Melting behavior in ultrathin metallic nanowires

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The thermal stability of helical multiwalled cylindrical gold nanowires is studied using molecular-dynamics simulations. From our simulation, the melting temperature of gold nanowires is lower than the bulk value, but higher than that of gold nanoclusters. It is interesting to find that the interior melting temperature in ultrathin nanowires is lower than that of the surface melting. The melting starts from the interior atoms, while the surface melting occurs at relatively higher temperature. This unique thermodynamic behavior is closely related to the interior structures. We propose that the surface melting represents the overall melting in ultrathin metallic nanowires.

The melting behaviors of nanoparticles and nanorods have been demonstrated dramatically different from the bulk both experimentally and theoretically.[1–13] It is well known that the melting process of a crystalline starts from the surface layer and propagates into the interior. Thus the surface melting temperature is significantly lower than the bulk melting point. Similarly, one may ask whether the surface melting temperature is lower than the overall melting temperature in clusters and nanowires. Berry considered that "dynamic coexistence" or surface melting occurs in the melting process of small clusters before the overall melting.[3] For crystalline nanowires, Gulseren *et al.* found that the surface melting temperature for Pb wires was also lower than the total melting temperature.[4] Experimentally, surface melting was observed in the melting process of nanoparticles and nanorods.[5–7] In particular Schmidt *et al.* found a broad peak in the heat capacity of Na_{139}^+ clusters, which implies a coexistence of solidlike and liquidlike phases before the overall melting.[8] Two major effects, a large surface-to-volume ratio and a quantum confinement effect in finite-size systems, are responsible for these different melting behaviors in these nanostructures. Surface atoms have fewer nearest neighbors and weaker binding, which may lead to an earlier surface melting behavior. On the other hand, a close relationship between the melting and the structural characters was found in the clusters.[14,15]

Recent studies demonstrated that ultrathin metallic nanowires have quite different structural properties from those of bulk, clusters, and crystalline nanowires.[16–23] Helical multiwalled cylindrical structures were found in metallic nanowires of the 1–3-nm size range both experimentally and theoretically.[16–19,22,23] These structures are expected to bring about some bizarre melting features different from the above-mentioned systems. To our knowledge, fewer efforts have focused on their thermodynamics so far, although such ultrathin metallic nanowires have attracted great interest.[20,21]

Furthermore, an ultrathin nanowire has some characteristics similar to either cluster or bulk solids. It may provide an opportunity for comprehensively understanding these types of matter states and their relations. For example, the surface-to-volume ratio is a nonzero value in these nanostructures, while it approaches zero in bulk systems. Surface and core atoms are expected to play different roles during the melting process. However, it is difficult definitely to distinguish overall melting and surface melting in clusters from experiments, because the cluster's signal spectrum will not exist when surface melting occurs. Alternatively, we may employ an ultrathin gold nanowire as a representation to explore these problems.

In this paper the thermal stabilities of gold nanowires with helical multiwalled cylindrical structures are studied using molecular dynamical simulations. We start from optimized structures from previous works,[19] which were supported by electron microscopy images.[16,17] The interaction between gold atoms was described by a glue potential,[24] and the periodic boundary condition is applied along the wire axis to model the nanowires with sufficient length. The length of supercell is chosen as the same in Ref. 19, which contains a reasonable scheme to attain the helical structures in the nanowire. To characterize the thermal behavior of nanowires, we monitor the root-mean-square (rms) fluctuation of the interatomic bond distances δ defined by

$$\delta = \frac{2}{n(n-1)} \sum_{i<j}^{n} \frac{(\langle r_{ij}^2 \rangle_t - \langle r_{ij} \rangle_t^2)^{1/2}}{\langle r_{ij} \rangle_t},$$

and the heat capacity C per atom, which is related to the energy E fluctuation by the relation

$$C = \frac{(\langle E^2 \rangle - \langle E \rangle^2)}{n k_B T^2},$$

where $r(i,j)$ denotes the distance between the nuclei i and j, n is the total number of the atoms in the nanowire, k_B is the Boltzman constant, and $\langle \cdots \rangle$ indicates the thermal statistical averages in the canonical ensemble after equilibration.

The constant temperature molecular dynamics (MD) method of Hoover[25] is employed to exploit the thermal prop-
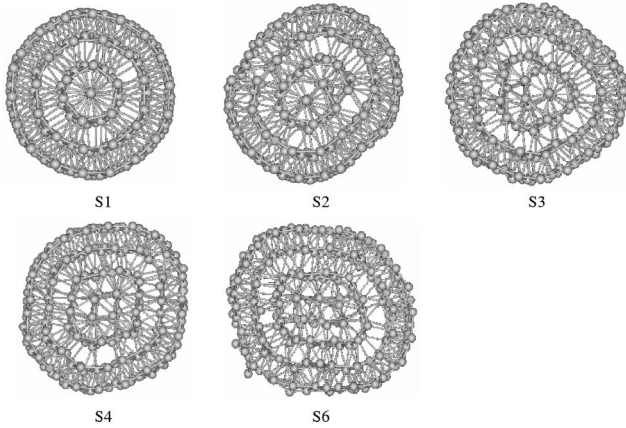
FIG. 1. Morphology of some representative gold nanowires with triple shells.

FIG. 2. Structure evolution of gold nanowire $S1$(18-12-6-1) with elevated temperature.

erties of gold nanowires. The MD time step is chosen as 2.15×10^{-15} s. The initial 10^5 steps are used to bring the system into equilibration, and further 10^6 steps are used to record the thermal average of the physical quantities. We study five representative helical triple-shelled gold nanowires with various core structures, i.e., single atom centered, double-chain, triangular, tetragonal, and six-atom-parallelogram centered (see Fig. 1). These wires can be noted as $S1$, $S2$, $S3$, $S4$, and $S6$. Table I summarizes the starting melting temperature T_{ini} and the overall melting temperature T_m of these structures, which are estimated from the curves of rms bond length fluctuation δ, heat capacity C, and binding energy E. The overall melting temperature T_m reflects the stability of the whole system, while the starting melting temperature T_{ini} describes the early stage of melting and sensitively depends on wire structures.

As shown in Table I, the overall melting temperatures T_m are almost the same for all the wires studied, and are slightly lower than the bulk melting point (1357 K).[24] Experimentally, Liu *et al.* reported that the melting point of Pt nanowire is about 400 °C.[11] The melting temperature of 4.6-nm Pd nanowire was found as only 300 °C, much lower than the bulk value (1445 °C).[12] A similar phenomenon was also found in the case of metal clusters. The depression of the melting point can be attributed to the low dimension and large surface-to-volume ratio in these nanostructures. However, the melting temperatures obtained for gold nanowires are much higher than those of gold nanoclusters with comparable sizes.[26–29] This effect might be understood by the one-dimensional periodicity and the well-reconstructed surface based on helical multishelled structures.

On the other hand, different starting melting temperatures T_{ini} are found for gold wires with different interior structures

TABLE I. Melting temperature for different interior structures of a Au nanowire.

Melting temperature (K)	$S1$	$S2$	$S3$	$S4$	$S6$
T_{ini}	300	550	650	700	650
T_m	1100	1100	1050	1100	1100
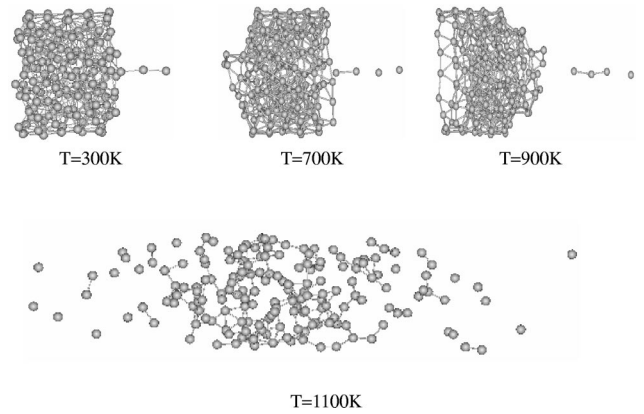
(see Table I). Wire $S1$ (as described by a multiwalled structural index:[22,23] 18-12-6-1, noted as $A5$ in Ref. 19) starts to melt at a rather lower temperature than the other ones, while wire $S4$ (21-15-9-4) has a relatively higher starting melting temperature. Such difference in T_{ini} can be related to their different interior structures. Moreover, since T_{ini} is related to the stability of the interior atoms, the relatively lower starting melting temperature T_{ini} implies that the interior melting occurs at an earlier stage of nanowire melting. It is worth noting that the overall thermal stabilities for all the wires studied are similar, which might be understood by their common multiwalled helical packing, despite their different interior structures. We investigate the structural difference of these wires, and find that the average coordination numbers (ACN's) of core atoms are much different in different interior structures while the ACN's of their surface atoms is similar. For example, the ACN's of core atoms in $S1$, $S2$, $S3$, $S4$, and $S6$ are 7.5, 8.0, 8.67, 8.69, and 8.08, while the ACN of surface atoms are 6.65, 6.75, 6.94, 7.02, and 6.97, respectively. Thus the interior melting temperature is lowest for the $S1$ wire, but highest for the $S4$ wire.

We discuss the structural evolution of gold nanowires during the melting process. Figure 2 shows several snapshots taken from the structural trajectories of the $S1$ wire at different temperatures. It is interesting to find that the interior atoms diffuse along the wire axis direction at a rather low temperature. As shown in Fig. 2, the central atoms first move along the wire at 300 K, while the helical outer shells are almost invariant. With a rise in temperature, the central atoms continue to move away from the original supercell. Such an atomic motion can create defects in the interior region of nanowires. Thus, up to 700 K, the atoms in the first shell (from interior to outer) should have fewer nearest neighbors and begin to diffuse along the axis direction (see Fig. 2). Similarly, the atoms in the second shell are also involved in the migration at higher temperature $T = 900$ K. However, the outer most shell still maintains a helical surface structure. As the temperature is high enough, the surface atoms in the outermost shell eventually start to migrate. As shown in Fig. 2, the helical structure of the nanowire surface is broken at 1100 K, corresponding to the overall melting. Therefore, we conclude that interior atoms diffuse prior to
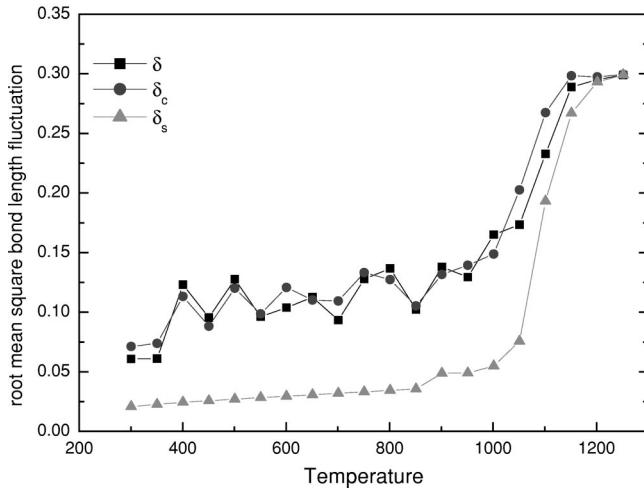
FIG. 3. The rms bond length fluctuation in the $S1(18\text{-}12\text{-}6\text{-}1)$ structure is ploted as a function of temperature for the entire system (δ), the core atoms (δ_c), and the surface atoms (δ_s).

surface atoms, and that no surface melting takes place before the overall melting of the gold nanowires.

To further illustrate the interior melting phenomena and to distinguish the role of surface and core atoms in the melting process, Fig. 3 plots the rms bond length fluctuation of the surface atoms (δ_s), core atoms (δ_c), and the total atoms (δ) for the $S1$ wire as functions of temperature. The bond length fluctuation of the core atoms have trends similar to that of the whole wire, but significantly different from the surface. In the temperature range of 350–1000 K, δ_s of the surface atoms is very small and almost invariable, while δ_c and δ have substantial fluctuations. In this melting region, the core atoms begin to diffuse along the axis and become "wet," while the surface atoms remain "solidlike." These results again confirm that the melting mainly comes from the diffusion of core atoms, and that no surface melting occurs at the beginning of the melting. Moreover, δ_c fluctuates around 0.12 at low temperature, consistent with the Lindemann criterion for equilibrium melting of simple crystals,[30] indicating that interior melting takes place. For all the three cases (core, surface, and overall) there is a rapid raise of the rms bond length fluctuation in a narrow temperature region (1000–1150 K), indicating that surface atoms are now involved in the melting process. Afterward, the surface atoms play an important role in the melting of a nanowire in the high-temperature region. Above 1150 K, all three quantities have a large, constant, and smooth variation, corresponding to the completely melting status. Together with Fig. 2, we argue that the surface melting represents the overall melting in the ultrathin multiwalled nanowires.

The above interior melting behavior is obviously different from that of the bulk, cluster, and crystalline nanowire, where the surface melting usually occurs before the overall melting. In bulk solids, after the melting of surface layers, the rest of the internal atoms can still be seen as an analogous bulk. Much more energy is needed to make the "rest bulk" molten. Therefore, the surface melting temperature of solids should be lower than their overall melting point. In the cases of clusters and crystalline nanowires, surface atoms have fewer nearest neighbors and are thus more weakly bound and less constrained compared to the core atoms. Thus surface atoms are easier to diffuse and become liquidlike. However, the present structures of gold nanowires are helical multi-walled cylindrical. The interaction among same-shell atoms is stronger than that of neighboring-shell atoms. To reach a well-tightened helical multi-walled structure, the helical match may cause a fewer number of atoms in the interior shells, especially for the center chain (only four atoms). We further investigated the structural characteristics of these wires, and found that the interior melting can be attributed to the special structure. In these helical multiwalled gold wires, although the coordination numbers of the interior atoms are larger than those of surface atoms, their average interatomic distances are also larger than those of surface atoms. Taking the $S1$ wire as an example, the average interatomic distance of center chain is 2.87 Å, which is larger than those of other shells (for the first interior shell it is 2.84 Å, for the second interior shell 2.81 Å, and for the outer shell 2.71 Å). Moreover, the average interatomic distances between shells are 2.81, 2.90, and 2.72 Å, respectively. Thus interior atoms with larger interatomic distances have less binding from the wire compared to surface atoms. Therefore, these center atoms in nanowires can break away from the binding sites in the wire prior to surface atoms, and diffuse at a rather low temperature. For other wires such as $S2$, $S3$, $S4$, and $S6$, similar structural characteristics are found, that is, the average inter-atomic distances of interior atoms are larger than those of surface atoms. Therefore, we hold that the interior melting behavior mainly comes from their special structures: the larger interatomic distance of core atoms and the shorter in-teratomic distance of surface atoms. In addition, in the optimization process of the ground-state structure, we found that the formation of a helical structure in the outer shell occurs earlier than in the interior shell. This implies that the surface is dynamically more stable than the interior part. Experimentally, Wu et al. found that the melting of a Ge nanowire starts from the two ends of the wire and move toward the middle.[13] These imply that the melting behavior for nanowires dramatically differs from those for nanorods and bulk.[7]

To clarify our ideas further, we separate the function of surface atoms and core atoms by fixing the surface atoms artificially and allowing the interior atoms to move, or vice versa. All the rms bond length fluctuation δ, δ_{fc}, and δ_{fs} are calculated for the entire system, representing no constraint, fixed core atoms and a fixed surface, respectively. We still take the wire $S1$ as an example. As shown in Fig. 4, regardless of the large difference among δ, δ_{fc}, and δ_{fs} curves, the full melting temperatures (which correspond to a large, smooth, and constant rms bond length fluctuation) in the three cases are about 1150 K. δ_{fs} has a considerable jump at low temperature (400 K), while δ_{fc} is almost invariable up to 800 K. This indicates that surface atoms with a helical structure are thermodynamically more stable. For the case of a fixed surface and no constraint, although δ_{fs}'s are just nearly half of δ, their general trends are similar. The small absolute value of δ_{fs} comes from the fixed surface atoms, which contribute nearly zero to the rms bond length fluctuation. Therefore, we propose that there should be no essential difference
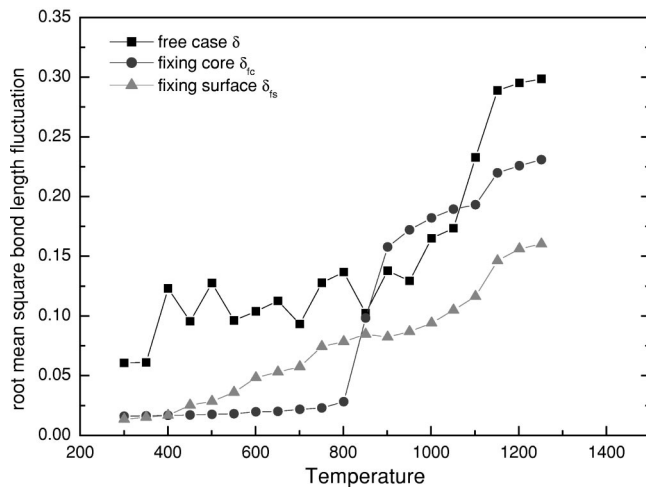
FIG. 4. Melting behavior in the 18-12-6-1 structure with fixed interior atoms, fixed surface, and no constraint.

between the first two cases. These results also support that the melting comes from the interior atoms at low temperature and that the surface melting represents the overall melting.

To check the validity of the current results, we have used the same MD code to study the melting of clusters and obtained results similar to previous Monte Carlo (MC) simulations.[31,32] We have also exploited the melting process of gold nanowires by MC simulations and observed similar interior diffuse behaviors. Moreover, to examine the effect of the periodic bound condition on the melting behavior, we rescaled the supercell length to two and three times the original one. The melting temperatures were also about 1100 K and the observed melting process is similar to the above

results. This proves that the periodic boundary condition has little effect on the simulation results. It should also be pointed out that we limit our discussion in this paper to helical structures. As mentioned above, this kind of helical structure is prevalent in free-standing metal nanowires in the small diameter range.[16–22] Therefore, the current results for interior melting behavior in ultrathin gold nanowires are significant, and might be a common feature in these ultrathin metallic nanowires.

In summary, the thermal behavior of helical multiwalled gold nanowires has been studied and the main points are as follows. (1) The melting process starts from the interior region, and no surface melting occurs at lower temperature. We further argued that interior melting behavior occurs prior to surface melting, and that surface melting represents the overall melting in ultrathin metallic nanowires. (2) The overall melting temperature of gold nanowires is lower than the bulk value, but higher than gold nanoclusters. (3) The surface and core atoms play different roles in the melting behaviors of these nanowires. The core atoms have a dominating effect on the melting at the beginning stage, and the surface atoms are involved in the melting at higher temperature region. The core melting is closely related to the interior atomic structural characters. (4) The interior melting behavior is ultimately attributed to the helical multiwalled structure, where interior atoms have larger interatomic distances compared to the surface atoms.

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