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The effect of carbon nanotube chirality on the spiral flow of copper atoms in their cores

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HIGHLIGHTS

- We model the transportation of copper atoms in armchair and zigzag CNT channels.
- The spiral flow of copper atoms occurs in a semiconductor–semiconductor CNT.
- The compact copper mass is predicted to occur at 673 K with a 4 V bias voltage.

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ABSTRACT

The effect of carbon nanotube (CNT) chirality on the flow of copper atoms along its core has been investigated using molecular dynamics simulations. The investigation is conducted using CNTs of different chirality, and different flow conditions such as temperatures, bias voltages and the initial positions of the copper atoms. The results show that the atoms flow in a spiral fashion along the CNT channels. The effect is most evident in the CNT channel with zigzag CNTs. The movement of the copper atoms is more erratic when the temperature is increased at a low biased voltage, regardless of the types of channel used. The initial positions of the copper atoms affect the way they converge as they move downstream along the channel. A bias voltage of 4 V favours the initiation of a spiral flow, especially when the position of the copper atoms is far from the central axis of the channel.

1. Introduction

Applications of carbon nanotubes (CNTs) in various fields [1–3] have shown much prospect in recent years. The filling of various materials in CNTs, in particular, has been gaining much attention [4–6]. Through various experiments and simulations [7,8], the studies on the filling of metal atoms in CNTs have been carried out extensively in order to demonstrate the method and outcome of the filling processes. Zhang and Wang have filled CNTs with copper atoms using a method based on a microwave plasma-assisted chemical vapour deposition system [9], whereas Schebarchov and Hendy have shown the capillary effect of palladium atoms in CNTs using molecular dynamics (MD) simulations [10,11]. Another important study, which shows the mechanical and structural properties of metal nanowires, CNTs and metal-filled CNTs, is conducted by Soldano and Mariscal on the iron-filled CNTs using simulations [12].

The well defined morphologies, thickness and other interesting characteristics of the single-walled carbon nanotube (SWCNT) have made this material an interesting structure for studying fillings of metal atoms in its interior. The chirality (mirror symmetric of two CNT tubules) and diameter of the CNTs can be determined by the chiral vector, which suggests either the armchair or the zigzag CNT tubules [13]. The chiral vector is also used to determine whether the electronic structure of a CNT is metallic or semiconducting [14]. Although the SWCNT is generally defined as a straight channel, various defects of the SWCNT have been reported on several occasions [15,16]. One of these defects exists in the form of pentagon–heptagon pairs in the network of the CNT [17]. The joining of nanotubes with different diameters, for example, can result in the formation of the pentagon–heptagon pair defects. The joining of CNTs with dissimilar diameters can be achieved experimentally, as demonstrated by Jin et al. [18]. The combination of two dissimilar CNTs results in a junction that acts as a nozzle or a diffuser, depending on the direction of the flow in the particular channel [19]. The role of a junction in a CNT channel is thus crucial in affecting the flow of the materials along a CNT channel [20].

As part of the studies of filled CNTs, the delivery of atoms along CNTs is equally as important as the type of filled materials chosen.

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One such example is the study of the mass delivery driven by the bend kink in SWCNTs [21]. Besides that, atoms can also be transported along CNTs using electromigration processes [22]. The transport of metal atoms using electromigration processes has also been observed in an experiment [23] and presented in MD simulations [24,25]. By manipulating the electric field along the nanotubes, an electromigration force is created to drive metal atoms along CNTs. The electromigration is dependent on diffusion and a driving force. The metal atoms which have filled CNTs will migrate in a direction opposing the electric field, i.e., in the direction of the electron flow.

The mass transport of various metals along CNTs has been achieved by Regan et al. using a voltage gradient [26]. This experiment demonstrated the mechanism of an atomic-scale mass transport using CNTs as a delivery system. It is possible that the mass distribution in the experiment is controlled, since the direction and the rate of the mass transport are affected by the external electrical drive. In nanorobotic spot welding, the mass delivery of copper in CNTs is achieved through the application of electromigration [27]. Dong et al. have demonstrated the flow of copper through CNTs using the nanorobotic manipulation. The bias voltage required for the transportation of copper in these nanotubes is between 1.5 and 2.5 V, with CNT outer diameters ranging from 40 to 80 nm. The copper in CNTs is melted due to the effect of the Joule heating on the metal.

The transport mechanism of metal atoms in CNT channels on a nanometre scale has received considerable attention. MD simulation by Hwang et al. has demonstrated the filling and flow process of copper atoms in CNT channels [28], whereas the effect of the CNT junction size on the flow of copper has been addressed by Lim and Zhong [29]. However, the flow processes of the metal atoms in CNTs of different chirality are yet to be discovered. Although CNTs are looked upon as delivery systems for metal atoms, the processes for the formation of nanowires in which CNTs are used as templates should not be neglected either. The difference in the chirality of the CNTs affects the distribution of carbon atoms throughout the wall of the CNT channels, especially at the CNT junction. Such a variation may indirectly alter the flow phenomenon of the encapsulated metal atoms. The flow processes of the metal mass along the core of CNT channels due to different CNT chirality are thus important for further investigation. In this study, we focus on the flow of copper atoms along CNTs of different chirality, and the various factors affecting the configuration of copper atoms along the channels such as the temperature, the bias voltage and the initial position of the copper atoms.

2. Computational methodology

The simulations of copper flow are performed in this study using copper atoms as the transported particles in different CNT channels. The MD code is written using MATLAB [30]. In the simulations, the copper atoms are confined within two CNT channels that are modelled as nonpolarized, single-walled, armchair and zigzag CNT channels. The CNT channels are generated using CoNTub [31]. Each of the CNT channel consists of one CNT junction, joined by two nanotubes of different diameters. For the purpose of comparing the effect of the CNT chirality on the flow of copper atoms, a (5,5)–(4,4) CNT channel with a junction joined by two armchair CNTs, a (8,0)–(7,0) and a (9,0)–(6,0) CNT channels with junctions joined by two zigzag CNTs are constructed. The (5,5), (4,4), (9,0) and the (6,0) CNTs are known to be metallic, whereas the (8,0) and the (7,0) CNTs are known to be semiconductors [13]. The CNT channels are chosen such that the differences in the diameters between the different channels are as minimal as possible. This ensures that the study is not affected by the geometrical differences between the two CNT channels. The (5,5)–(4,4) CNT channel has 828 carbon atoms, with a diameter of 6.8 Å for the (5,5) nanotube and a diameter of 5.4 Å for the (4,4) nanotube. The (8,0)–(7,0) CNT channel has 795 carbon atoms, with a diameter of 6.3 Å for the (8,0) nanotube and a diameter of 5.5 Å for the (7,0) nanotube. The (9,0)–(6,0) CNT channel has 765 carbon atoms, with a diameter of 7.0 Å for the (9,0) nanotube and a diameter of 4.7 Å for the (6,0) nanotube. All of the CNT channels are approximately 112 Å in length, spanning the z coordinate between −53 and 59 Å. The CNT channels are fixed in space.

There are a total of 28 copper atoms in each of the CNT channels. The copper atoms are placed close to the wider opening of the channel end initially. Before the nonequilibrium MD simulations were performed, energy minimization and equilibrium MD runs had been made.

The copper atoms in the system are modelled using the embedded-atom method [32] with the cutoff distance between two atoms as $r_{\text{cut}} = 1.65a_0$ ($a_0 = 3.615$ Å). The total internal energy of a metal system of N atoms can be described as:

$$E_{\text{tot}} = \sum_{i}^{N} F_i(\varsigma_i) + \sum_{j(i\neq j)}^{N} \varphi(R_{ij}), \tag{1}$$

where R_{ij} is the separation distance between atoms i and j, $F_i(\varsigma_i)$ is the embedded function in the universal form as suggested by Banerjea and Smith [33], and $\varphi(R_{ij})$ is the two-body potential as an analytical form similar to the model function given by Rose et al. [34].

The force on the copper atom is derived from Equation (1) in order to evaluate the magnitude of the acceleration of the copper atom. The force on the copper atom can be expressed as follows [35,36]:

$$\xi_i = -\sum_{j=1\, j\neq i}^{N} \left[\frac{\mathrm{d}\varphi(R_{ij})}{\mathrm{d}R_{ij}} + \left(\frac{\mathrm{d}F_i}{\mathrm{d}\varsigma_i} + \frac{\mathrm{d}F_j}{\mathrm{d}\varsigma_j} \right) \left(\frac{\mathrm{d}\varsigma(R_{ij})}{\mathrm{d}R_{ij}} \right) \right] \frac{R_{ij}}{|R_{ij}|}, \tag{2}$$

where ξ_i represents the force on the ith copper atom, N is the total number of copper atoms in the system and j is the number of neighbouring copper atoms surrounding the ith copper atom. R_{ij} is the distance between the ith copper atom and the jth copper atom. $\mathrm{d}\varphi(R_{ij})/\mathrm{d}R_{ij}$ is the spatial gradient of the two-body potential between the ith copper atom and the jth copper atom with respect to the distance between them. The following two terms, $\mathrm{d}F_i/\mathrm{d}\varsigma_i$ and $\mathrm{d}F_j/\mathrm{d}\varsigma_j$, are the derivatives of the `embedding function' for the ith copper atom and jth copper atom respectively. $\varsigma(R_{ij})$ is the electron density provided to the embedded ith copper atom by its surrounding j copper atoms.

The interaction between copper and carbon can be expressed in the form [37],

$$E_{\text{Cu-C}}(r) = \sum_{i<j} \left[\frac{C_{12}(i,j)}{r_{ij}^{12}} - \frac{C_6(i,j)}{r_{ij}^{6}} \right], \tag{3}$$

where r is the distance between two atoms, $C_6 = 41.548$ (eV Å^6) and $C_{12} = 2989.105$ (eV Å^{12}). The simple pair potential is used to describe the interaction between copper and carbon in this study because simulation predictions due to this potential for copper and carbon atoms are supported by experimental findings [38,39]. The cutoff distance is set at 10 Å [40]. The driving force (F_{em}) for the copper atoms is induced due to the electromigration process. The equation is expressed as [41]:

$$F_{\text{em}} = (Z_{\text{d}} + Z_{\text{w}})eE = \left(Z_{\text{d}} + \frac{K_{\text{m}}}{\gamma(T)} \right) eE, \tag{4}$$