

Metallic Beta-Phase Silicon Nanowires: Structure and Electronic Properties

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Electronic band structure and energetic stability of two types of $\langle 110 \rangle$ and $\langle 001 \rangle$ oriented silicon nanowires in β -Sn phase with the surface terminated by hydrogen atoms were studied using density functional theory. It was found that β -Sn nanowires are metastable with zero band gap against to nanowires in diamond phase. The relative energy of the studied wires tends to the energy of the bulk silicon crystal in β -Sn phase.

Introduction. Silicon nanowires (SiNW) are the most perspective elements of nanotechnology. SiNW can be used in nanoelectronics as field-effect transistors, diodes, logic gates, and more. A huge number of theoretical [1–6] and experimental [7–10] papers devoted to investigation of properties of SiNW were published in the last years.

The structure and properties of silicon nanowires and nanorods under high pressure is almost a virgin field. Only two papers [11, 12] devoted to this topic were published. In these works a study of the silicon nanowires in different high-pressured phases was reported. In particular, it was found that the SiNWs start to transform from initial diamond to β -Sn phase in the range of 7.5 to 10.5 GPa [11, 12].

Despite of low activity of investigations of high pressured nanowires a plenty of experimental [13–16] and theoretical [17–20] studies of the high-pressure phases of bulk silicon were carried out. The existence of silicon nanowires in new phases opens a new promising field in the nanomaterial science due to their useful electronic properties. In particular, the silicon nanowires in β -Sn phase have larger bulk modulus than the bulk module of corresponding crystal [11].

The main goal of this paper is an *ab-initio* study of hydrogen-covered thin SiNWs β -Sn phase. [11, 12]. The stability, electronic properties of the structures were calculated and compared with SiNW in diamond phase. Also, the dependence of transition pressure upon the size of the SiNW was observed.

Method of calculations. The electronic structure calculations of a set of silicon nanowires were carried out using density functional theory (DFT) in the frame-

work of local density approximation [21–23] with periodic boundary conditions using Vienna Ab-initio Simulation Program [24–26]. We used a planewave basis set, ultrasoft Vanderbilt pseudopotentials [27] and a plane-wave energy cutoff equal to 200 eV. To calculate the equilibrium atomic structures, the Brillouin zone was sampled according to the Monkhorst-Pack [28] scheme with a 0.1 \AA^{-1} k -points density grid. To avoid interactions with the wire periodic image, the neighboring SiNWs were separated by 15 \AA in the tetragonal supercells. During atomic structure minimization, structural relaxation was performed until the change in total energy was less than 10^{-3} eV/atom.

At the DFT level of theory the lattice parameter of the β -Sn phases of bulk silicon was predicted with an error of 1.5% ($a_{\text{calc}} = 4.76 \text{ \AA}$, $a_{\text{exp}} = 4.69 \text{ \AA}$ [16], $(c/a)_{\text{calc}} = 0.551$ [17, 19], $(c/a)_{\text{exp}} = 0.550 \pm 0.002$ [16], 0.554 [14]). The energy difference between the diamond and β -Sn phases of silicon is 0.22 eV/atom, which is in close agreement with previous DFT calculations of 0.22 [17] and 0.21 eV/atom [20].

Results and discussion. The atomic structures of silicon in diamond ($m3m$ cubic unit cell) and β -Sn phases ($4/mmm$ tetragonal unit cell) are presented in Fig.1a. Different symmetries dictate the different notations of the crystallographic directions of the crystals. a and b crystallographic axes of the β -Sn unit cell are rotated on 45° relative to the corresponding axes of the diamond cell. Due to this and $a = b \neq c$ in the tetragonal unit cell, the equivalent $\langle 100 \rangle$, $\langle 010 \rangle$ and $\langle 001 \rangle$ directions in diamond phase correspond to equivalent $\langle 110 \rangle$, $\langle \bar{1}10 \rangle$ and non-equivalent $\langle 001 \rangle$ directions in β -Sn phase. We studied the $\langle 110 \rangle$ (Fig.1b) and $\langle 001 \rangle$ (Fig.1c) oriented SiNWs truncated from the bulk silicon in β -Sn phase and compared them with

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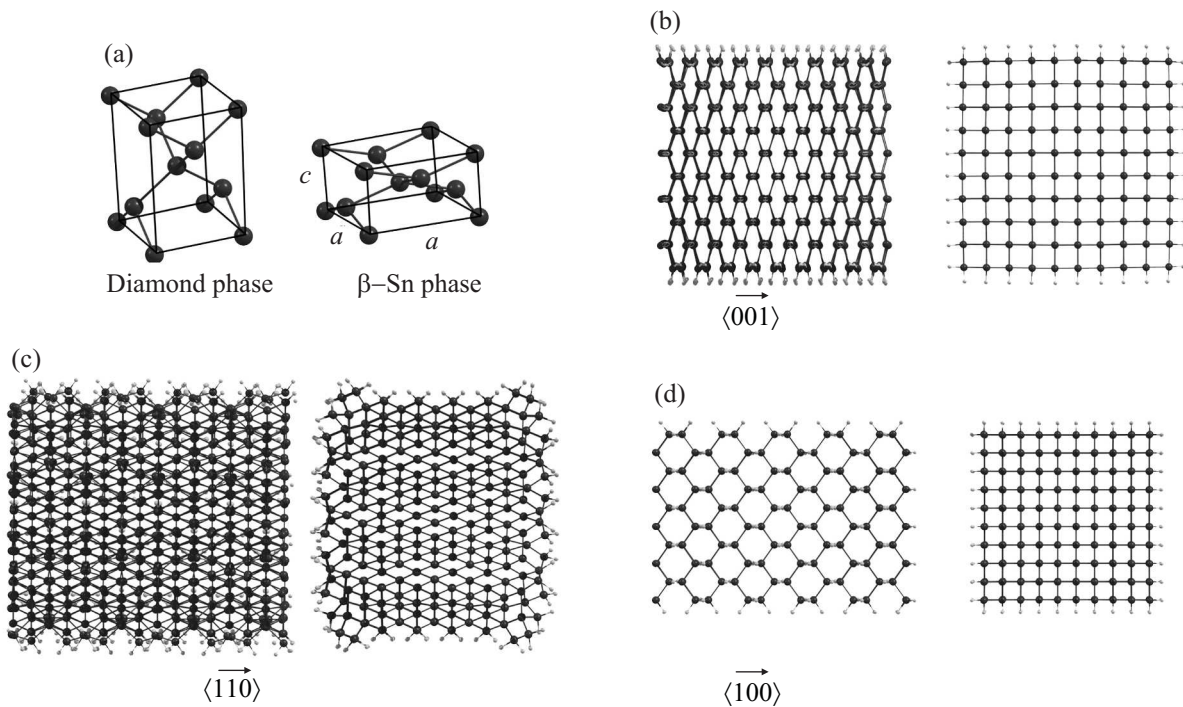


Fig.1. (a) The bulk silicon unit cells in diamond and β -Sn phases; Side and cross-section views of (b) $\langle 001 \rangle$ SiNW in β -Sn phase, (c) $\langle 110 \rangle$ SiNW in β -Sn phase and (d) $\langle 100 \rangle$ SiNW in diamond phase

$\langle 100 \rangle$ wires of different effective sizes truncated from the bulk silicon in diamond phase (Fig.1d). The size of studied SiNW was chosen according to [10] where the nanometer-size silicon wires were produced.

To study the electronic structure and energetic stability of SiNWs, the uniformly hydrogen-covered silicon nanowires were calculated. Hydrogen passivation prevents reconstruction of the surface of silicon wires under the study and conserves the conducting properties of the materials. For example, unpassivated $\langle 100 \rangle$ oriented silicon nanowires in diamond phase reveal metallic properties, whereas hydrogen passivation restores the semi-conducting band gap [1, 6].

It was found that in comparison with the parent crystal, the deviation of the Si-Si bond lengths inside both $\langle 001 \rangle$ and $\langle 110 \rangle$ oriented β -Sn SiNWs is less than 1.5% with wider distribution of the bond lengths on the wires surface. Orientation and the surface relaxation of the $\langle 110 \rangle$ β -Sn SiNWs determine wider bond length deviation on the surface (up to 4.4 %). The $\langle 001 \rangle$ oriented β -Sn wires display smaller surface relaxation with deviation of the bond lengths on the surface up to 2.7%.

To determine the effective size of the nanowires under study, the area of perpendicular cross-section of the species [2, 3] was used. Some other methods, like the determination of a single effective diameter of a nanowire

as the smallest diameter taken from a perpendicular cross section [3] or the smallest cylinder containing a nanowire [4, 5] are not unambiguous and cannot be applied to species with complex shapes and different facets. The cross-section of SiNW was taken as the polygonal region which was defined by the surface hydrogen atoms.

The 1D nature and high surface tension of the wires are expected to imply an increasing of the strain of the structures. The dependence of SiNWs relative energies upon the cross-section area is presented in Fig.2. The nanowires relative energy is defined as energy per atom of a wire of given cross-section area relatively to the energy per atom of bulk silicon in diamond phase.

The dependence of nanowires relative energy upon the size can be approximated by the power law. The data points of the energy were fitted to $E_{rel} = A \cdot S^c + E_0$ where E_0 is the energy of the corresponding crystal, S is the cross-section area, A and c are fitting parameters. The E_0 for SiNWs in diamond phase was defined as 0 and for SiNWs in β -Sn phase as 0.22 eV/atom. The A and c parameters calculated using E_0 values are presented in Table.

The SiNWs in diamond phase are energetically favorable the SiNWs in β -Sn phase with close cross-section areas. The difference of the energies of the wires in β -Sn phase of different orientations tends to zero with increasing of the wire size. In the paper [29] was concluded that

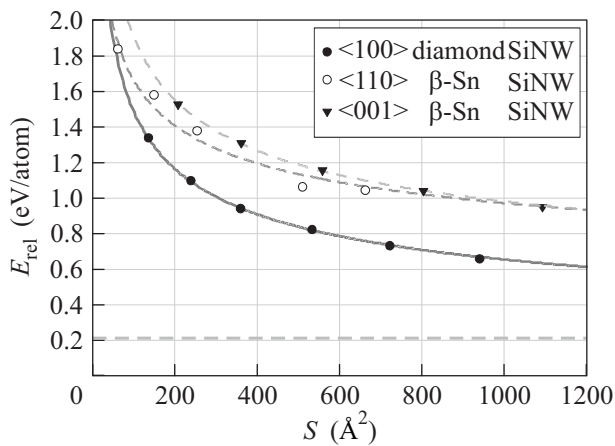


Fig.2. The relative energy (E_{rel}) as a function of SiNW cross-section area. E_{rel} of SiNWs in β -Sn phase of $\langle 110 \rangle$ orientation is marked by empty circles with dashed approximating curve. The SiNWs in β -Sn phase of $\langle 001 \rangle$ orientation is marked by filled triangles with dashed approximating curve. The relative energy of SiNWs in diamond phase is marked by filled circles with solid approximating curve. The relative energy of bulk silicon in β -Sn phase is marked by horizontal dashed line

strain- and defect-free β -Sn silicon nanocrystals and microcrystals would appear to be metastable at ambient conditions therefore we believe that studied nanowires remains in β -Sn phase after compression release.

A and c parameters of approximating curves of dependences of strain energies upon cross-section area of the studied SiNWs

	SiNW in diamond phase oriented in $\langle 100 \rangle$ direction	SiNW in β -Sn phase oriented in $\langle 110 \rangle$ direction	SiNW in β -Sn phase oriented in $\langle 001 \rangle$ direction
A	7.859	5.373	8.439
c	-0.3603	-0.285	-0.3483

SiNWs in β -Sn phase display metallic properties like bulk β -Sn silicon. In the case of the bulk obtained results agree with previously reported experimental [14, 15] and theoretical [18] papers. It should be mentioned that metallic nature of β -Sn SiNW and diamond SiNW without surface passivation is different. The metallic properties of β -Sn SiNW is induced by high pressure whereas metallic behavior of diamond SiNW without surface passivation is induced by the surface states [6].

The electronic band structures of the nanowires oriented in the same direction are similar. Also the band structure of studied SiNWs is similar to parent crystal bands in the corresponding directions. For example, the band structures of bulk silicon in β -Sn phase and $\langle 001 \rangle$ silicon nanowire in β -Sn phase with cross-section area

$19 \text{ \AA} \times 19 \text{ \AA} = 361.2 \text{ \AA}^2$ are presented in Fig.3a and 3b, respectively. Also the density of states of the studied

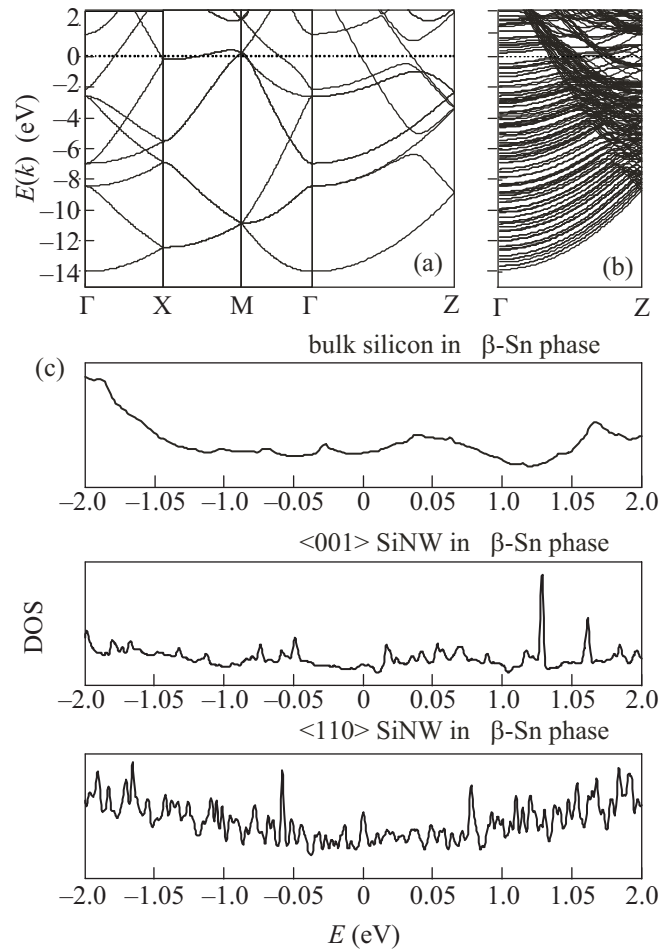


Fig.3. The electronic band structure of (a) bulk silicon in β -Sn phase, (b) $\langle 001 \rangle$ SiNW in β -Sn phase. Symmetry notations of Miller and Love [30], (c) density of states of bulk silicon in β -Sn phase, $\langle 001 \rangle$ SiNW with cross-section area 361.2 \AA^2 and $\langle 110 \rangle$ SiNWs with cross-section area 510.4 \AA^2 in β -Sn phase. The Fermi energies are equal to zero

structures is calculated. For example, DOSes of bulk silicon, of $\langle 110 \rangle$ and $\langle 001 \rangle$ silicon nanowire in β -Sn phase are presented in Fig.3c.

It was found that bulk silicon in β -Sn phase is superconductor [31] therefore we expect that β -Sn SiNW would display superconducting properties too.

Conclusions. The stability and electronic properties of $\langle 110 \rangle$ and $\langle 001 \rangle$ oriented thin silicon nanowires in β -Sn phase were studied and compared with $\langle 100 \rangle$ nanowires in diamond phase. It was shown that SiNWs in β -Sn phase display higher strain energy and zero band gap like in the parent crystal. The pro-

nounce dependence of transition pressure upon the size for thin SiNW was observed.

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1. A. K. Singh, V. Kumar, R. Note, and Y. Kawazoe, *Nano Lett* **5**, 2302 (2005)
2. P. B. Sorokin, P. V. Avramov, A. G. Kvashnin et al., *Phys. Rev. B* **77**, 235417 (2008)
3. R. Q. Zhang, Y. Lifshitz, D. D. D. Ma et al., *J. Chem. Phys.* **123**, 144703 (2005)
4. J. F. Justo, R. D. Menezes, and L. V. C. Assali, *Phys. Rev. B* **75**, 45303 (2007).
5. P. V. Avramov, A. A. Kuzubov, A. S. Fedorov et al., *Phys. Rev. B* **75**, 205427 (2007)
6. R. Rurali and N. Lorente, *Phys. Rev. Lett.* **94**, 26805 (2005).
7. Y. Li, F. Qian, J. Xiang, and C. M. Lieber, *Materials Today* **9**, 18 (2006)
8. J. D. Holmes, K. P. Johnston, R. C. Doty, and B. A. Korgel, *Science* **287**, 1471 (2000).
9. Y. Huang, X. Duan, and C. M. Lieber. *Small* **1**, 142 (2005).
10. D. D. D. Ma, C. S. Lee, F. C. K. Au et al., *Science* **299**, 1874 (2003).
11. H. K. Poswal, N. Garg, S. M. Sharma et al., *J. Nanoscience and Nanotechnology* **5**, 729 (2005).
12. Y. Wang, J. Zhang, J. Wu et al., *Nano Lett.* **8**, 2891 (2008).
13. S. Minomura and H. G. Drickamer, *J. Phys. Chem. Solids* **23**, 451 (1962).
14. J. C. Jamieson, *Science* **139**, 762 (1963).
15. M. C. Gupta and A. L. Ruoff. *J. Appl. Phys.* **51**, 1072 (1980).
16. J. Z. Hu, L. D. Merkle, C. S. Menoni, and I. L. Spain. *Phys. Rev. B* **34**, 4679 (1986).
17. R. J. Needs and R. M. Martin. *Phys. Rev. B* **30**, 5390 (1984).
18. K. Gaál-Nagy, A. Bauer, P. Pavone, and D. Strauch, *Comp. Mat. Sci.* **30**, 1 (2004).
19. K. J. Chang and M. L. Cohen. *Phys. Rev. B* **31**, 7819 (1985).
20. K. Mizushima, S. Yip, and E. Kaxiras, *Phys. Rev. B* **50**, 14952 (1994).
21. P. Hohenberg and W. Kohn, *Phys. Rev* **136**, B 864 (1964).
22. W. Kohn and L. J. Sham, *Phys. Rev* **140**, A1133 (1965).
23. D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett* **45**, 566 (1980).
24. G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).
25. G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (1994).
26. G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
27. D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
28. H. J. Monkhorst and J. D. Pack. *Phys. Rev. B* **13**, 5188 (1976).
29. L. E. Brus, J. A. W. Harhless, and F. H. Stillinger, *J. Am. Chem. Soc* **118**, 4834 (1996).
30. S. C. Miller, W. F. Love, *Tables of Irreducible Representations of Space Groups and Co-Representations of Magnetic Space Groups*, Boulder: Pruett; 1967.
31. J. Wittig, *Z. Phys.* **195**, 215 (1966).