application. CNTs could be metalized in order to use them for interconnect systems. This was already accomplished during our previous studies using small amounts of Co adatoms [10]. A reduction of the band gap is needed for the application of CNTs in sensor devices. For sensors, CNTs with small band gaps are required to obtain sensor currents which are well measurable. Simulations are essential to identify the most suitable

* Corresponding author.
E-mail address: florian.fuchs@s2009.tu-chemnitz.de (F. Fuchs).

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metals for the various desired applications and to judge the stability of the binding with the nanotubes. It was shown that particles inside CNTs tend to move along the CNT when an external voltage is applied [12–14]. A similar behavior is expected for particles or adatoms on a CNT surface. This could strongly reduce the lifetime of devices as, in the worst case, the atoms would simply migrate to one of the contacts. Hence, it is important to study the stability of adsorbed metal on the CNT surface and at the contacts.

2. Model system

2.1. Metal adatoms on the CNT surface

For studying metal atoms on a CNT surface we use the semiconducting (8,4) CNT, which has 112 carbon atoms per unit cell and a diameter of about 8.31 Å. We choose this specific tube because it has a small band gap of about 0.74 eV. Furthermore, the diameter of the tube is not unrealistically small, which minimizes possible curvature effects. Nevertheless, it has a manageable system size for complex ab initio studies. All calculations are performed for a single CNT unit cell. We set periodic boundary conditions in all three spatial dimensions and therefore investigate a CNT of infinite length with a selected number of adatoms per unit cell. The lateral extent of the box-shaped unit cell is set to 24.58 Å, so that interactions between periodic neighbors of CNTs are negligible.

The metal atom is added on the CNT surface above the bond of two neighboring carbon atoms, which is the most stable position according to [17]. It will be shown later, that there are only small differences compared to other positions and how an energetically even more favorable position is found. The differences on the electronic properties between these energetically very similar positions are below 0.04 eV and are therefore negligible for judging the electronic properties. For simplicity a uniform and regular decoration of the metal atoms on top of the CNT is considered in the present study. This leads to a chainlike orientation of the adatoms (only one exception will be discussed later, see Section 4.1 for details). Three unit cells of such a setup are shown in Fig. 1a.

Our study is focused on Pd atoms as decoration metal because it is already used in technology to create low-Ohmic contacts [15] and shows excellent wetting properties on CNTs [16]. Finally, it is a well suited candidate for calculations due to the lack of spin

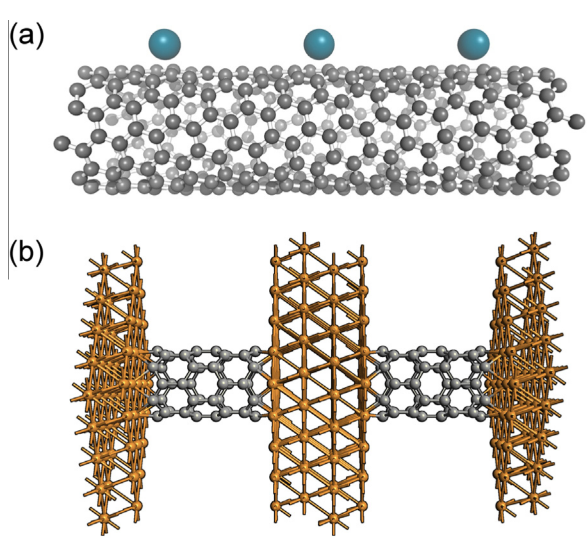

Fig. 1. (a) Model of a Pd decorated (8,4) CNT. Three unit cells are shown with one Pd adatom per unit cell. The system is periodic in all three dimensions, but the distance to neighbored CNTs is huge. (b) Model of a (6,0) CNT between flat Cu (1 1 1) surfaces, two unit cells are shown. The system is periodic in all three dimensions.

effects – unlike many other metals – when added on CNT surfaces [17]. Spin unpolarized calculations, which are computationally cheaper, are therefore sufficient to get physically correct results.

2.2. CNT-metal contact

The model system used for studying CNT metal contacts consists of a metallic (6,0) CNT which is sandwiched between two flat metal (1 1 1) surfaces. So called end contacts are studied, meaning that the CNT is not embedded into the metal but oriented perpendicular to the metal surface in a way that the tube axis is centered on a surface metal atom. There is a finite contact distance between the CNT and the metal which is subject to variation. The system is periodic in all directions. Two unit cells of such a system are depicted in Fig. 1b for the case of Cu contacts. The six fcc metals Al, Cu, Pd, Pt, Ag, and, Au are studied, which are all non-ferromagnetic.

3. Simulation details

For electronic structure simulations of CNTs a vast variety of different simulation approaches are possible [20]. Recently, we published comparative studies of electron transport in CNTs using density functional theory (DFT), extended Hückel theory, and tight-binding [18,19].

As the number of atoms per unit cell is relatively small for the topic discussed here, DFT is a well-suited method for our calculations. The simulations of the metal decoration are performed using the SIESTA package [21], which is based on local atomic orbitals and pseudopotentials. A double zeta polarized basis set was used. The number of k-points along the tube was set to 20 and the mesh cutoff for solving the Poisson equation was set to 100 Ha.

To verify our results, we use the plane wave based DFT code Quantum Espresso (QE) [22] with ultrasoft pseudopotentials. The kinetic energy cutoff of the wavefunctions and for charge density/potential was set to 15 Ha and 120 Ha respectively. Due to the different basis, this method is suitable to verify our results.

While the structures are optimized by SIESTA using the conjugate gradient (CG) method with maximum forces of 0.02 eV/Å, the Quantum Espresso optimizations are based on the Broyden–Fletcher–Goldfarb–Shanno algorithm with maximum forces of 0.01 eV/Å. The presented results on metal adatom decoration, unless otherwise indicated, are calculated with SIESTA.

For the results corresponding to the CNT metal contacts, the software package Atomistix ToolKit [23,24] was used, which is as SIESTA based on local atomic orbitals and pseudopotentials. In this case, the number of k-points and the mesh cutoff was set to 1 (since the unit cell is large) in each spatial region and 75 Ha respectively.

All calculations used for this work are performed using the GGA functional of Perdew, Burke, and Ernzerhof [25].

4. Results and discussion

4.1. Properties of Pd decorated CNTs

To judge the electronic properties of the system, we calculate the band structure (Fig. 2) for all configurations of Pd adatoms and extract the band gap E_{gap}. The band gap of a pristine (8,4) CNT is at about 0.74 eV. This value is in good agreement with comparable DFT calculations [26], but smaller than experimental results (where values above 1.1 eV were found [27,28]). However, as the influence of the metal on the electronic properties of the tube is the main focus of this work, the change of the band gap