Atomistic Modeling on Structures of ultrathin copper nanotubes

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ABSTRACT

We have performed atomistic simulations for helical multi-shell (HMS) Cu nanowires and nanotubes. Our investigation on HMS Cu nanowires and nanotubes has revealed some physical properties that were not dealt in previous works that considered metal nanowires. As the diameter of HMS nanowires increased, their cohesive energy per atom decreased but their optimal lattice constants were almost constant. Shell-shell or core-shell interactions mainly affected on the lattice constant and the diameter of HMS nanowires or nanotubes. Our MD simulations showed that a part of ultrathin Cu nanotubes collapsed into the empty core at low temperature and this is main mechanism for the transformation from ultrathin nanotube to nanowire structures. This study showed that HMS Cu nanotubes can keep their own structures when the internal stress on HMS nanotubes are zero or toward the outside.

Keywords: Ultrathin copper nanotube, Helical multi-shell structure, Atomistic simulation

1 INTRODUCTION

Recently, ultrathin metal nanowires have aroused growing interest in condensed matter physics; for example, Takayanagi's group has fabricated ultrathin gold [1-3] and platinum [4] nanowires. Many theoretical studies on ultrathin nanowires have been done using atomistic simulations for several metals, and these have simulated straight-line uniform ultrathin nanowires containing helical multi-shell (HMS) structures, such as Ag [5], Al [6], Au [7-10], Ti [11], Cu [12,13], and Zr [14]. Unlike a hexagonal network for carbon nanotubes, each shell of the HMS structures is formed by a triangular network which is similar to the {111} atomic sheet of *fcc* crystals. The <110> atomic rows in each {111} sheet make a helix that coils around the axis of metal nanowires. The n - n'- n''- n''' HMS nanowires, then, are composed of coaxial tubes with n, n', n'', n''' helical atom rows ($n > n' > n'' > n'''$).

In addition to studies on novel helical structures of ultrathin nanowires, the melting behavior of ultrathin nanowires has been investigated for Pb [15], Au [16], Cu [17], and Ti [18]. The compression of the HMS Au nanowires [19] and the tensile testing of the HMS Cu nanowires [20] have also been performed using a classical molecular dynamics (MD) simulations. The resonance of ultrathin Cu nanobridges was investigated using a classical MD simulation [21]. In study on defects in the HMS Cu nanowires [22], the vacancy formation energy was lowest in the core of a HMS-type nanowire, a vacancy formed in the outer shell of a HMS-type nanowire naturally migrated toward the core, and an onion-like cluster with a hollow was also formed. These provided basic information on the formation of hollow HMS-type metal nanowires. Recently an evidence of a suspended a 13-6 HMS Pt nanotubes was reported in experiments [4] and Bilalbegovic [23] also showed the structure of the 16-10 Au nanotube compared with double-wall carbon nanotubes in a classical MD simulation.

Although the previous works have given support for metal nanowires of the HMS structures, further investigations, in areas such as non-linear ultrathin nanowires, funnel-shaped nanowires, defects in nanowires, and metal tubular structures like carbon nanotubes need to be made in order to understand the physical properties of nanowires, and for the successful application of nanowires to nanoscale devices. Therefore, this investigation focuses on copper HMS nanotubes and provides basic physical information on the structural properties of HMS-type nanotubes.

2 COMPUTATIONAL METHODS

For the Cu-Cu interactions, we used a well fitted many-body potential function of the second-moment approximation of the tight-binding (SMA-TB) scheme [24]. The optimal atomic arrangements were obtained using the steepest descent (SD) method, which is the simplest of the gradient methods, and so this was called the gradient descent method. The structures of ultrathin metal nanowires found using the embedded atom model (EAM) potential [6,8-10,16,19] have been the same with those found using the SMA-TB potential [7,11,12,14,18]. These results have been found in the motifs [6,10-12,7], the cohesive energies per atom as a function of diameter [6,25], bond angle distributions [6,11,12] and melting properties [15,26] of nanowires. Table 1 shows all the structures that are investigated in this paper. We selected the series of the 5-1 and 6-1 HMS nanowires investigated in previous works [12,14], the 6-0 and 13-6 nanotubes found in experiments [4] and the 16-10 nanotube found in a MD simulation [23]. Circular folding of {111} sheet made each shell of the HMS nanowires and nanotubes. The HMS nanowires and nanotubes were relaxed using the SD method. While the cores of the HMS nanowires are filled with atomic strand, the cores of the HMS nanotubes are empty. Each shell is composed of thirty atomic layers along the wire axis, and periodic boundary condition (PBC) is applied to supercells of nanowires and nanotubes. Table 1 shows the number of atoms in supercells. The

optimal lengths of PBCs of nanowires and nanotubes are related to the diameters of those, and this will be discussed in Table 1 in next chapter.

3 RESULTS AND DISCUSSION

Table 1 shows the optimal lattice constants, the cohesive energy per atom and the mean diameter of the shell composed of 6 atoms for the optimal structures of nanowires and nanotubes based on the SMA-TB potential. We calculated optimal lattice constants of nanowires and nanotubes along the wire axis as follows; Using the structures of Table 1, as the lattice constants (a) of those increased by 0.0001 Å from 2.22 Å, the optimal structure of each step was obtained from the SD method and then the cohesive energies per atom ($E(a)$) of those were calculated. The points at the lowest cohesive energy ($E_{\min}$) are the optimal lattice constants that are shown in Table 1. The optimal lattice constant of the 15-10-5-1 HMS nanowire is 0.0063 Å higher than those of the 5-1 and 10-5-1 HMS nanowries, 2.25 Å. For the 6-1 HMS series, as the diameter increases, the optimal lattice constant slightly decreases. However, since the differences between the optimal lattice constants of HMS nanowires are within 0.0177 Å, the optimal lattice constants of HMS nanowires are almost constant irrespective of the diameter of HMS nanowires. As the lattice constant increases, some sharp curves of the cohesive energy for of the 16-11-6-1 HMS nanowire are shown since its diameter increases or decreases more or less.

We also calculated the optimal lattice constants of nanotubes by using the same procedure, and results obtained are shown in Table 1. The optimal lattice constant of the 6-0 nanotube is much smaller than those of the HMS nanowires. However, in the case of the 13-6 and 16-10 HMS nanotubes, its lattice constant is higher than that of the 6-0 nanotube because of interaction between the inner and outer shells, and is similar to those of the HMS nanowires within 1.4 %. Therefore, this result appears that the shell - shell or core - shell interactions mainly affects on the lattice constants of the HMS nanowires or nanotubes. For the HMS nanowires, since their cores are filled with a linear atomic strand and their shells are made by circular folding of {111} sheets, both the distance between atoms in core and the height of triangles in outer shell are mainly related to the lattice constants of the HMS nanowires. However, since the HMS nanotubes are only made by circular folding of {111} sheets, the height of triangles is only related to the lattice constants of the HMS nanotubes. In Table 1, the lattice constant of the 6-0 nanotube is 93.33 % of that of the 6-1 nanowire. In the case of the 6-0 nanotube, when the length of a side of normal triangle is 1, the height of triangle is $\sqrt{3}/2 = 0.866$. In the case of the 6-1 nanowire, when both the length of a side of normal triangle and the distance between atoms in core strand are 1, the average between the height of triangle, $\sqrt{3}/2$, and the distance between atoms in core strand, 1, is $(2+\sqrt{3})/4 = 0.933$. Therefore, the lattice constant of the 6-0 nanotube is 92.82 % of that of the 6-1 nanowire from above two values. This value, 92.82 %, is in good agreement with 93.33 % obtained from our simulation. From these results, since the 6-1 nanowire has the atomic strand of core, the lattice constants and the diameters of the 6-1 nanowire are different with those of the 6-0 nanotube. In the case of double-shell nanotube, the 13-6 nanotube, the interaction between inner and outer shells also makes the longer lattice constant than a single-shell nanotube.

In previous works, the cohesive energies per atom (E_{coh}) for nanowires have been linearly proportional with the reciprocal of diameter (D) [6,27], and are expressed as follows,

$$E_{coh} \approx E_{bulk} + n / D , \qquad (3\text{-}1)$$

where E_{bulk} is the cohesive energy of atom of bulk material and n is a constant. As the number of shells in the HMS nanowires increases, their cohesive energy per atom increases and the relation following Eq. (3-1) has been shown in our previous work [27]. In this investigation, since we considered only the 6-0, 13-6 and 16-10 HMS nanotubes, this paper could not provide relationship between the E_{coh} and D for HMS nanotubes. However, our results show that the E_{coh} of the 13-6 and 16-10 HMS nanotube with double shell are lower than that of the 6-0 nanotube with a single-shell.

While the number of atoms of the 5-1 nanowire is equal to that of the 6-0 nanotube, since the E_{coh} of the 5-1 nanowire is lower than the E_{coh} of the 6-0 nanotube. This means that the 5-1 nanowire is more stable than the 6-0 nanotube in a potential energy point of view. Our classical molecular dynamics simulations of the 6-0 nanotube showed that the 6-0 nanotube was transformed into a nanowire with complex structures including the structure of a 5-1 nanowire, and this will be discussed below. For the 16-10 Cu nanotube, the value for the potential energy per atom obtained is 0.4844 eV/atom higher than that for the Cu bulk, -3.544 eV/atom. Considering the cohesive energy for the Cu bulk material, the cohesive energy for the 16-10 Cu nanowire is only 86.33 % of the bulk. The cohesive energy per atom for the 16-11-6-1 nanowire is 0.2999 eV/atom higher than that the bulk material and is 91.54 % of the bulk. Therefore, one can see that the studied Cu nanotubes are more unstable structures than the HMS Cu nanowires from the potential energy point of view. When the number of atoms composingr nanowire is the same as that composing nanotube, since the cohesive energy per atom for the nanowire is much lower than that for the nanotube, it is very difficult for tube-like structures to be obtained from a simulated annealing method.

We calculated the mean diameter (D_{6s}) of the shell composed of 6 atoms for the 6-1 and 11-6-1 HMS nanowires and the 6-0 and 13-6 HMS nanotubes. In the case of the 11-6-1 HMS nanowire, since the outer shell slightly compresses the inner shell, the D_{6s} of the 11-6-1 HMS nanowire is slightly smaller than the D_{6s} of the 6-1 nanowire. The D_{6s} of the HMS nanotubes is larger than the D_{6s} of the HMS nanowires. While the lattice constant of the

6-1 nanowire is larger than that of the 6-0 nanotube, the D_{6s} of the 6-1 nanowire is shorter than D_{6s} of the 6-0 nanotube. Therefore, the difference between volumes of the 6-1 nanowire and the 6-0 nanotube is 2.296 %, and this result implies that a 6-0 nanotube is a different geometry of shell composed of 6 atoms in the condition of constant volume. In this work, the distance between shells of the nanotubes is 2.165 Å.

In previous work [22], as the diameter of HMS nanowire increased, the vacancy formation energy of its core decreased rapidly. MD simulations also showed that vacancy migrated from the outer shell to the inner shell and to the core. Since the formation energy of a vacancy was lowest at the core and the vacancy migrated towards the lower energy states, the vacancy migrated to the core. Therefore, these results implied that vacancies would be most frequently found in the core of a HMS nanowire. This interpretation is in good agreement with previous result that showed an evidence of metal nanotube and high-resolution transmission electron microscopy (HRTEM) images of a 6-0 and a 13-6 HMS Pt nanotubes. Therefore, we investigated an 11-6-1 HMS nanowire with a hollow region. Some core atoms in the center region of the 11-6-1 HMS nanowire was omitted and then this structure was relaxed by the SD method and transformed into the structure. The region with a hollow of the 11-6-1 HMS nanowire disappeared due to the pressure on the inner shell, 20.663 GPa. These results show that a hollow region disappears because forces exerted on atoms of inner or outer shell acted on the direction toward the core. On the analogy of this result, when the pressure acting on the inner shell of a HMS nanotube are zero or very low, the nanotube will be a stable structure. This interpretation is also related to the mean diameter (D_{6s}) of the shell composed of 6 atoms. As shown in Table 1, the D_{6s} of nanotubes is larger than the D_{6s} of nanowires. Especially, the D_{6s} of the 13-6 Cu HMS nanotube have the largest in this work, and this is because the interaction between the inner and outer shells is attractive. Takayanagi group also showed the HRTEM image of a 13-6 Pt HMS nanotube obtained from a suspended nanowire made by electron-beam thinning method [4].

We also investigated the internal energy curve per atom for the 16-10 Cu nanotube. The Cu nanotube was heated up in step via scaling the atomic velocities with zero total linear and angular momenta. On heating, temperature was increased from 0 K by 50 K interval, but it was changed in steps of 10 K near the structural transition temperatures. At each temperature, MD runs of $2 \cdot 10^5$ steps were made with a time step of 0.5 fs (total 100 ps). The mean kinetic temperature $k_B T = [2/(3N-6)]\left\langle \sum_{i=1}^{N} (mv_i^2/2) \right\rangle$, where the angular brackets denote averaging over time and k_B is the Boltzman constant, supply the energy to atoms in nanotube, and the internal energy curve of the nanotubes with the kinetic temperature, as shown in Fig. 4, were obtained from the last 10^3 steps. A code base on constant temperature molecular dynamics scheme has carried out all simulations in this paper and in previous works [13,17,22].

Figure 1 shows the internal energy per atom as a function of temperature and also includes some atomic structures to show the structural transition of the 16-10 Cu nanotube. Below 150 K, the 16-10 nanotube maintained a tubule structure. From 160 to 200 K, a part of nanotubes collapesed to block the tube, but most of nanotube were hollow regions as shown in Fig. 4. When the nanotube caved in, a little downward curvature in the internal energy curve was achieved at the point of 160 K in Fig. 4. Above 200 K, the curve rapidly decreased and the 16-10 Cu nanotube was transformed into a Cu nanowire because the structure of nanotube collapsed, and then the hollow region rapidly decreased and the hollow region of nanowire disappeared at 300K. In the previous MD simulation work [23] for a 16-10 Au nanotube based on a glue model potential [28], Bilalbegovic showed the high temperature stability of the 16-10 Au nanotube, and showed that several atoms evaporated into the empty core at 900 K. Both studies show the degradation of the inner shell toward the empty core, and his results are similar to our results except that several atoms evaporated into the empty core at a high temperature. However, our results show that several atoms on the inner shell of the 16-10 Cu nanotube did not evaporate into the empty core at high temperature but some part of the 16-10 Cu nanotube collapsed into the empty core at low temperatures. It is seemed that thus difference may be due to both the differences of the materials and the empirical potential used. While the glue model potential [28] used in Bilalbegovic's work considers only the interactions between the first neighbours, the SMA-TB potential used in this work covers the long-range interactions that are important effects in metallic materials. More detailed study has to be investigated by future works. We also performed MD simulations for the 6-0 Cu nanotube at very low temperatures. Since the cutoff distance, 5.30 Å, for the SMA-TB potential is longer than the diameter of the 6-0 Cu nanotube, the 6-0 Cu nanotube was crushed and transformed into a nanowire in the case of MD simulations at just 30 K. For carbon material, since a single graphite sheet is stable structure, a single shell carbon nanotube also is stable. However, for copper material, since a single {111} sheet is unstable structure, a single shell Cu nanotube also is unstable. The cohesive energy per atom for a Cu {111} sheet is –2.523 eV that is higher than that for the 6-0 Cu nanotube. Though HMS Cu nanotubes are more stable than a Cu {111} sheet, our MD simulation results show that the structures of ultrathin Cu nanotubes are unstable and limited below very low temperature, since the potential energies of Cu nanotubes are much higher than that of Cu nanowires.

4 CONCLUSION

This study on HMS Cu nanowires and nanotubes has revealed some physical properties that were not dealt in previous works that considered metal nanowires. As the

diameter of nanowires increased, their cohesive energy per atom decreased but their optimal lattice constants were almost constant. Shell-shell or core-shell interactions mainly affected on the lattice constant and diameter of HMS nanowires or nanotubes. Simulation result of an 11-6-1 HMS nanowire with a hollow region showed that the region with a hollow disappeared because of the pressure acting on the inner shell. Cu nanotubes were unstable structures from the potential energy point of view and MD simulations showed that the structures of Cu nanotubes were limited very low temperature. Our MD simulations also showed that a part of ultrathin Cu nanotubes collapsed into the empty core at low temperature and this is main mechanism for the transformation from ultrathin nanotube to nanowire. From this study, we conclude as follows: For copper material, when the internal stress on HMS nanotubes are zero or toward the outside, the HMS nanotubes can be maintained at just low temperatures.

Structure	N	a (Å)	E_{coh} (eV)	D_{6s} (Å)
5-1	180	2.2500	-2.90327	-
10-5-1	480	2.2500	-3.09703	-
15-10-5-1	930	2.2563	-3.20678	-
6-1	210	2.2435	-2.94216	4.788440
11-6-1	540	2.2396	-3.15202	4.734468
16-11-6-1	1020	2.2386	-3.24411	4.691218
6-0	180	2.0913	-2.58686	5.012518
13-6	570	2.2184	-2.98825	5.405746
16-10	720	2.2185	-3.05957	-

Table 1. For structures of HMS Cu nanowires and nanotubes, the number of atoms in supercell, the optimal lattice constant along the wire axis (a), the cohesive energy per atom (E_{coh}), and the mean diameter of shell composed of 6 atoms (D_{6s}).

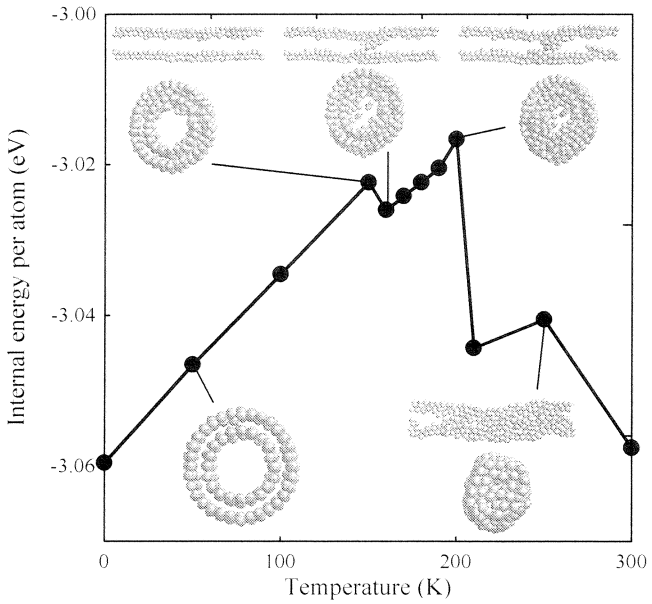

Figure 1. Internal energy per atom as a function of temperature for the 16-10 Cu nanotube and the cross-sectional side views of the 16-10 nanotube at 150, 160, 200, and 250, respectively.

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