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Anisotropic in-plane thermal conductivity in multilayer silicene

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ABSTRACT

We systematically study thermal conductivity of multilayer silicene by means of Boltzmann Transportation Equation (BTE) method. We find that their thermal conductivity strongly depends on the surface structures. Thermal conductivity of bilayer silicene varies from 3.31 W/mK to 57.9 W/mK with different surface structures. Also, the 2×1 surface reconstruction induces unusual large thermal conductivity anisotropy, which reaches 70% in a four-layer silicene. We also find that the anisotropy decreases with silicene thickness increasing, owing to the significant reduction of thermal conductivity in the zigzag direction and its slight increment in the armchair direction. Finally, we find that both the phonon-lifetime anisotropy and the phonon-group-velocity anisotropy contribute to the thermal conductivity anisotropy of multilayer silicene. These findings could be helpful in the field of heat management, thermoelectric applications involving silicene and other multilayer nanomaterials with surface reconstructions in the future.

1. Introduction

Many theoretical and experimental results showed that the quantum confinement and surface effects can remarkably reduce the thermal conductivity of nanomaterials while maintaining their electronic conductivity at high level, which make them great potential applications in the thermoelectric [1,2]. For example, Boukai et al. [3] found that by altering the nanowire size and impurity doping levels, approximately 100-fold improvement of ZT over bulk Si can be achieved in a broad temperature range. Also, Hochbaum et al. [4] proposed a way of increasing ZT via controlling the roughness of silicene nanowires. The combined effects of quantum size and surface reconstruction in multilayer silicene are expected to induce exotic thermal transport properties different from either monolayer silicene or bulk Si, which may make it suitable for the thermoelectric applications. Since thermal conductivity of monolayer silicene and bulk Si had been well explored, the investigation on multilayer silicene is helpful for understanding thermal conductivity evolution from two dimensional (2D) to three dimensional (3D) systems.

The existing researches on thermal conductivity of 2D materials mainly focus on the ones with weak van der Waals (vdW) interlayer interactions where no surface reconstruction appears. The multilayer graphene [5–7], MoS_2 [8], and black phosphorus [9–11] are such kind of 2D materials which had been well studied. Whereas, the thermal conductivity of 2D materials with strong interlayer interactions is poorly understood so far. The multilayer silicene, which has been both theoretically predicted and experimentally synthesized, can be an ideal material for such an investigation [12–14]. The silicon materials present complex surface reconstructions, which are usually neglected for thermal conductivity investigations due to their small specific surface area. However, the reconstruction effect can be significant when a material's thickness becomes ultra thin, i.e., multilayer silicene. Previous studies showed that multilayer silicene exhibits special surface reconstructions which induce intriguing electronic property [12,14]. Naturally, one also expects the surface reconstruction to play a key role in its thermal transport property.

On the other hand, both experimental and theoretical studies showed that surface reconstruction in 2D materials can induce large anisotropy. For example, black phosphorus and phosphorene exhibit distinct thermal transport anisotropy owning to their puckered structures [9,10]. The thermal transport anisotropy is closely relevant to the thermomechanical reliability of functional devices

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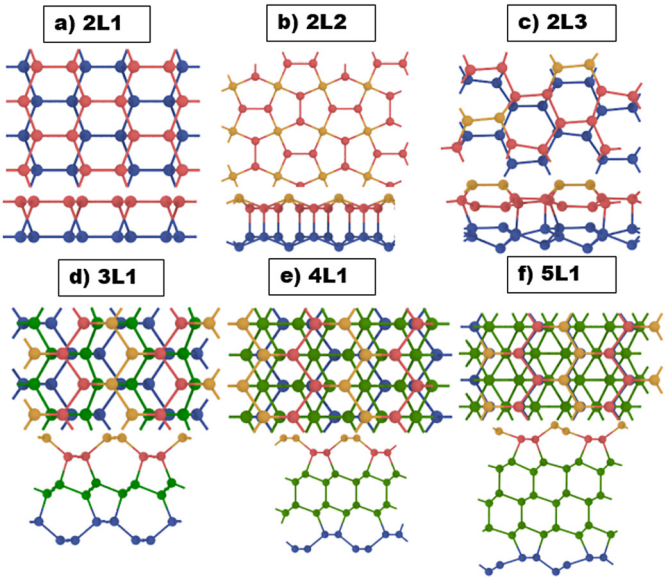

Fig. 1. (Color online.) Top view and side views of typical structures of multilayer silicene. The buckling Si atoms on the top layer are labeled as yellow balls, and the red balls represent the remaining Si atoms on the top layer. All the Si atoms on the bottom layer are labeled as the blue balls. The green balls represent Si atoms in the middle layers. The orientation of top view of the cells is armchair in the x direction and zigzag in the y direction in the figure. The structures exhibit obvious and pretty different surface reconstruction.

in nanoelectronics. In particular, alternative flexible substrate and active layer materials with increased thermal conductivity are desirable to prevent thermomechanical failures which have become a big challenge in flexible devices based on 2D materials [15,16]. Revealing the surface reconstruction effect on thermal conductivity anisotropy of multilayer silicene could stimulate the studies of covalently bonded 2D materials for the potential applications in the nanoelectronics.

2. Computational details

The thermal conductivity of multilayer silicene structures are studied with the BTE method realized in ShengBTE [17]. In order to save the computing expense, the latest classical Mod potential [18] implemented on the large scale parallel molecular dynamics software package (LAMMPS) is chosen [19]. This potential is able to reconstruct the elastic constant, melting point and phase transition of silicon materials. The potential parameters have been constructed for different type of silicene structures by fitting its bond angles to give accurate melting point and elastic constants, and for bulk Si with experimental equilibrium bond lengths which leads to smaller binding energy than that predicted by the first-principles calculations.

The atomic structures of multilayer silicene that were predicted to be stable by Guo et al. [14] are shown in Fig. 1. For convenience, we define the names of these structures as “nLxs”, where “n” is a pure number, representing the number of layers, “L” means layer, “x” distinguishes different structures (concrete 1, 2, 3 etc.) and “s”=“a” or “z”, corresponds to the silicene edge along the length direction, i.e., “a” for armchair) and “z” for zigzag. We also show in Table 1 the structure names and minimum repeat cell periodicities of these multilayer silicene.

Silicene structures are fully optimized using the conjugate gradient method. The finite displacement method (FDM) realized in Phonopy [20] and Thirdorder [17] are applied to extract the second- and third-order force constants (FCs) respectively, in which hundreds of slightly displaced supercells are generated. The obtained forces are calculated and used to calculate the FCs with the numerical differential calculation. The supercells of $3 \times 3 \times 1$ primitive cells are adopted to make the in-plane dimension above 40 Å, which ensure the accuracy of calculated forces. Following the previous studies [21,12], we choose Si (111) layer spacing of 3.14 Å as the interlayer thickness d because the thickness of two dimensional silicene is hard to strictly determined, since it’s a common constant for all the structures, the conclusion is independent on the absolute value of d, so a experimental value makes sense here.

Table 1
The thermal conductivity and its anisotropy of different multilayer silicene, along with the average heat capacity (kJ/m^3/K) of zigzag (Cv_z) and armchair (Cv_a) directions, respectively.

	Minimal period	$\kappa_{z,\infty}$	$\kappa_{a,\infty}$	χ	Cv_z	Cv_a
2L1	1×1	42.10	57.92	27.31%	165.8	166.7
2L2	$\sqrt{2} \times \sqrt{2}$	31.11	31.11	0%	38.44	38.44
2L3	2×2	3.311	5.624	41.13%	22.42	22.42
3L1	2×1	31.44	14.05	55.29%	52.22	52.46
4L1	2×1	20.37	6.114	69.98%	37.71	37.89
5L1	2×1	19.33	6.419	66.78%	29.17	29.32
6L1	2×1	17.78	6.527	63.29%	23.73	23.86
8L1	2×1	17.56	7.461	57.51%	17.26	17.36

The thermal conductivity tensor can be calculated as

$$\kappa^{\alpha\beta} = \sum_{k\sigma} c_{k\sigma} v^{\alpha}_{k\sigma} v^{\beta}_{k\sigma} \tau_{k\sigma} \tag{1}$$

where $c_{k\sigma}$ is the heat capacity of phonon mode, $v^{\alpha}_{k\sigma}$ is the mode group velocity, and $\tau_{k\sigma}$ is the phonon lifetime. The heat capacity is calculated by

$$c_{k\sigma} = \frac{\hbar\omega_{k\sigma}}{V} \frac{\partial f(\omega_{k\sigma}, T)}{\partial T} \tag{2}$$

where $f(\omega, T) = 1/[exp(\frac{\hbar\omega}{k_b T}) - 1]$ is the Bose–Einstein distribution function.

The calculations of $c_{k\sigma}$, $v^{\alpha}_{k\sigma}$, and $\tau_{k\sigma}$ require the second- and third-order FCs as inputs, where the detailed formulas are referred to the work of Li [17]. To avoid underestimation of thermal conductivity, the iteration method is used instead of the relaxation time approximation (RTA). A $45 \times 45 \times 1$ Monkhorst–Pack q-point mesh is adopted for the convergence on the summation.

3. Results and discussion

The surface reconstruction has substantial influence on thermal conductivity of multilayer silicene. Fig. 2(a) presents the length dependence of thermal conductivity of three structures of bilayer silicene. One can see that the thermal conductivity converges quickly with cutoff phonon mean free path (MFP) in of 2L2 structure, while it is a bit slowly in 2L1 and 2L3 structures. Also, the cutoff MFPs of 2L1 structure are distinct in the armchair and zigzag directions. These features can be attributed to the different scattering intensity caused by the surface reconstructions. It is known that the ballistic phonon transport is dominating when the length of the sample is smaller than the MFP, whereas the diffuse phonon transport is dominating when the length is larger than the MFP. An empirical formula had been proposed by Thomas [22] to characterize the thermal conductivity from ballistic to diffuse phonon-transport region, which is

$$\kappa = \kappa_{\infty}(1 - e^{-\frac{L}{L_c}}) \tag{3}$$

where κ_{∞} is the fitted full scattering thermal conductivity, L_c is the transition length from the ballistic transportation to the diffuse transportation. Here we find that the length dependence of thermal conductivity of multilayer silicene can also be well described

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