탄소나노튜브 속에 성장된 구리 나노와이어의 구조

최원영, 강정원, 송기오, 황호정
중앙대학교 전자전기공학부 반도체 공정소자 연구실

Structures of Ultrathin Copper Nanowires Encapsulated in Carbon Nanotubes

Won Young CHOI, Jeong Won KANG, Ki Oh SONG and Ho Jung HWANG
Computational Semiconductor Laboratory, Department of Electronic Engineering, Chung-Ang Uni.

Abstract

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 consisted of coaxial cylindrical shells. As the diameter of copper nanotubes increased, the encapsulated copper nanowires have the face centered cubic structure as the bulk. Both the semiclassical orbits in a circle and the circular rolling of a triangular network can explain the structures of ultrathin multishell copper nanowires encapsulated in carbon nanotubes.

Key Words : 탄소나노튜브, 분자동력학

1. Introduction

Carbon nanotubes (CNTs) filled with various materials are of great interest in materials science and technology because of their interesting structures. CNTs filled with metals represent a fascinating new material and are the effective route to exploit one-dimensional nanocables with various uses. These CNTs 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 CNTs employing different methods. Previous studies reported two kinds of methods on filling the CNTs. One is that CNTs 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 CNTs 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 CNTs 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 CNTs growth, because carbon solubility in bulk copper is very small, making it difficult to form a stable carbide [19]. However, CNTs filled with copper have been prepared [16,17]. Therefore, the

Cu nanowire structures encapsulated in CNTs should be investigated. Atomistic simulations have been 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 detail 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 CNTs using an atomistic simulation.

2. Methods

For carbon-carbon, a many-body empirical potential, the Tersoff-type potential [20], was used. For carbon-copper, a universal repulsive potential, the Moliere potential function [21], was used. 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 [22]. The SMA-TB-type potential function has been used in atomistic simulation studies of nanoclusters [23-27] and ultrathin nanowires [28]. This potential is in good agreement with other potentials and with the experiments for bulk [22] and low-dimensional systems [29]. 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 CNTs, 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 nanowire reached 40 Å. The free boundary condition was then applied to the axis of the nanowires. The zigzag (n, n) CNTs with n = 5-15 were investigated to encapsulate ultrathin Cu nanowires.

3. Results and discussion

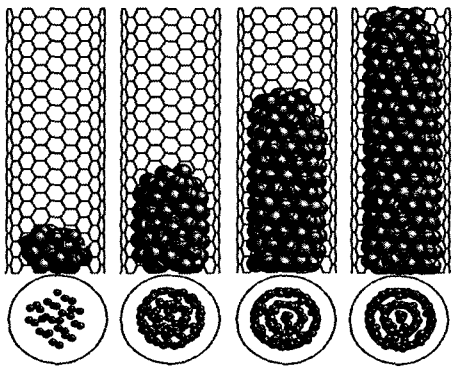

Fig. 1. Four snapshots for Cu nanowires growth in (10, 10) CNT. from the left side, the numbers of the inserted Cu atoms are 30, 100, 200 and 307, respectively. In each case, a side(top) and a top(bottom) views are showed.

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 CNTs obtained from our simulations. In general, the stable structures of the ultrathin Cu nanowires encapsulated in CNTs 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.

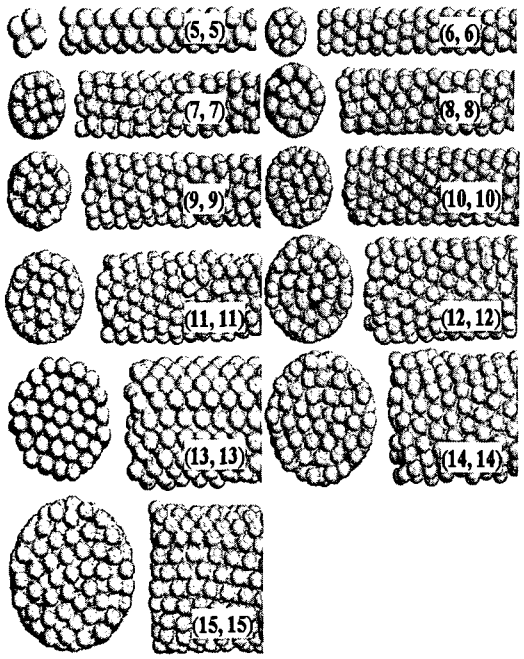

Fig. 2. Morphologies of ultrathin Cu nanowires encapsulated in CNTs. In each case, a top(left) and a side(right) views are presented.

The lateral surface of each shell exhibits a near-triangular network. Such helical multishell structures have been theoretically predicted for Al, Pb [30, 31], Cu [32], Au [33-38], and Ti nanowires [28] and recently experimentally observed in Au [39-42] and Pt [43] nanowires. To characterize the multishell structures, Yanson *et al.* [44] used the classical orbits inside a circle and labeled the orbits of nanowires as (M, Q), where M is the number of vertices and Q is the winding number, and Kondo and Takayanagi [41] 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* [28] used this notation. Since the thinnest magic nanowire consists of a single tube and a central strand, Tosatti *et al.* [35] used an (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) CNTs below n = 12, the ultrathin multishell structures of Cu nanowires are generally obtained, whereas for (n, n) CNT above n = 13, the cross-sectional shapes of Cu nanowires are similar with the hexagonal close-packed structures, {111} facet. 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 good agreement with the previous result for the ultrathin Au nanowires [45]. Wang *et al* [33] obtained the multishell Au nanowires for small diameters but the FCC structural Au nanowires for the diameters above 30Å.

In discussion of our simulation results, we briefly review regular polygons inside a circle, which are applicable to cylindrical nanowires. A series of semiclassical orbits inside a circle is elementary geometry obtained by using the classical dynamics of a circular billiard ball on a circular billiard table [44, 46, 47]. Due to momentum conservation, only the balls direction and position [46, 47] determine its motion. The periodic orbits for the circular billiard ball are the regular polygons shown in Fig. 3. Each of these orbits can be characterized by a three-integer numbers $\beta(\upsilon, \omega, n)$, where υ is the number of turning points at the boundary during on period and ω measures how many times the trajectory encircles the center during the fundamental period. . Therefore the winding number is ω, and the number of vertices is υ. Obviously, we have $\upsilon \geq \omega$. If there is a maximum common divisor n between υ and ω,

the orbit is an n-fold repetition of a primitive periodic orbit (see (2,1,1), (4,2,2), (6,3,3), and (3,1,1), (6,2,2), and (9,3,3) in Fig. 3).

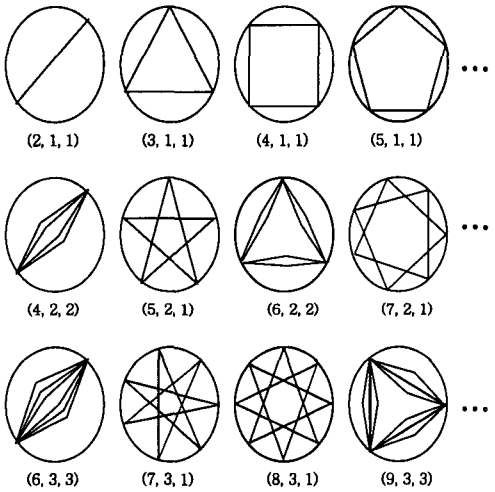

Fig. 3. Series of semiclassical inscribed inside a circular cross section, which are applicable to spheres (clusters) and cylinders (nanowires) alike.

Introducing an angle $\Phi_{v\omega}=\pi\omega/v$, the length of a periodic orbit is $L_{v\omega}=2v\,R\sin\Phi_{v\omega}$ from simple geometry, where R is the radius. The structures of ultrathin Cu nanowires encapsulated in CNTs obtained from our simulations can be compared with the closed classical periodic orbits in a circular billiard with reflective walls. Each nanowire has a {111}-like surface. Previous simulation works on nanowire elongation deformation showed that a rectangular {100} nanowire transforms in to a cylindrical nanowire with a {111}-like surface by stretching [48]. In order to carry out a more detailed study of cylindrical multishell nanowire structures, we investigated the spreading sheets of nanowires.

Figure 4 shows the spreading sheets of nanowires encapsulated in (5, 5), (7, 7), and (10, 10) CNTs, 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. 5.

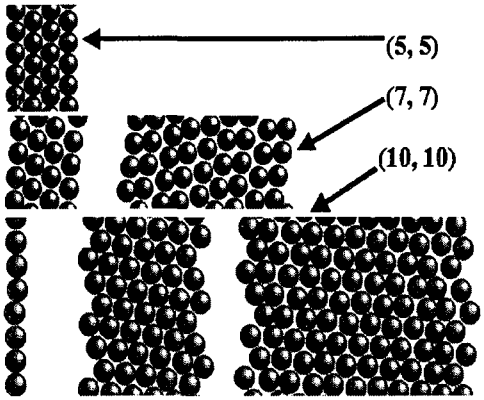

Fig. 4. Spreading sheets of three ultrathin Cu nanowires encapsulated (5, 5), (7, 7), and (10, 10) CNTs.

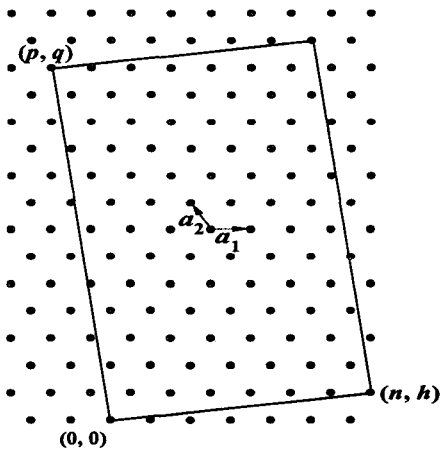

Fig. 5. Triangular network sheet. An (n, h) shell is made by cylindrically rolling a triangular lattice. A (p, q) is the axis vector of the (n, h) shell. p : q = (n-2h) : (2n-h), and $h \le n/2$

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 $h \le n/2$. 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 $(n^2 + h^2 \quad nh)^{1/2} / 2\pi$ Å and decreases for increasing

h, as the strands progressively align with the axis, where d_0 is the distance from the atomic center to the wire center. 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). In 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 1. The KT indices for both (7, 7) and (8, 8) CNTs are a 9-4, whereas the T indices for (7, 7) and (8, 8) CNTs are the (9,3)(4,2) and the (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 $\tan^{-1}(\sqrt{3}h/(2n-1))$. Our results shows that both semiclassical orbits in a circle and circular rolling of the triangular network can explain the structures of ultrathin multishell Cu nanowires encapsulated in CNTs.

	Structure indices	
nanotube (n, n)	KT index n-n′-n″	T index Orthogonal vectors
5	4	(4,2)
6	5-1	(5,0)(1,1)
7	9-4	(9,3)(4,2)
8	9-4	(9,1)(4,1)
9	10-4	(10,2)(4,0)
10	11-6-1	(11,1)(6,1)(1,1)
11	14-8-2	(14,1)(8,1)(2,1)
12	16-10-2	(16,2)(10,3)(4,2)

4. Summary

In summary, we have investigated the structures of ultrathin copper nanowires encapsulated in carbon nanotubes using a structural optimization process applied to the steepest descent scheme. The stable structures of the cylindrical ultrathin copper nanowires in CNTs are multi-shell 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 copper 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 copper nanowires in carbon nanotubes.

References

[1] G. Che, B.B. Lakshmi, C.R. Martin, and Fisher E R *Langmuir* **15,** 750 (1999).

[2] M. Ajayan and S. Iijima *Nature* **361,** 333 (1993).

[3] S. C. Tsang, P. J. F. Harris, and M. L. H. Green *Nature* **362,** 520 (1993).

[4] P. M. Ajayan, T. W. Ebbesen, T. Ichihashi, S. Iijima, K. Tanigaki, and H. Hiura *Nature* **362,** 522 (1993).

[5] S. C. Tsang, Y. K. Chen, P. J. F. Harris, and M. L. H. Green *Nature* **372,** 159 (1994).

[6] P. M. Ajayan, O. Stephan, Ph. Redlich, and C. Colliex *Nature* **375,** 564 (1995).

[7] D. Ugarte, A. Chatelain, and W. A. De Heer *Science* **274,** 1897 (1996).

[8] C. Guerret-Piecourt, Y. Le Bouar, A. Loiseau, and H. Pascard *Nature* **372,** 761 (1994).

[9] P. M. Ajayan, C. Colliex, J. M. Lambert, P. Bernier, L. Barbedette, M. Tence, and O. Stephan *Phys. Rev. Lett.* **72,** 1722 (1994).

[10] Y. Yosida *Appl. Phys. Lett.* **64,** 3048 (1994).

[11] A. A. Setlur, J. M. Lauerhaas, J. Y. Dai, and R. P. H. Chang *Appl. Phys. Lett.* **69,** 345 (1996).

[12] C. N. R. Rao, R. Sen, B. C. Satishkumar, and A. Govindaraj J. Chem. *Soc. Chem. Commun.* **15,** 1525 (1998)

[13] N. Grobert, W. K. Hsu, Y. Q. Zhu, J. P. Hare,

H. W. Kroto, D. R. M. Walton, M. Terrones, M. Ruhle, R. Escudero, and F. Morales *Appl. Phys. Lett.* **75,** 3363 (1999).

[14] S. Liu and J. Zhu *Appl. Phys. A: Mater. Sci. Process.* **70,** 673 (2000).

[15] Y. Gao, J. Liu, M. Shi, S. H. Elder, and J. W. Virden *Appl. Phys. Lett.* **74,** 3642 (1999).

[16] G. Y. Zhang and E. G. Wang *Appl. Phys. Lett.* **82,** 1926 (2003).

[17] X-R Ye, Y. Lin, C. Wang, and C. M. Wai *Adv. Mater.* **15,** 316 (2003).

[18] B. W. Smith, M. Monthioux, and D. E. Luzzi *Nature* **396,** 323 (1998).

[19] V. Ivanov, J. B. Nagy, Ph. Lambin, A. Lucas, X. B. Zhang, X. F. Zhang, D. Bernaerts, G. Van Tendeloo, S. Amelinckx, and J. Van Landuyt *Chem. Phys. Lett.* **223,** 329 (1994).

[20] J. Tersoff *Phys. Rev.* B **39,** 5566 (1989).

[21] R. Smith, M. Jakas, D. Ashworth, B. Oven, M. Bowyer, I. Chakarov, and R.Webb *Atomic and Ion Collisions in Solids and at Surface* edited by R Smith (Cambridge University Press) (1997).

[22] F. Cleri and V. Rosato, *Phys. Rev.* B **48,** 22 (1993).

[23] K. Michaclian, N. Rendon, and I. L. Garzon, *Phys. Rev.* B **60,** 2000 (1999).

[24] F. J. Palacios, M. P. Iniguez, M. J. Lopez, and J. A. Alonso, *Phys. Rev.* B **60,** 2908 (1999).

[25] L. Rongwu, P. Ahengying, and H. Yukun, *Phys. Rev.* B **53,** 4156 (1996).

[26] T. X. Li, S. Y. Yin, Y. L. Ji, B. L. Wang, G. H. Wang, and J. J. Zhao, *Phys. Lett.* A **267,** 403 (2000).

[27] H. Lei, J. Phys.: Condens. Matter **13,** 3023 (2001).

[28] B. Wang, S. Yin, G. Wang, and J. Zhao, *J. Phys.: Condens. Matter* **13,** L403 (2001).

[29] J. W. Kang and H. J. Hwang, *J. Korean Phys. Soc.* **38,** 695 (2001).

[30] O. Gulseren, F. Erolessi, and E. Tosatti, *Phys. Rev. Lett.* **80,** 3775 (1998).

[31] F. Di Tolla, A. Dal Corse, J. A. Torres, and E. Tosatti, *Surf. Sci.* **456,** 947 (2000).

[32] H J Hwang and J W Kang, *J. Phys. Soc.* **40,** 283 (2002).

[33] B. Wang, S. Yin, G. Wang, A. Buldum, and J. Zhao, Phys. *Rev. Lett.* **86,** 2046 (2001).

[34] G. Bialalbegoviæ, *Phys. Rev.* B **58,** 15412 (1998).

[35] E. Tosatti, S. Prestipino, S. Kostlmeier, A. Dal Corso, and F. D. Di Tolla, *Science* **291,** 288 (2001).

[36] G. Bialalbegoviæ, *Solid State Commun.* **115,** 73 (2000) .

[37] J. A. Torres, E. Tosatti, A. Dal Corso, F. Ercolessi, J. J. Kohanoff, F. D. Di Tolla, and J. M. Soler, *Surf. Sci.* **426,** L441 (1999).

[38] G. Bialalbegoviæ,Comput. Master. Sci. **18,** 333 (2000).

[39] Y. Kondo and K. Takayanagi, *Phys. Rev. Lett,* **79,** 3455 (1997).

[40] H. Ohnishi, Y. Kondo, and K. Takayanagi, *Nature* **395,** 780 (1998).

[41] Y. Kondo and K. Takayanagi, *Science* **289,** 606 (2000).

[42] V. Rodribues, T. Fuhere, and D. Ugarte, *Phys. Rev. Lett.* **85,** 4124 (2000).

[43] Y. Oshima, H. Koizumi, K. Mouri, H. Jirayama, and K. Takayanagi *Phys. Rev.* B **65,** 121401 (2002).

[44] A. I. Yanson, I. K. Yandson, and J. M. van Ruitenbeek, *Phys. Rev. Lett.* **84,** 5832 (2000).

[45] B. Wang, S. Yin, G. Wang, A. Buldum, and J. Zhao, *Phys. Rev. Lett.* **86,** 2046 (2001).

[46] S. M. Reimann, M. Brack, A. G. Magner, J. Blaschke, and M. V. N. Murthy, *Phys. Rev.* A **53,** 59 (1996)

[47] C. Hoppler and W. Zwerger, *Phys. Rev.* B **59,** 5881 (1996).

[48] J. W. Kang and H. J. Hwang, *J. Korean Phys. Soc.* **38,** 695 (2001).