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Electronic structure, lattice dynamics and thermoelectric properties of silicon nanosphere-nanoribbon layered structure from first-principles calculation

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ABSTRACT

How to further optimize the thermoelectric figure of merit of silicon (Si) nanostructure? Constructing the layered structure composed of two different Si nano morphologies should be viewed an effective approach. The figure of merit of the layered structure could be further optimized by tuning the different contribution from the composed nano morphologies on the electron and phonon transport. In order to reveal the thermoelectric transport mechanism, the electronic structure, the lattice dynamics and the thermoelectric properties of Si nanosphere, Si nanoribbon and the layered structure composed of the two nano morphologies were investigated through first-principles calculation, lattice dynamics simulation and Boltzmann transport theory. The results suggest that the figure of merit of the layered structure is improved significantly in whole although its specific thermoelectric parameters are unsatisfactory as compared to the single nano morphologies. Therefore we provide a complete understanding on the thermoelectric transport of the layered structure and an effective route to further optimize the figure of merit of Si nanostructure.

1. Introduction

Thermoelectric materials, which can convert temperature difference into electric energy and vice versa, have been employed in many applications, such as space exploration mission and renewable energy in automobile. With no moving parts thermoelectric devices possess huge advantage in long-duration operation reliability. The conversion efficiency of thermoelectric materials is often evaluated by a dimensionless figure of merit (*ZT*), which is determined by electrical conductivity, Seebeck coefficient and thermal conductivity. The thermoelectric material with a high conversion efficient requires a high electrical conductivity, a large Seebeck coefficient and meanwhile a low thermal conductivity. However, the above parameters are hardly optimized simultaneously due to the existing conflicts among the thermoelectric variations, which restrict the further improvement in *ZT*. So a profound and complete understanding on the electron and phonon transport in thermoelectric materials is essentially necessary so as to realize the synergetic optimization in *ZT* value.

Silicon (Si), a foundation stone of our modern semiconductor industry for its rich reserve, extensive application and low cost, had been initially selected as the potential thermoelectric material used in a high temperature (above 1100 K). However, the faced challenge is its very poor *ZT* value (less than 0.001 at room temperature). Si crystalline possesses a small electrical conductivity, a large Seebeck coefficient and a huge thermal conductivity. Thus the strategy in improving its *ZT* value has always focused on the reduction in the thermal conductivity contributed from phonons. Alloying Si with Ge, is proved to be an effective way in reducing the thermal conductivity of Si crystalline due to the resulted strong scattering effect on electrons and phonons. As a result, SiGe alloys are firstly used as the thermoelectric generator in deep-space mission as reliable and long-lived power source. However, the optimal thermoelectric *ZT* value of SiGe alloys across the operating temperature is only 0.55, which induces a very low conversion efficiency less than 8%. Moreover, rare and expensive Ge raw materials are needed. Hence, it is of significance to improve the *ZT* value of Si crystalline so as to replace the expensive SiGe alloys.

Nanostructing, as an effective approach to obtain a high *ZT* value, has been widely employed to thermoelectric materials [1]. The electrical conductivity, the Seebeck coefficient and the thermal conductivity of nanostructured material could be improved obviously by tuning the density of states, the mobility of carriers and the scattering effect [2–4]. In experiments, many nanostructured Si materials with

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different morphologies such as nanotubes, nanowires, nanorods, nanoribbons and nanospheres were synthesized. The *ZT* value at 1100 K of Si nanospheres was enhanced to 0.7 [2]. The phonon thermal conductivity of Si nanospheres was reduced by 90% while the electrical conductivity was decreased slightly, which consequently resulted in a large enhancement of 3.5 times in *ZT* [5]. Si nanowires exhibited a 100-fold reduction in thermal conductivity, which yielded a large *ZT* value of 0.6 [1,6]. By controlling the anisotropy and the surface roughness the *ZT* value of Si nanowires was increased as much as 20 times as compared to Si crystalline due to the large reduction in phonon thermal conductivity [7,8]. Moreover, the cross section shape would play an important role in the enhancement in *ZT* value of Si nanowires since the extremely small size was often accompanied by a strong quantum confinement effect [9,10]. Importantly, Si nanoribbons possessed a unique thermoelectric transport [11]. The thermoelectric properties of Si nanoribbons could be improved obviously by introducing randomly distributed vacancies and/or defects [12,13]. Decreasing the size of nanoribbons and introducing defects were considered as two effective ways to further optimize the *ZT* value of Si nanoribbons [14].

More recently, fabricating the layered structure composed of two different nano morphologies has been regarded as an effective way to further optimize the figure of merit of nanostructured materials. By introducing carbon nanotubes into Bi_2Te_3 nanospheres, the thermal conductivity of the layered structure was suppressed significantly and thereby the figure of merit was improved largely [15]. By introducing $(Bi_{0.2}Sb_{0.8})_2Te_3$ nanospheres into carbon nanotubes the phonon thermal conductivity of the layered structure was decreased by 31 per cent [16]. By introducing Sb_2Se_3 nanowires into Bi_2Te_3 nanospheres, the Seebeck coefficient of the layered structure was increased obviously while the phonon thermal conductivity was reduced significantly. By introducing Bi nanowires into Bi nanotubes, the thermal conductivity of the layered structure was reduced by a factor of 5 and thus its figure of merit was increased by more than 10 times [17,18]. Due to the strong interface scattering effect the thermal conductivity of Bi-Te core/shell nanowires was reduced to a tenth of Si crystalline [19]. The thermoelectric transport mechanism in different nano morphology was very different. Nanowires had a small thermal conductivity, nanospheres possessed a strong grain scattering while nanoribbons had a high electrical conductivity [20]. $MoS_2/MoSe_2$ mixed-layer compound was investigated by using first principles calculation. The thermoelectric properties of the $MoS_2/MoSe_2$ layered structure could be improved largely by tuning the different contribution from the composed nano morphologies on the electron and phonon transport [21].

To the best of our knowledge, however, the theoretical studies on the thermoelectric transport in the layered structure composed of two different nano morphologies are still lacking up to now. It is also unclear whether the electronic structure and the lattice dynamics of the layered structure can function as its promising thermoelectric properties. Therefore, our work aims to provide a complete understanding on the thermoelectric transport in Si nanosphere, Si nanoribbon and the layered structure composed of the two different nano morphologies through first-principles calculation, lattice dynamics simulation and Boltzmann transport theory.

2. Modeling and calculation methods

Si nanosphere, Si nanoribbon and the layered structure composed of the two nano morphologies were modeled through the Visualizer module of Materials Studio 8.0. Si nanosphere was fabricated by building a nanocluster with a diameter of 2.0 nm and of total 220 atoms. And then a vacant crystal lattice with same symmetry and lattice constants was built. Finally the nanocluster was moved into the center of the vacant lattice (seen in Fig. 1a). Si nanoribbon was built according to the following steps. Firstly, Si crystalline was modeled. Secondly, 6×6×3 superlattice was built. Thirdly, a surface along [1 1 1] plane was cleaved, in which the cap bonds on the surface were not passivated with H atoms. Fourthly, the extra atoms outside the surface were all removed. Lastly, a vacuum slab with a thickness of 0 Å was added perpendicularly to [1 1 1] direction. Thus the Si nanoribbon with a length of 2.0 nm and a width of 2.0 nm was realized (seen in Fig. 1b). The layered structure was built by fabricating a layer structure in which Si nanoribbon, Si nanosphere and Si nanoribbon were selected as the first, the middle and the last layer respectively (seen in Fig. 1c). In experiments, the layered structure could be fabricated by physically mixing Si nanosphere powders and Si nanoribbon powders prepared via a hydro/sovol thermal route.

The detailed calculation of the electronic structure and the thermoelectric properties could referred to our previous work [22,23]. The phonon dispersion, the phonon density of states and the phonon thermal conductivity κ_p were calculated through the General Utility Lattice Program (GULP) integrated in Materials Studio 8.0 [24]. The obtained parameters of the electronic structure, the lattice dynamics and the thermoelectric properties at 1200 K of Si nanosphere, Si nanoribbon and the layered structure are summarized in Table 1.

3. Results and discussion

3.1. Electronic structure

The band structure of Si nanosphere, Si nanoribbon and the layered structure is presented in Fig. 2a–c, respectively. As for Si nanosphere (seen in Fig. 2a), the bands near Fermi level distribute smoothly along all the high symmetric points, exhibiting a typical isotropic characteristic. In addition, there exists no bandgap between the valence band top (VB) and the conductor band bottom (CB), indicating a typical semimetal behavior. However, Si crystalline belongs to a typical semiconductor with a bandgap of 0.63 eV [22]. Such transition from semiconductor to semimetal has been observed in other nanostructured materials [25]. It can also be seen from Fig. 2a that the band width in CB for Si nanosphere is very narrow (from 0 eV to 0.45 eV), which means a large effective mass of carriers (1.25 m_e). Similarly, Si nanoribbon also exhibits a typical semimetal characteristic (seen in Fig. 2b). However, the bands of Si nanoribbon distribute sharply in the both sides while smoothly in the middle, showing a typical anisotropic characteristic. Additionally, its band width in CB is increased obviously (from 0 eV to 1.2 eV), which implies a small effective mass of carriers. As for the layered structure (seen in Fig. 2c), its anisotropy is decreased obviously. Moreover, there exists a narrow bandgap of about 0.045 eV near Fermi level in the layered structure, suggesting a typical semiconductor characteristic. On the other hand, the band width in CB of the layered structure is also very narrow (from 0 eV to 0.55 eV), which indicates a large effective mass of carriers.

The density of states (DOS) of Si nanosphere, Si nanoribbon and the layered structure is shown in Fig. 3. As for Si nanosphere, the density of states at Fermi level is 6 electrons/eV and no bandgap is observed, exhibiting a typical semimetal characteristic. Such small DOS of Si nanosphere may be a main reason for its small electrical conductivity. Pseudogap energy, an energy difference between the nearest two peaks at Fermi level in DOS curve, can reflect the covalent bonding strength between the parent atoms. Furthermore, the phonon vibrational frequency is positively proportional to the square root of the force constant. Therefore the phonon thermal conductivity could be estimated qualitatively by the obtained pseudogap energy. The pseudogap energy of Si nanosphere is 0.583 eV, which means a relatively weakened covalent bonding, a lowered phonon vibration frequency and thus a largely suppressed phonon thermal conductivity. However, Si nanoribbon exhibits a large enhancement in the concentration of carriers at Fermi level (41 electrons/eV). Meanwhile the pseudogap energy of Si nanoribbon is increased obviously (1.015 eV), indicating a strong force constant, a high phonon vibration frequency and thereby a high phonon thermal conductivity. As for the layered structure, its concentration of carriers and pseudogap energy are intervenient