Structures of ultrathin copper nanowires encapsulated in carbon nanotubes

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We have investigated the structures of copper nanowires encapsulated in carbon nanotubes using a structural optimization process applied to the steepest descent method. The results showed that the stable morphology of the cylindrical ultrathin copper nanowires in carbon nanotubes is multishell packs consisting of coaxial cylindrical shells. As the diameter of carbon nanotubes increased, the encapsulated copper nanowires have the face-centered-cubic structure as the bulk. The circular rolling of a triangular network can explain the structures of ultrathin multishell copper nanowires encapsulated in carbon nanotubes.

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I. INTRODUCTION

Carbon nanotubes (CNT's) filled with various materials are of great interest in materials science and technology because of their interesting structures. CNT's filled with metals represent a fascinating new material and are the effective route to exploit one-dimensional nanocables with various uses. These CNT's covering metal nanowires have significant potential in data storage nanotechnology due to their size. In addition, the carbon shells provide an effective barrier against oxidation and consequently ensure a long-term stability of the metal core.[1–5] Various materials, such as metals or their compounds,[2–17] even fullerenes,[18] have been successfully used to fill CNT's employing different methods. Previous studies reported two kinds of methods for filling the CNT's. One is that CNT's are initially opened at the capped tube ends[2–7] and subsequently filled with molten materials through capillary action[2,4,6] or with metal oxides using wet chemical techniques.[5,7] The other is an *in situ* filling method. Metals or metal compounds can be filled into the CNT's by arc-discharge technique using a graphite anode impregnated with the filling material.[8–11] *In situ* filling of Fe, Co, or Cu can also be achieved in chemical vapor deposition systems[12–17] by pyrolysis of organometallic compounds.[12–14]

Although several groups have successfully obtained metal-filled CNT's or nanoparticles by catalytic method and several reaction models have been proposed, the structural properties of the encapsulated materials are still not very clear. Copper acts weakly as the catalyst for the growth of CNT's because carbon solubility in bulk copper is very small, making it difficult to form a stable carbide.[19] However, CNT's filled with copper have been prepared.[16,17] Therefore, the Cu nanowire structures encapsulated in CNT's should be investigated. Atomistic simulations have played important roles in scaling down to nanometer scales and can help in the elucidation of their properties and in the development of methods for their fabrications and applications. Computational materials sciences have also provided detailed microscopic information on the physical properties of several nanotubes. In this present work, we described a study of the structures of ultrathin Cu nanowires capsulated in CNT's using an atomistic simulation.

II. METHODS

For carbon-carbon interaction, a many-body empirical potential, the Tersoff-type potential,[20] was used. For carbon-copper interaction, a universal repulsive potential, the Molière potential function,[21] was used. Kong *et al.*[22] have shown that a weak ionic bonding is formed between the CNT and the Cu chain, resulting in a reduction of the charge at the contact region for the states near the Fermi lever and a further increase of the contact resistance. The binding energy and the optimal interatomic distance between copper and carbon are well known, about 0.1–0.144 eV/atom and 2.2–2.285 Å, respectively.[23,24] Yang *et al.*[25] recently obtained about 0.25 and 0.52 eV/atom binding energy for Au and Al chain adsorbed on the CNT. Therefore, the interaction between Al, Cu, Au metals, and CNT has a lower binding energy. Especially since the interaction between Cu metal and CNT has a very low binding energy, this makes it difficult to form a stable copper-carbide compound. Therefore, copper metal acts weakly as the catalyst for the growth of CNT's. Although the Molière potential is not the most suitable interatomic potential of Cu-C, because of the very weak binding energy between Cu and C, the results obtained from the Molière potential shows that it is reasonable in the results. The interaction between copper atoms is described by a well-fitted potential function of the second moment approximation of the tight binding (SMA-TB) scheme.[26] The SMA-TB-type potential function has been used in atomistic simulation studies of nanoclusters[27–31] and ultrathin nanowires.[32] This potential is in good agreement with other potentials and with the experiments for bulk[26] and low-dimensional systems.[33] The physical values for copper calculated by the SMA-TB scheme are in agreement with the other results.

In our study of the structures of ultrathin Cu nanowires encapsulated in CNT's, atomistic simulations were as follows: (1) We defined a nanotube with a diameter; then an atom was inserted into the bottom of the nanotube. (2) Another atom was inserted into the bottom of the nanotube, and the atomic configuration was relaxed using the steepest descent (SD) scheme. (3) After sufficient relaxation, another atom was inserted into the bottom of the nanotube, and the atomic configuration was again relaxed using the SD scheme. This simulation was repeated until the length of the

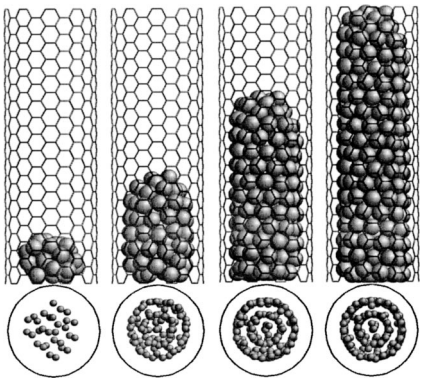

FIG. 1. Four snapshots for Cu nanowires growth in (10,10) CNT. From the left side, the numbers of the inserted Cu atoms are 30, 100, 200 and 307, respectively. In each case, side (top) and a top (bottom) views are showed.

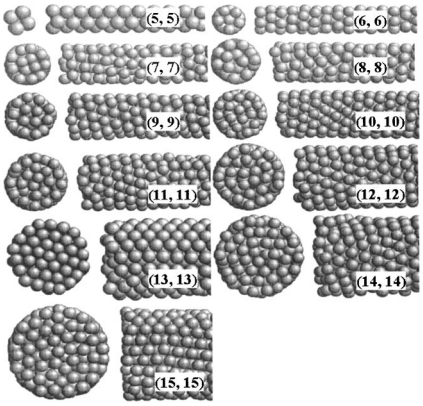

FIG. 2. Morphologies of ultrathin Cu nanowires encapsulated in CNT's. In each case, top (left) and a side (right) views are presented.

nanowire reached 40 Å. While the reflective boundary condition was applied to the bottom, as shown in Fig. 1, the free boundary condition was then applied to the other side. Although the SD method generally cannot guarantee that the global minimum is found, since the CNT acts as a cylindrical tube and guards the copper nanowires, the local minimized structures obtained from the SD method can be extended into the global minimized structures in the case of the ultrathin CNT's. This is obviously found in the results showing that Cu nanowires encapsulated in the ultrathin CNTs have ordered periodic structures. To confirm this, we performed the molecular dynamics (MD) simulations based on simulated annealing for some cases applied to the periodic boundary conditions. The MD simulations used the same MD methods as was used in our previous works.[34,35] The MD code used the velocity Verlet algorithm, a Gunsteren-Berendsen thermostat to keep constant temperature, a periodic boundary condition along the wire axis, and neighbor lists to improve computing performance. MD time step is 5×10^{-4} ps. The zigzag (n,n) CNT's with $n=5-15$ were investigated to encapsulate ultrathin Cu nanowires in CNT's.

III. RESULTS AND DISCUSSION

Figure 1 shows four snapshots for Cu nanowire growth in (10,10) CNT. From the left side, the numbers of the inserted Cu atoms are 30, 100, 200, and 307, respectively. As the Cu nanowire grows, the Cu nanowire is stabilized into a multishell structure with an atomic strand of the core, as shown in the bottom figures of Fig. 1. Figure 2 shows the structures of ultrathin Cu nanowires encapsulated in CNT's obtained from our simulations. In general, the stable structures of the ultrathin Cu nanowires encapsulated in CNT's are multishell packs composed of coaxial cylindrical shells. The copper nanowires in some cases have a single-atom chain at their center. Each shell is formed by rows of atoms wound helically upwards, side by side. The pitch of the helices for the outer and the inner shells are different. The lateral surface of each shell exhibits a near-triangular network. Such helical multishell structures have been theoretically predicted for Al, Pb,[36,37] Cu,[38] Au,[39–44] and Ti nanowires[32] and recently experimentally observed in Au (Refs. 45–48) and Pt (Ref. 49) nanowires. We performed the MD simulations based on the simulated annealing method for the Cu nanowires encapsulated in (5,5), (6,6), (10,10), and (13,13) CNT's. Since the melting temperatures of freestanding Cu nanowires or nanobridges are below 700 K in our previous work,[50,51] the quenching rate in the MD simulations is selected by 1 K/ps from 700 K to 10 K. The lowest energy structures obtained are the same with those obtained from the geometric optimization based on the SD method. The freestanding Cu nanowire on the same structure with the Cu nanowire encapsulated in (5,5) CNT was unstable and broken at the very low temperature in our previous MD simulations,[50,51] whereas the Cu nanowire encapsulated in (5,5) CNT maintained its structure below 520 K. This reason is that the wall of CNT guards the encapsulated Cu nanowire. The melting temperatures of freestanding Cu nanowires are very low, whereas those of CNT's are very high. Therefore, the wall of CNT increases the stability of Cu nanowires encapsulated in CNT. This result is also identical with the MD simulations of the other encapsulating nanowires. Thus more detailed work on thermal stability and properties will be presented and discussed in our future paper.

To characterize the multishell structures, Kondo and Takayanagi[47] introduced the notation n-n'-n''-n''' to describe a nanowire consisting of coaxial tubes with n, n', n'', n''' helical atom rows $(n>n'>n''>n''')$. Wang *et al.*[32] used this notation. Since the thinnest magic nanowire consists of a single tube and a central strand, Tosatti *et al.*[41] used the index (n,h) to denote a tube consisting of n closely packed strands forming a maximal angle ranging from 30° ($n=0$) to 0° ($h=n/2$) with respect to the tube axis. Although the index of Kondo and Takyanagi (KT index) is useful and easy to determine for multishell nanowire structures, the chirality information on nanowires cannot be characterized. The index of Tosatti *et al.* (T index) provides both chirality information and helical atom rows in the shells. In this work, we use those notations, the KT and the T indices, to denote cylindrical multishell nanowire structures.

For (n,n) CNT's below $n=12$, the ultrathin multishell structures of Cu nanowires are generally obtained, whereas

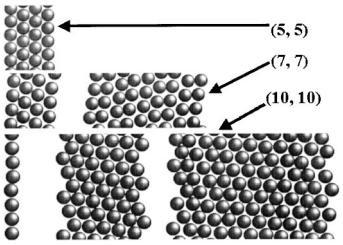

FIG. 3. Spreading sheets of three ultrathin Cu nanowires encapsulated (5,5), (7,7), and (10,10) CNTs.

for (n,n) CNT above $n=13$, the cross-sectional shapes of Cu nanowires are similar to the {111} facet of hexagonal-close-packed structures. These results mean that as the diameter of CNT decreases, the encapsulated Cu nanowires have the multishell structures. However, as the diameter of CNT increases, the encapsulated Cu nanowires have the face-centered-cubic (fcc) structure as the bulk. This result is in good agreement with the experiments observed for evidence of fcc lattices[16,17] and with the ultrathin Au nanowires optimized by a genetic algorithm.[39] Wang *et al.*[39] obtained the multishell. Au nanowires for small diameters but the fcc structural Au nanowires for the diameters above 30 Å.

Each nanowire has a {111}-like surface. Previous simulation works on nanowire elongation deformation showed that a rectangular {100} nanowire transforms into a cylindrical nanowire with a {111}-like surface by stretching.[52] In order to carry out a more detailed study of cylindrical multishell nanowire structures, we investigated the spreading sheets of nanowires. Figure 3 shows the spreading sheets of nanowires encapsulated in (5,5),(7,7), and (10,10) CNT's, which are generally composed of a triangular network. To investigate the spreading sheets, we explain the T index of the triangular network sheet as shown in Fig. 4. The tube unit cell is given by the orthogonal vector (n,h) and the wire axis vector (p,q), in which $p:q=(n-2h):(2n-h)$, and $h\leqslant n/2$. All other tubes, except $(n,0)$ and $(n,h/2)$, are chiral, and (n,h) and $(n,n-h)$ are symmetrical with one another. At a constant n value, the wire center-to-center radius is given by $d_0(n^2+h^2-nh)^{1/2}/2\pi$Å and decreases for increasing h, as

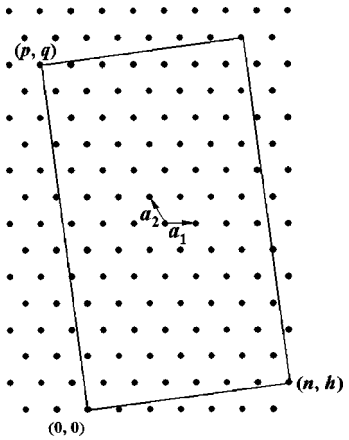

FIG. 4. Triangular network sheet. An (n,h) shell is made by cylindrically rolling a triangular lattice. (p,q) is the axis vector of the (n,h) shell. $p:q=(n-2h):(2n-h)$, and $h\leqslant n/2$.

the strands progressively align with the axis, where d_0 is the distance between the neighboring atoms in the triangular network sheet. The total number of atoms per shell is $N=2(n^2+h^2-nh)$, and the number in the central strand is q. In this paper, the central strand is denoted by (1,1). For example, nanowires denoted by the KT index 4 can be denoted by (4,0), (4,1), and (4,2) using the T index. Therefore, the nanowire structure indices of KT and T are shown in Table I. The KT indices for both (7,7) and (8,8) CNT's are a 9-4, whereas the T indices for (7,7) and (8,8) CNT's are (9,3)(4,2) and (9,1)(4,1), respectively. As mentioned above, at constant n value, the wire diameter is linearly proportional to $d_0(n^2+h^2-nh)^{1/2}/\pi$, and the chirality angle is given by $\tan^{-1}[\sqrt{3}h/(2n-1)]$. Table I also compares the radii obtained with the radii calculated. The calculated radii are in good agreement with the obtained radii with the different d_0. While d_0 of the more close-packed Cu nanowire in (7,7) CNT is 2.41 Å, d_0 of the less close-packed Cu nanowire in (10,10) CNT is 2.73 Å. The average d_0 is 2.609 Å. Due to the curvature effect, the average interatomic distance between Cu atoms is 2.591 Å, which is slightly higher than the equilibrium interatomic distance in the bulk, 2.56 Å, for the

TABLE I. The structure indices, radii, and d_0 of Cu nanowires encapsulated in CNTs obtained from our simulation. The KT index is the index of Kondo and Takyanagi (Ref. 47), and the T index is the index of Tosatti *et al.* (Ref. 41). Obtained radii of Cu nanowires are compared with the values calculated using the T index.

Nanotube (n,n)	Radius (Å)	Structure indices: KT index n-n'-n''	Structure indices: T index Orthogonal vectors	Radius (Å): Simulation	Radius (Å): Calculation	d_0 (Å)
5	3.379	4	(4,2)	1.439	1.437	2.61
6	4.059	5-1	(5,0)(1,1)	2.061	2.057	2.59
7	4.738	9-4	(9,4)(4,2)	2.996	2.982	2.41
8	5.418	9-4	(9,1)(4,1)	3.590	3.593	2.64
9	6.097	11-4	(11,2)(4,0)	4.280	4.285	2.55
10	6.777	11-6-1	(11,1)(6,1)(1,1)	4.578	4.636	2.73
11	7.456	14-8-2	(14,1)(8,1)(2,1)	5.552	5.525	2.66
12	8.136	16-10-2	(16,2)(10,3)(4,2)	6.152	6.151	2.68

interatomic potential function used. The optimized interatomic distance in the isolated Cu chain was 2.49 Å obtained from *ab initio* calculation.[22] The distances between C atoms and Cu atoms on the outer shells are 2.0 to 2.4 Å. These values are in good agreement with the range obtained from *ab initio* calculation, 2.06 to 2.42 Å. Our results show that the circular rolling of the triangular network can effectively explain the structures of ultrathin multishell Cu nanowires encapsulated in CNT's.

IV. SUMMARY

In summary, we have investigated the structures of ultrathin Cu nanowires encapsulated in carbon nanotubes using a structural optimization process applied to the steepest descent scheme. The stable structures of the cylindrical ultrathin Cu nanowires in CNT's are multishell packs composed of coaxial cylindrical shells. The theory of semiclassical orbits in a circle helped to explain the properties of the structures of the cylindrical ultrathin Cu nanowires. An investigation of the spreading sheets of the nanowires acquired from our simulations showed that a coaxial cylindrical shell could be obtained by circular rolling of a triangular network sheet with an orthogonal vector. As the diameter of the nanowire is increased, the encapsulated Cu nanowires have the face-centered-cubic structure as the bulk. Further works will show more specific theoretical and experimental works on such subjects as thermal effects, electronic properties, nanowire fabrication using the quantum calculation, and the experiments, thus overcoming our limited simulation work on Cu nanowires in carbon nanotubes.

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