Vol 18 No 7, July 2009
1674-1056/2009/18(07)/2920-05

Chinese Physics B

© 2009 Chin. Phys. Soc.
and IOP Publishing Ltd

Thermal stability of silicon nanowires: atomistic simulation study*

Liu Wen-Liang(刘文亮)†, Zhang Kai-Wang(张凯旺), and Zhong Jian-Xin(钟建新)

Department of Physics, Xiangtan University, Xiangtan 411105, China

(Received 9 June 2008; revised manuscript received 30 July 2008)

Using the Stillinger–Weber (SW) potential model, we investigate the thermal stability of pristine silicon nanowires based on classical molecular dynamics (MD) simulations. We explore the structural evolutions and the Lindemann indices of silicon nanowires at different temperatures in order to unveil atomic-level melting behaviour of silicon nanowires. The simulation results show that silicon nanowires with surface reconstructions have higher thermal stability than those without surface reconstructions, and that silicon nanowires with perpendicular dimmer rows on the two (100) surfaces have somewhat higher thermal stability than nanowires with parallel dimmer rows on the two (100) surfaces. Furthermore, the melting temperature of silicon nanowires increases as their diameter increases and reaches a saturation value close to the melting temperature of bulk silicon. The value of the Lindemann index for melting silicon nanowires is 0.037.

Keywords: molecular dynamics, silicon nanowires, thermal stability, melting points
PACC: 6322, 7115Q, 9160K

1. Introduction

Compared with bulk materials, low-dimensional nanoscale materials with large surface areas and possible quantum confinement effects, exhibit distinct properties. Semiconductor nanowires are promising nanomaterials for novel electronic,[1] optoelectronic,[2] and sensing[3] applications. The thermal stability of nanowires is of critical importance for their implementation as building blocks in nanoscale electronic and photonic devices. Silicon nanowires with various morphologies were found to be able to form at different temperatures, in addition, many other types of Si nanostructures were also found to have significant yields.[4] These nanostructures are believed to evolve from Si nanowires through spheroidization, a process that involves material transport along individual nanowires. It was also found[4] that annealing temperatures played an important role in determining the relative ratios of these nanostructures in the products. Therefore, it is possible to control the morphology and crystallinity of Si nanostructres by simply varying the temperature. On the other hand, it is well known that the surface structure of bulk silicon is sensitive to the ambient temperature.[5]

In recent years, considerable attention has been paid to the thermal stability of small cluster and 1D nanostructures.[6] It has been well documented that the melting point of a solid material is greatly reduced when it becomes of nanostructure.[7] It is reasonable to assume that the melting behaviour of semiconductor nanowires evolves gradually from a nanoscale material behaviour towards a bulk material behaviour as their diameter increases. However, it is very difficult to confirm this assumption experimentally. Molecular dynamics (MD) simulations can give a valuable insight into the physical essence of nanowires when the dependence of their thermodynamic behaviour on their diameter size is attempted to be clarified. A review of the available literature reveals that the majority of published theoretical and experimental studies concentrate primarily on the melting phenomena of nanoscale clusters and other 1D nanostructures.[6] In contrast, the thermal stability of semiconductor nanowires has received relatively little attention. It is necessary to develop a quantitative understanding of their thermodynamic properties, since semiconductor nanowires have a number of important potential applications in nanoscale electronic devices.[1−3] An understanding of the thermal stability of semicondutor nanowires is essential for many important applications.

*Project supported by the National Natural Science Foundation of China (Grant No 10774127).
†Corresponding author. E-mail: wlliu1981@gmail.com

In order to quantitatively investigate the melting temperature of silicon nanowires, we used empirical rules. Empirical rules, such as the Lindemann criterion, have long been used to characterize the melting transitions of solids and have been found to be very useful for identifying the onset of melting.[8−13] However, it is unknown whether the Lindemann criterion holds for semiconductor nanowires. In the present paper, we employ pristine silicon nanowires to investigate the melting behaviour of semiconductor nanowires and obtain the Lindemann index for melting transitions. We investigate the atomic-level melting behaviours of silicon nanowires by observing the morphological change of silicon nanowires at different temperatures. Meanwhile, we examine the critical Lindemann parameter δ which is used for determining whether silicon nanowires are melting. The rest of the present paper is organized as follows. In Section 2, the Stillinger-Weber (SW) potential model[4] is described. The results and a brief discussion are presented in Section 3. Finally, some conclusions drawn from the present study are given in Section 4.

2. Method

The interaction potential employed for the present study has an SW form,[14] which is one of the most suitable potentials for teterahedral semiconductors such as bulk materials. The potential was used to reproduce bulk structures, but it has been also successfully applied to nanowires and clusters.[14,15] These calculations have demonstrated that the empirical SW potential for silicon nanostructures can be employed to study the thermal properties of homogeneous materials of silicon. In addition, the potential can handle dangling bonds, wrong bonds, and excess bonds in bulk silicon very well. Therefore, this potential should be reliable to study the thermal stability of silicon nanowires.

In our molecular dynamics simulation, the many-body SW potential is used to describe the Si–Si interaction and the cut-off distance is chosen to be 1nm. Periodic boundary conditions are applied only along the axial direction of a silicon nanowire. Sufficient vacuum space is provided in non-axial directions to model the one-dimensional system. Temperature is controlled by the velocity scaling method and an NTV (constant-particle number/constant-temperature/constant-volume dynamics) ensemble is employed for the simulation environment. In all the simulations, a time step of 2 fs is used. Successive equilibrium calculations are carried out by increasing the temperature in steps of of 100 K. For each temperature step, the cell maintains equilibrium for 200 ps.

We use the distance-fluctuation Lindemann index to identify the melting temperature of silicon nanowires. For a system of N atoms, the local Lindemann index for the ith atom in the system is defined as[15,16]

$$\delta_i = \frac{1}{N-1} \sum_{j(\neq i)} \frac{\sqrt{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle_T^2}}{\langle r_{ij} \rangle_T}$$

and the system-averaged Lindemann index is given by

$$\delta = \frac{1}{N} \sum_i \delta_i,$$

where r_{ij} is the distance between the ith and jth atoms and $\langle \ldots \rangle_T$ denotes the thermal average at temperature T. The Lindemann index is small and increases slowly and linearly with temperature increasing before melting due to the stable constraint of the atomic potentials and the linear increase in kinetic energy. On the melting side, however, the index is expected to be sensitive to temperature change and deviate from linear behaviour.

3. Results and discussion

Figure 1 shows three silicon nanowires with different surface structures, which are cited from our previous studies.[17] The three silicon nanowires are oriented along the [110] direction and bounded by the

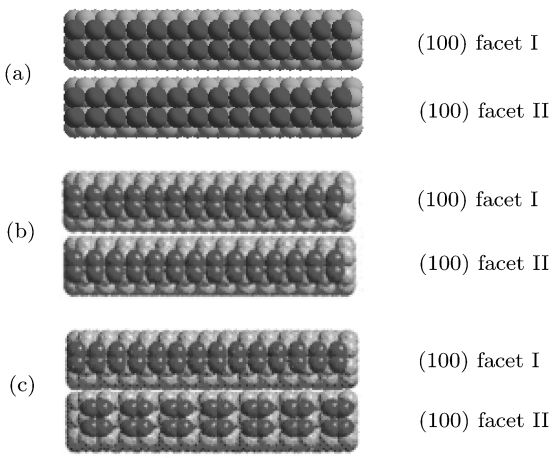


Fig.1. (a) NW1, (b) NW2 and (c) NW3 Si nanowires with different (100) surface structures along the [110] direction bounded by (100) surfaces and (110) surfaces.

(100) and (110) surfaces in lateral directions. The silicon nanowires have different (100) surface structures, namely, nanowires without reconstructions in Fig.1(a) for NW1 and nanowires with surface dimmer reconstructions in Figs.1(b) and 2(c). The dimmer rows on the two (100) surfaces are parallel to each other, in Fig.1(b) for NW2 and are perpendicular to each other in Fig.1(c) for NW3. Figure 2 shows the images of atom positions projected onto the plane of the nanowires (parallel to the axis of the nanowires) for NW1, NW2, and NW3 in Figs.2(a), 2(b) and 2(c) respectively. We discuss the structural evolution of silicon nanowires during the melting process. Figure 2 shows that the morphologies of silicon nanowires undergo significant changes around the melting point, indicating that the melting point of silicon nanowires is between 900 and 1300 K. It is clear that the disorder increases with the increase in temperature. This provides direct evidence of melting the silicon nanowires. Above 1300 K, the silicon nanowires collapse into liquid-like droplets. It is interesting to note that the atoms diffuse along the wire axis direction as a rise in temperature occurs.

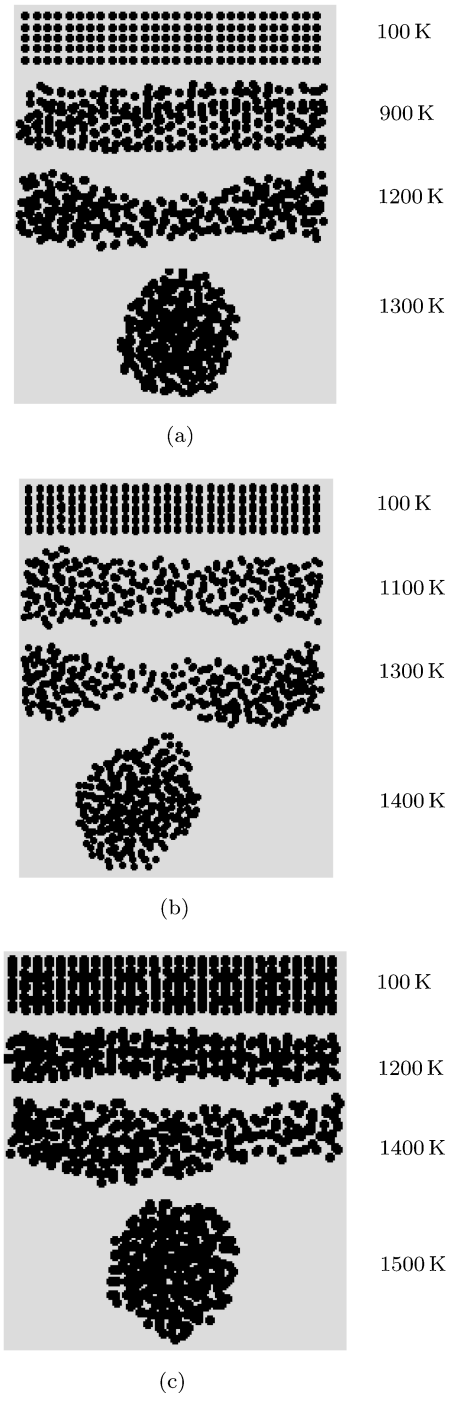


Fig.2. Structural evolutions of (a) NW1, (b) NW2 and (c) NW3 Si nanowires with temperature.

To precisely locate the melting temperature, we calculate the Lindemann indexes at different temperatures. Figure 3 shows the temperature dependences of the Lindemann index of silicon nanowires and several atomic plots at different temperatures illustrating the melting process. The Lindemann index is small and increases slowly and linearly with the increase of temperature before melting due to the stable constraint of the atomic potentials and the linear increase in kinetic energy. However, the index is expected to be sensitive to the temperature change and deviate from the linear behaviour. Therefore, silicon nanowires are melted when the Lindemann index deviates from the linear behaviour. The temperature dependences of Lindemann index δ in Fig.3 show that δ exhibites very different behaviours around 900, 1100 and 1200 K. It is evident that the melting points of the three types of silicon nanowires are 900, 1100 and 1200 K, respectively. They turn into liquid-like droplets at 1300, 1400 and 1500 K, respectively. It is also clear that the melting process can be divided into three stages

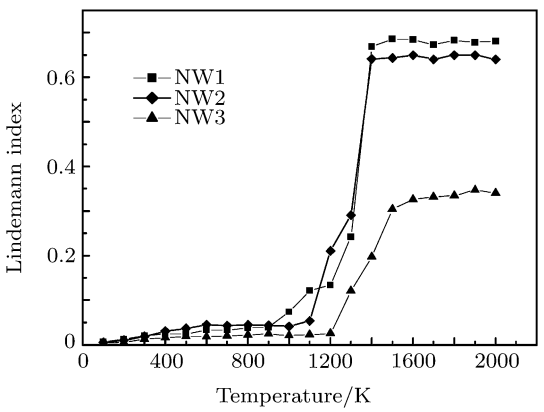


Fig.3. Temperature dependences of the Lindemann index for NW1, NW2 and NW3 Si nanowires.

in Fig.3. Below melting point, the Lindemann index δ increases slowly and linearly with the increase of temperature, showing a typical behaviour of atomic thermal vibration around the original position. The Lindemann index starts to deviate from the linear behaviour and sharply increases around the melting temperature. The melting points of the three types of silicon nanowires are different from each other by about 100–200 K, which is important to homogeneous materials of silicon.

We also investigate the effect of size on the melting of silicon nanowires with [100] axial direction and [100]-oriented facets. Initial structures with different diameters are directly cut from bulk silicon. We name these nanowires Si3, Si4, Si5, Si6, Si7, Si8, and Si9 with diameters ranging from 0.859 to 2.715 nm. Figure 4 shows the temperature dependences of the Lindemann index of these silicon nanowires. It is evident that the melting points of these silicon nanowires are 400, 800, 900, 1100, 1200, 1300 and 1500 K, respectively. Corresponding to the melting temperatures of silicon nanowires, the Lindemann indices are 0.0345, 0.0344, 0.0362, 0.0371, 0.0388, 0.0350 and 0.0421 with an average value of 0.037.

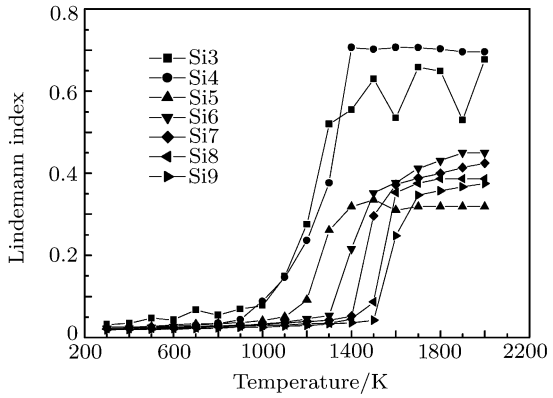


Fig.4. Temperature dependences of the Lindemann index for un-optimized Si nanowires along the [100] direction bounded by (100) surfaces, with diameters of Si3, Si4, Si5, Si6, Si7, Si8, and Si9 nanowires being 0.859, 1.086, 1.385, 1.629, 1.920, 2.172, and 2.715nm, respectively.

Our computation results are comparable with recent measurements. Temperature was found to be the critical factor for controlling both the diameter of silicon nanowires and the formation of various kinds of silicon nanowire-related morphologies, and silicon nanowires were found to grow in a temperature range from 1150 to 1500 K, whose diameter decreased remarkably with the growth temperature decrease. The experimental results indicated that the melting temperature of the silicon nanowires was lower than that of bulk silicon (1683 K) and decreased with the diameter of the nanowires decreasing. It is very difficult to confirm our computation results in experiment directly for different diameters of silicon nanowires, since what we simulate here is pristine silicon nanowires. For silicon nanowires with different surface structures, it is more difficult to distinguish discrepancies among their melting points experimentally. We predicted theoretically the melting point of pristine silicon nanowires which is in agreement with the relevant measured value.[4]

The remarkable reduction in melting temperature of silicon nanowires has several important implications. First, the annealing temperature necessary for the synthesis of defect-free nanowires might only be a small fraction of the annealing temperature required for the bulk material. It is thus possible to perform zone-refining to purify nanowires at a modest temperature. Second, a reduction in melting point enables one to cut, interconnect, and weld nanowires at a relatively mild temperature. This capability may provide a new tool to integrate these 1D nanostructures into functional devices and circuitry. Third, as the thickness of nanowires is reduced to a smaller and smaller length scale, their stabilities may be extremely sensitive to the change in ambient condition, such as temperature fluctuation and residual stress variation. Driven by Rayleigh instability, nanowires may spontaneously undergo a spheroidization process to break up into shorter segments at room temperature to reduce the relatively high free energy associated with a 1D system, when their diameter is sufficiently small or their bonding between constituent atoms is too weak.

4. Conclusions

Using molecular dynamics simulation and the Lindemann index for melting, we study the melting behaviour of silicon nanowires. We investigate the morphological changes of silicon nanowires at different temperatures and adopt the Lindemann index to accurately confirm the melting temperature of the silicon nanowires. From the morphological change of silicon nanowires, we can clearly learn the melting behaviour of the silicon nanowires. We also find that the critical Lindemann parameter in a range of 0.1–0.15, which is widely used for determing the melting temperatures of bulk solids, is not applicable to silicon nanowires.

The melting of silicon nanowires occurs when the Lindemann index δ is in a range of 0.03–0.05 with an average value of 0.037. Silicon nanowires with surface reconstructions have higher thermal stability than those without reconstructions. Silicon nanowires with perpendicular dimmer rows on their two (100) surfaces have higher thermal stability than the nanowires with parallel dimmer rows on their two (100) surfaces. Our results show that the melting temperatures of silicon nanowires with small diameters are much lower than that of bulk silicon. The melting temperature of silicon nanowires increases with the increase of the diameter of the nanowires and eventually reaches a value corresponding to the melting temperature of bulk silicon, 1683 K.

References

[1] Chung S W, Yu J Y and Heath J R 2000 *Appl. Phys. Lett.* **76** 2068
Cui Y and Lieber C M 2001 *Science* **291** 851
Huang y, Duan X F, Cui Y, Lauhon L J, Kim K H and Lieber C M 2001 *Science* **294** 1313
Duan X F, Huang Y, Cui Y, Wang J F and Lieber C M 2004 *Nature* **409** 66
Zheng G, Lu W, Jin S and Lieber C M 2004 *Adv. Mater.* **16** 1890

[2] Duan X F, Huang Y, Agarwal R and Lieber C M 2003 *Nature* **421** 241
Huang M H, Mao S, Feick H, Yan H Q, Wu Y Y, Kind H, Weber E, Russo R and Yang P D 2001 *Science* **292**
Wang J F, Gudiksen M S, Duan X F, Cui Y and Lieber C M 2001 **293** 1455
Gudiksen M S, Lauhon L J , Wang J, Kim K H and Lieber C M 2002 *Nature* **415** 617

[3] Cui Y, Wei Q Q, Park H K and Lieber C M 2001 *Science* **293** 1289
Wang W U, Chen C, Lin K, Fang Y and Lieber C M 2005 *Proc. Natl. Acad. Sci.* U.S.A. **102** 3208
Patolsky F, Zheng G, Hayden O, Lakadamyali M, Zhuang X and Lieber C M 2004 *Proc. Natl. Acad. Sci.* U.S.A. **101** 14017

[4] Pan Z W, Dai Z R, Xu L, Lee S T and Wang Z L 2001 *J. Phys. Chem.* B **105** 2507
Peng H Y, Pan Z W, Xu L, Fan X H, Wang N, Lee C S and Lee S T 2001 *Adv. Mater.* **13** 317

[5] Buffat P and Borel J P 1976 *Phys. Rev.* **13** 2287
Wu Y and Yang P 2001 *Adv. Mater.* **13** 520
Wu Y Y and Yang P D 2000 *Appl. Phys. Lett.* **77** 43

[6] Cleveland C L, Luedtke W D and Landman U 1999 *Phys. Rev.* B **60** 7
Wang B L, Wang G G, Chen X S and Zhao J J 2003 *Phys. Rev.* B **67** 193403
Werner R 2005 *Eur. Phys. J.* B **43** 47
Fang K C and Weng C I 2005 *Nanotechnology* **16** 250
Zhang K W, Meng L J, Li J, Liu W L, Tang Y and Zhong J X 2008 *Acta Phys. Sin.* **57** 7 (in Chinese)

[7] Tabata T, Aruga T and Murata Y 1987 *Surf. Sci. Lett.* **179** L63
Fukaya Y and Shigeta Y 2003 *Phys. Rev. Lett.* **91** 12

[8] Lindemann F A 1910 *Phys. Z.* **11** 609
Hansen J P and Verlet L 1969 *Phys. Rev.* **184** 151
Wen H L, Palberg T and Simon R 1993 *Phys. Rev. Lett.* **70** 1557
Stillinger F H 1995 *Science* **267** 1935

[9] Wen H L 1994 *Phys. Rep.* **237** 249

[10] Bilgram J H 1987 *Phys. Rep.* **153** 1

[11] Young D A and Alder B J 1974 *J. Chem. Phys.* **60** 1254
Meijer E J and Frenkel D 1991 *J. Chem. Phys.* **93** 2269

[12] Stillinger F H and Stillinger D K 1990 *J. Chem. Phys.* **93** 6013
Zhou Y, Karplus M, Wichert J M and Hall C K 1997 *J. Chem. Phys.* **107** 1069
Zhou Y and Karplus M 1997 *Proc. Natl. Acad. Sci.* U.S.A. **94** 14429
Zhou Y, Vitkup D and Karplus M 1999 *J. Mol. Biol.* **285** 1371
Wang J L, Chen X S, Wang G H, Wang B L, Lu W and Zhao J J 2002 *Phys. Rev.* B **66** 085408

[13] Zhou Y Q, Karplus M, Ball K D and Berry R S 2002 *J. Chem. Phys.* **116** 5
Zhang K W, Stocks G M and Zhong J X 2007 *Nanotechnology* **18** 285703

[14] Stillinger F and Weber T A 1985 *Phys. Rev.* B **31** 5262

[15] Wang Z G, Zu X T, Gao F and Weber W J 2006 *J. Appl. Phys.* **100** 063503

[16] Ding F, Bolton K and Rosen A 2005 *Eur. Phys. J.* D **34** 275

[17] Liu W L, Zhang K W, Xiao H P, Meng L J, Li J, Stocks G M and Zhong J X 2007 *Nanotechnology* **18** 215703