Atomistic simulations of the tensile and melting behavior of silicon nanowires*

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Abstract: Molecular dynamics simulations with Stillinger–Weber potential are used to study the tensile and melting behavior of single-crystalline silicon nanowires (SiNWs). The tensile tests show that the tensile behavior of the SiNWs is strongly dependent on the simulation temperature, the strain rate, and the diameter of the nanowires. For a given diameter, the critical load significantly decreases as the temperature increases and also as the strain rate decreases. Additionally, the critical load increases as the diameter increases. Moreover, the melting tests demonstrate that both melting temperature and melting heat of the SiNWs decrease with decreasing diameter and length, due to the increase in surface energy. The melting process of SiNWs with increasing temperature is also investigated.

Key words: Si nanowires; molecular dynamics; tensile behavior; melting behavior
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1. Introduction

In recent years, one-dimensional semiconductor nanostructures have attracted great interest for their tremendous technological potential in nanoscale devices[1, 2]. Utilizing the structure at the nanometer level is key technology in the development of electronic devices and elements of nanoelectromechanical systems (NEMS). Therefore, it is important to understand the mechanical properties for engineering usefulness, such as design of reliability in service. Silicon nanowires (SiNWs) appear to be an especially appealing choice due to their compatibility with conventional Si-based electronic technology. Recently, SiNWs have been synthesized by solution techniques[3], an oxide-assisted catalyst-free method[4, 5], and a metal-catalytic vapour-liquid-solid method[6–8]. High resolution electron microscopy experiments have shown that the resulting SiNWs carry cores with monocrystalline bulk structures[7, 9].

Theoretical investigations, based on quantum mechanical principles, have been conducted to calculate the properties of the SiNWs[10–15]. Attention was mainly paid to the microstructural and electronic properties of the SiNWs. The mechanical strength of the nanowires plays an important role in maintaining the structural integrity of the structures, devices, or systems. However, such calculations are very complicated and expensive. Size-dependent and thermodynamical properties of nanowires are still unattainable using such methods. Molecular dynamics (MD) simulations are nowadays being used to study the mechanical behavior and deformation mechanisms of nanostructures. A number of studies have used MD simulations to analyze the tensile failure modes in metal nanowires[16–19]. Metal nanowires have been found to exhibit unique physical behavior under tensile load. However, studies on the mechanical characteristics of SiNWs are less reported[20, 21]. Although empirical methods carry a considerable simplification of the underlying atomistic processes, they still represent an alternative to access these important nanowire properties[20, 22].

This paper is mainly concerned with the tensile and melting behavior of SiNWs. The effects of the temperature, the strain rate, and the cross-sectional dimension on the mechanical properties are studied. The size effect on the melting temperature of SiNWs is also investigated.

2. Simulation method

Figure 1 shows the optimized structures of single crystalline SiNWs. The geometry is the same as those of the nanowires in Refs. [7, 9]. It is oriented along the [110] direction and has a hexagonal cross-section with four (111) and two (100) lateral surfaces.

The atomic interactions are described using the Stillinger–Weber (SW) potential[23]. The empirical SW interatomic potential consists of two- and three-body interaction terms and was originally fitted to describe crystalline and liquid silicon phases. The two-body potential describes the formation of a chemical bond between two atoms. The three-body

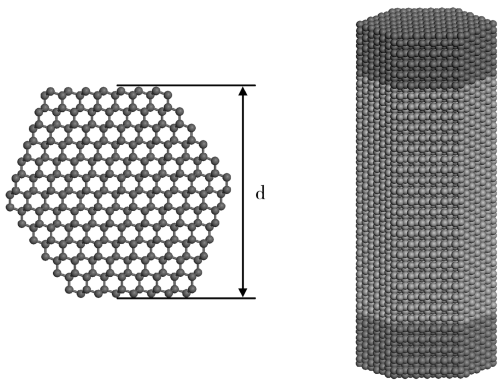

Fig. 1. Top and side views of the optimized structures of single crystalline SiNWs.

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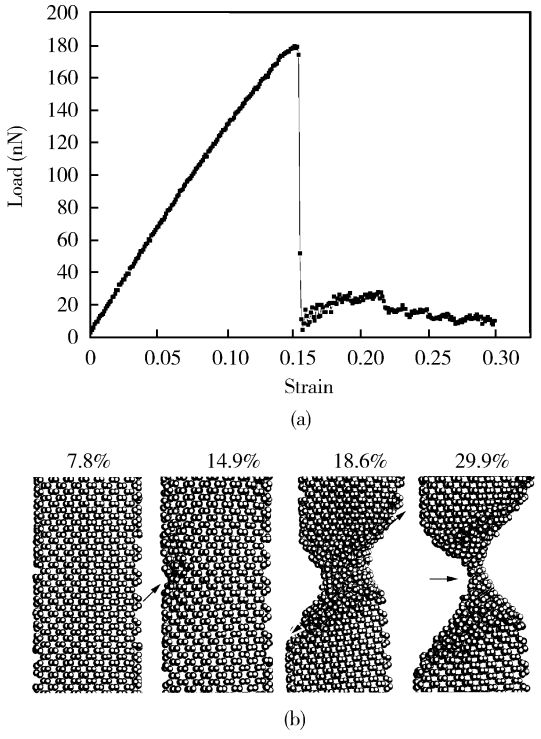

Fig. 2. (a) Load-strain curve of the SiNW with length 10 nm and diameter 3.89 nm, simulated with a strain rate of 0.04% ps^{-1} at 300 K; (b) Snapshots of atomic configurations at various strains.

potential is particularly suitable for structures in which the angles between two bonds made by the same atom are close to the tetrahedral angle. The SW potential has been used in the study of molten Si[23] as well as surfaces of crystalline Si[24]. The SW potential has also been adopted for the study of SiNWs and found to give good results for nanowire properties[20, 22]. Therefore, the SW potential should be reliable to study the mechanical properties of SiNWs.

The loading state in the present tension simulations is as follows: the load is applied along the axis, and five atomic layers, located at the top and bottom of the SiNWs, respectively, are set as fixed layers during each loading step; the other layers are set as thermal controlled layers, as illustrated in Fig. 1. The system temperature is controlled by rescaling the atom velocities[25]. The SiNWs are initially annealed at 700 K over a period of 10^6 time-steps, where each step is separated by an interval of 0.5 fs, and then the structures of the nanowires are dynamically relaxed at a given temperature for 50 ps with traction-free boundary conditions. Finally, stable configurations of the nanowires are obtained. The strain was then applied along the axial direction to study the mechanical properties of SiNWs. In order to investigate the relative influences of the temperature, the strain rate, and the cross-sectional dimension on the mechanical properties of the current SiNWs under tensile loading conditions, the computational simulations are carried out at temperatures in the range of 10 to 1200 K, with strain rates varying from 2×10^{-4} to 2×10^{-2} ps^{-1} and the wire diameters ranging from 3.89 to 6.14 nm. For the melting simulations, the initial configuration is relaxed at 300 K for 50 ps with traction-free boundary conditions. The heating process is simulated by a temperature increment of T = 100 K.

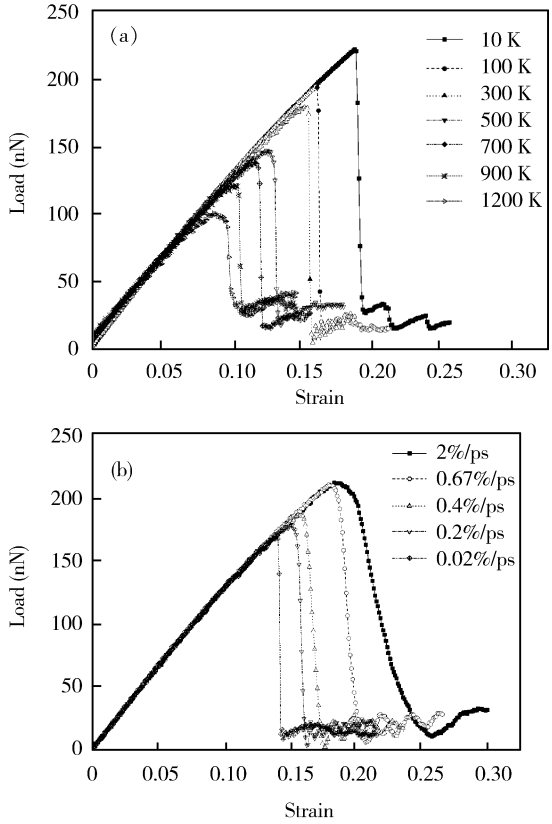

Fig. 3. Load-strain curves for the SiNWs under tensile load. The tensile behavior of the SiNWs is affected by (a) temperature and (b) strain rate.

However, a temperature increment of T = 50 K is applied near the melting region. For each temperature interval, the MD cell was relaxed for 50 ps.

3. Results and discussion

The computational results of the MD simulation are presented, and the deformation characteristics of the nanowire in uniaxial tension are shown first. The effects of the temperature, the strain rate, and the cross-sectional dimension on the mechanical properties of the nanowires are subsequently given. Finally, the melting process and associated properties of the SiNWs are presented.

3.1. Tensile properties of the SiNWs

Figure 2(a) shows an axial load-strain curve for a SiNW having a length of 10 nm and a diameter of 3.89 nm, which is simulated with a strain rate of 0.04%/ ps at 300 K. As shown in this figure, the load increases up to a maximum value of 179 nN corresponding to a strain of 0.15, then the load suddenly decreases to 11 nN, where the plastic zone is developed. For low strains ($\varepsilon < 0.05$), the load-strain relation is essentially linear in the elastic regime, and the Young's modulus can be directly evaluated in this elastic region. The Young's modulus is estimated to be 121.2 GPa according to the present model, which is consistent with experimental results of 93–180 GPa of SiNWs[26, 27]. The deformation process can be better understood by the wire evolution presented in Fig. 2(b). For small

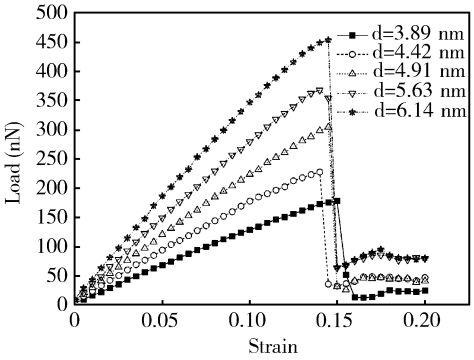

Fig. 4. Load-strain curves for different diameters.

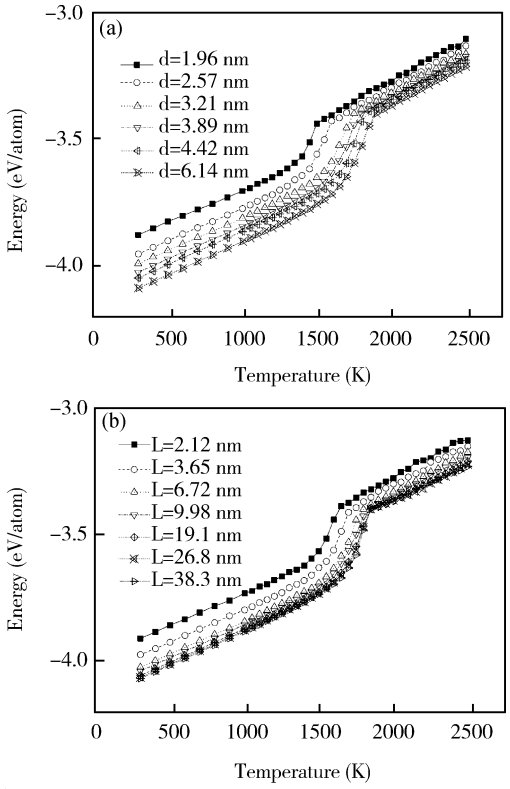

Fig. 5. Potential energy as a function of temperature for SiNWs. The melting properties of the SiNWs are affected by (a) diameter and (b) length.

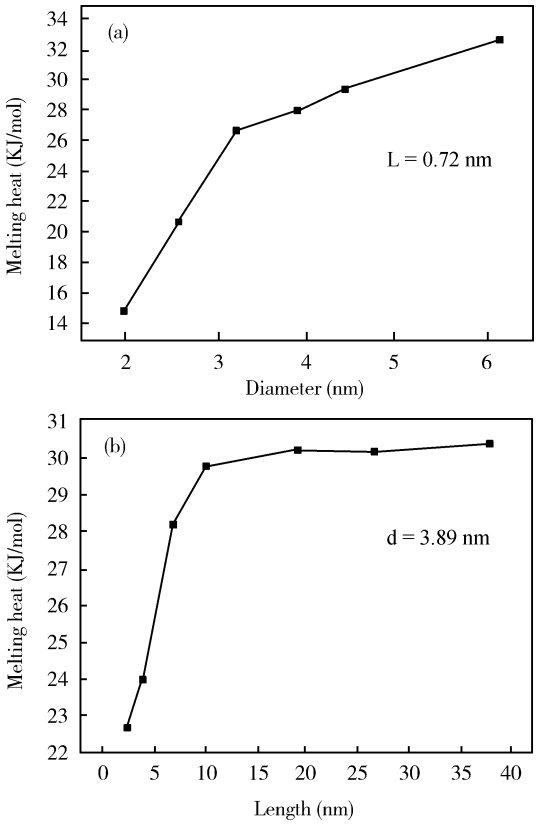

Fig. 6. Melting heat of SiNWs as a function of (a) diameter and (b) length .

strains, the bonds of the nanowire are just stretched and preserve their fourfold coordination in the nanowire, and no structural defects appear in this stage. For larger strains, bond breakage in the outmost layer is observed and spreads toward the central area as the strain increases. As the strain increases further, sliding along the $\{111\}$ plane takes place, and many atoms rearrange in the neck region. When a single crystal is stretched, the fundamental deformation mechanism is a shearing action based on the resolved shear stress on an active slip system. The silicon is a diamond structure and its slip plane is $\{111\}$[28], and in the present simulation the load is along the [110] orientation; the resolved shear stress on the $\{111\}$ plane induces sliding. After the formation of the neck, the plastic deformations evolve mainly through the reconstruction and rearrangement of the neck region, which was previously reported in other studies[16]. Beyond this region, the nanowire keeps the structure in order and has no further significant variation.

Since buckling occurs as a result of dynamic processes, the mechanisms of material deformation are influenced by both the temperature and the strain rate. Therefore, if material deformations in SiNWs are to be fully understood, the influence of these factors must be investigated. Figure 3 shows the effects of the temperature and the strain rate on the tension behavior. Figure 3(a) shows the axial load-strain curves of SiNWs with length 10 nm and diameter 3.89 nm, which are simulated within 10–1200 K with a strain rate of 0.04% ps^{-1}. The results clearly demonstrate that the critical load decreases as the temperature increases. In fact, for higher temperatures, the atomic structure has a relatively higher entropy, and the atoms vibrate about their equilibrium position with much larger amplitudes. In this case, a greater number of molecules may gain sufficient energy to overcome the activation energy barrier, and, hence, deformation occurs. This result suggests that a thermally activated process plays an activating role in the fracture of SiNWs. Figure 3(b) shows the axial load-strain curves of SiNWs with length 10 nm and diameter 3.89 nm, which are simulated at 300 K with strain rates varing from 0.02%/ps to 2%/ps. The strain rate adopted here is very high compared to that in experiment, because only a very short period of time can be simulated due to the time scale of molecular dynamics. One consequence of the short time scale is that very high strain rates are required to get a reasonable deformation within the available time[29]. For all strain rates, the load increases linearly with strain up to 0.13. Below this value, the load-strain curves almost completely overlap for all strain rates applied, indicating that no plastic deformation occurs and the

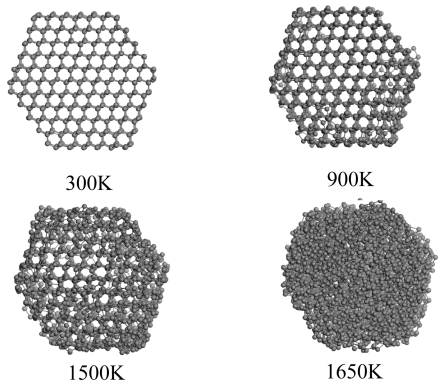

Fig. 7. Structural transitions of the SiNW with a diameter of 3.21 nm at different temperatures .

elastic modulus of a nanowire is insensitive to the strain rate. However, a slower strain rate may result in a lower critical load. Regarding the strain rate influence, the strain or deformation tends not to be uniformly distributed within the material, particularly when a large strain is applied. Hence, some regions of the nanowire are subjected to larger stresses or strains than other parts, and it is within these regions that defects will become evident first. When a lower strain rate is applied, the SiNWs have more time to induce adequate local deformation, and, hence, the onset of plastic deformation is accelerated. Therefore, a slower strain rate results in a lower critical load. The present results clearly demonstrate that the mechanical properties of SiNWs are sensitive to the strain rate and the temperature.

An important factor in evaluating the mechanical properties of a nanowire is the size effect. Physical and chemical properties of materials are expected to exhibit some dependencies on the dimensionality and the cross-sectional dimension. Figure 4 shows the axial load-strain curves for nanowires of length 10 nm with different diameters, which were simulated at 300 K with a strain rate of 0.04%/ ps. It is shown that the critical load decreases as the diameter of the nanowires decreases. Specifically, as the diameter decreases from 6.14 to 3.89 nm, the critical load decreases about 61%. The reason for this behavior may be due to the small atomic-coordination number and weak cohesion of the atoms near the surface. As compared with those in the bulk, the increasing dominance of the surface would degrade the strength of the structure.

3.2. Melting properties of the SiNWs

The effects of the cross-sectional dimension and the length on the melting properties of the SiNWs are studied. The variation of potential energies as a function of temperature is shown in Fig. 5. As can be seen from this figure, the energy generally increases with decreasing diameter and length of SiNWs at a given temperature, which indicates that the surface energy increases with decreasing diameter and length. The potential energies also increase linearly with increasing temperature and change abruptly when the melting takes place. The melting temperature is defined as a point of an abrupt change in the potential energies during the heating process. From Fig. 5, it is found that the melting temperature of SiNWs increases as the diameter increases and as the length increases, which is consistent with the fact that the melting behavior of nanostructure materials is strongly dependent upon size. Figure 6 shows the variation of the melting heat as a function of the diameter and the length of SiNWs, respectively. It is observed that the melting heat of SiNWs is lower than that of the bulk silicon (50.55 kJ/mol) and increases as the diameter increases or the length increases. It can be seen from Fig. 6 that the melting heat increases rapidly for relatively small sizes and increases slowly for larger sizes. Moreover, the melting heat converges to a definite value as the length increases. In general, the thermodynamic property of nanostructures is different from the bulk materials[30]. The change of the melting temperature of nanostructures depends on their surface. This indicates that the unstable surface of free-standing nanowires leads to a decrease in both of the melting temperature and the melting heat.

To understand the melting behavior of SiNWs, the structural evolution of the nanowire with a length of 6.72 nm and a diameter of 3.21 nm at different temperatures during the heating process is shown in Fig. 7. Before the melting takes place, the atoms of the SiNW oscillate at their equilibrium position. During the melting process, the unstable atoms on the edge move to the facet of the SiNW. It should also be noted that at 1500 K, which is 150 K below the melting point, several atoms in the central region of the nanowires are still located in the crystalline configurations. However, when the temperature is increased to 1650 K, none of the atoms are kept in their lattice configurations, and the atomic positions are disordered. The nanowire finally collapses, which indicates the melting of the nanowire.

4. Conclusions

In this paper, the classical MD method is used to simulate the tensile and melting behaviors of SiNWs. It is found that the tensile behavior of the SiNWs is strongly dependent upon the temperature, the strain rate, and the diameter of the SiNWs. The critical load decreases as the temperature increases, which indicates that a thermally activated process plays an activating role in the collapse of SiNWs. The critical load increases as the strain rate increases, but Young's modulus is independent of the strain rate. Regarding the size effect, it can be seen that the critical load increases when increasing the diameter. In addition, it is observed that the melting behavior is obviously size dependent. Both the melting temperature and the melting heat of the SiNWs decrease with decreasing diameter or length, due to the increase of the surface energy. This indicates that the unstable surface of free-standing nanowires leads to a decrease in both of the melting temperature and the melting heat. The melting process of SiNWs with increasing temperature is simulated in detail and it can be seen that the melting begins from the edge to the outside surface, and, finally, to the centre of the cross section of the SiNWs.

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