Cite this: *Nanoscale*, 2015, 7, 6014

Bilateral substrate effect on the thermal conductivity of two-dimensional silicon

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Silicene, the silicon-based counterpart of graphene, has received exceptional attention from a wide community of scientists and engineers in addition to graphene, due to its unique and fascinating physical and chemical properties. Recently, the thermal transport of the atomic thin Si layer, critical to various applications in nanoelectronics, has been studied; however, to date, the substrate effect has not been investigated. In this paper, we present our nonequilibrium molecular dynamics studies on the phonon transport of silicene supported on different substrates. A counter-intuitive phenomenon, in which the thermal conductivity of silicene can be either enhanced or suppressed by changing the surface crystal plane of the substrate, has been observed. This phenomenon is fundamentally different from the general understanding of supported graphene, a representative two-dimensional material, in which the substrate always has a negative effect on the phonon transport of graphene. By performing phonon polarization and spectral energy density analysis, we explain the underlying physics of the new phenomenon in terms of the different impacts on the dominant phonons in the thermal transport of silicene induced by the substrate: the dramatic increase in the thermal conductivity of silicene supported on the 6H-SiC substrate is due to the augmented lifetime of the majority of the acoustic phonons, while the significant decrease in the thermal conductivity of silicene supported on the 3C-SiC substrate results from the reduction in the lifetime of almost the entire phonon spectrum. Our results suggest that, by choosing different substrates, the thermal conductivity of silicene can be largely tuned, which paves the way for manipulating the thermal transport properties of silicene for future emerging applications.

Received 5th November 2014,

Accepted 9th February 2015

DOI: 10.1039/c4nr06523a

www.rsc.org/nanoscale

Silicene, a novel two-dimensional allotrope of silicon with a hexagonal honeycomb structure, similar to graphene, is now at the center of attention of a wide community of scientists and engineers in addition to graphene, due to its unique and fascinating physical properties.¹ Silicene was first mentioned in a theoretical study by Takeda and Shiraishi in 1994,² and then reinvestigated by Guzmán-Verri *et al.* in 2007.³ Experimentally, in recent years silicene sheets and silicene nanoribbons have been successfully grown on various metal substrates, such as Ag,^{4–6} Ir,⁷ and ZrB₂.⁸ The synthesis of free standing silicene remained difficult until recently. The experimental synthesis stimulated tremendous theoretical investigations of the physical properties of silicene. Although significant progress has been made in the theoretical investigation of the electronic transport properties of silicene,^{9–11} its thermal transport

(mainly phonons) properties have only recently been studied. For almost all nanoelectronics applications, thermal conductivity is one of the most important physical parameters in electronics design and operation. It is well-known that thermal transport plays a crucial role in many applications, such as heat dissipation,¹² thermal management,¹³ and electronic packaging.¹⁴ Therefore, there is an emerging need to characterize the thermal transport properties of silicene based nanostructures for the development of relevant micro/nanoelectronics.

To date, the research on thermal transport in silicene reported in the literature has been focusing on free standing silicene, mainly from atomistic simulations. Scalise *et al.* calculated the phonon dispersion curve of silicene, and found that silicene also has a flexural phonon branch,¹⁵ similar to the ZA branch of graphene. Li and Zhang adopted the Green-Kubo method to calculate the thermal conductivity of free standing silicene,¹⁶ and Pei *et al.*¹⁷ evaluated its thermal conductivity using a non-equilibrium molecular dynamics (NEMD) approach. Diverse thermal conductivity values were found, with different classical interatomic potentials. Very recently, we developed an improved Stillinger-Weber (SW) potential that can reproduce both the low-buckled structure

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and the majority of the phonon dispersion curves of silicene.¹⁸ Using the optimized SW potential, the thermal conductivity of silicene is predicted to be around $10 \text{ W m}^{-1} \text{ K}^{-1}$, which is in good agreement with the value obtained by combining first-principles based anharmonic lattice dynamics and the Boltzmann Transport Equation (BTE).^{19,20} It is now well understood that the thermal transport in silicene is dominated by the in-plane longitudinal modes, while the out-of-plane vibrations have small contributions to the total thermal conductivity.^{18–20} This phenomenon is attributed to the unique buckled structure found in silicene, which is fundamentally different from that of graphene, despite the similarity of their honeycomb lattice structures. Although a few studies have been dedicated to the thermal transport of free standing silicene by atomistic simulations, no research has been conducted for silicene supported on substrates. Supported silicene is, in fact, a common form in realistic applications: for example, it can be transferred onto an insulating substrate and gated electrically.²¹

In this paper, we report the results of nonequilibrium molecular dynamics simulations predicting the effects of different substrates on the thermal transport of silicene. A non-intuitive phenomenon, in which the thermal conductivity of silicene can be either enhanced or suppressed by choosing different substrates, was observed. This phenomenon is also fundamentally different from that of supported graphene, in which all experimental and theoretical investigations to date have shown that the substrate has a negative effect on its thermal conductivity.^{22–27} The different substrate effects between graphene and silicene can be attributed to the different effects induced by the substrate on the phonons, stemming from the different dominant thermal transport mechanisms in these two materials (out-of-plane flexural modes *vs.* in-plane longitudinal modes), due to the different intrinsic buckling distances – for graphene, the buckling distance is zero (purely planar), while silicene has a buckling of about $0.42 \text{ \AA}$.¹⁸

Our model system consists of a pristine silicene structure horizontally aligned on silicon carbide (SiC) substrates. The top and side view of typical supported silicene structures are shown in the top and middle panel of Fig. 1, respectively. In our MD simulations, we investigated two types of SiC substrate, namely, 6H-SiC and 3C-SiC substrates. Both the substrates are terminated with carbon atoms. The width of the substrates in the *x* direction is 6.6 nm , and the thickness along the *z* direction is about 1.5 nm . The length of the substrates in the *y* direction ranges from 22 to 602 nm . For silicene, the number of unit cells is $10 \times n$, with n ranging from 58 to 1580 , considering the lattice mismatch between silicene and the substrate. When constructing the initial structure, we fixed the width of silicene to be 10 unit cells, and then chose the closest box size in the *x*-direction that is a multiple for the substrates. Therefore, the total numbers of unit cells for the different substrates are different, namely, 22 unit cells for 6H-SiC and 15 unit cells for 3C-SiC. Throughout the entire simulation, the simulation box remained unchanged. Finally, this is equivalent to a strained effect (less than 2%) on the sub-

Fig. 1 (Top) Top view of silicene structure supported on 6H-SiC (left) and 3C-SiC (right) substrates. The 6H-SiC surface has a honeycomb lattice, and the 3C-SiC surface has an f.c.c. like structure. Color code: yellow, Si (silicene); cyan, C; pink, Si (substrate). (Middle) Side view of silicene supported on the 6H-SiC substrate. The left and right ends of the system and the bottom layer of the SiC substrate are fixed during the simulation and are highlighted in green. (Bottom) The corresponding temperature profile of the supported silicene and the SiC substrate.

strate, but for silicene there is no strain effect at all. The same procedure was applied to the *y*-direction. A periodic boundary condition was used in the *x* (transverse, armchair) direction, and fixed boundary conditions were used in the *y* and *z* directions (out-of-plane of silicene). We set 1 nm -long regions at both the ends in the *y* (longitudinal, zigzag) direction as rigid walls, and the outermost bottom layer in the SiC substrate was fixed. We used the optimized Stillinger-Weber potential (SW1)¹⁸ to describe the interatomic interactions in the supported silicene, and the Tersoff potential²⁸ to model the interatomic interactions in the SiC substrates. The interfacial interactions between silicene and the SiC substrates were described by the 12-6 Lennard-Jones potential as follows:

$$V(r) = 4\chi\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (1)$$

where r represents the distance between two atoms, ϵ is the energy that reflects their interaction strength, σ denotes the zero-across distance of the potential, and χ is a scaling factor that can be used to tune the interfacial interaction strength. The standard Si-Si and Si-C Lennard-Jones parameters ($\chi = 1$) are adopted from ref. 29 and 30, respectively. For clarity, the parameters are presented here: $\epsilon_{\text{Si-Si}} = 25.3416 \text{ meV}$, $\sigma_{\text{Si-Si}} = 3.39 \text{ \AA}$; $\epsilon_{\text{Si-C}} = 8.909 \text{ meV}$, $\sigma_{\text{Si-C}} = 3.326 \text{ \AA}$. It should be noted that, the real case in applications is related to the interfacial contact, which could be largely affected by many factors. For example, if the supported silicene does not have good contact

with the substrate, or the surface of the substrate is not perfectly flat (e.g. in the case of roughness), the interfacial interaction strength could be very weak. In this case, the assumption of van der Waals interactions is suitable, which corresponds to the scaling factor of $\chi = 1$. In the opposite case, if the silicene and substrate are in perfect contact, some chemical bonds might form at the interface, as demonstrated by recent *ab initio* calculations;³¹ thus, the interfacial interaction strength could be considerably larger than that for weak van der Waals interactions, and therefore corresponds to the scaling factor of $\chi \gg 1$. Because the exact interfacial interaction strength is unknown for the silicene/SiC interface, we tried to mimic situations in realistic applications as much as possible by simply changing the scaling factor χ .

All MD calculations were performed using the LAMMPS³² package, with a timestep of 0.1 fs throughout. We used the NEMD method to separately calculate the thermal conductivities of the supported silicene and the substrates. In the first stage of the NEMD simulations, we relaxed the system at 300 K for 0.1 ns using a Nosé-Hoover thermostat.^{33,34} After NVT (constant particles, volume, and temperature) relaxation, we froze the walls and continued to relax the system with an NVE (constant particles, volume, and no thermostat) ensemble for another 0.1 ns. Following equilibration, we computed the thermal conductivity of the system using the NEMD method. It is well known that using the NEMD method to compute thermal conductivity relies on a steady heat flux, which must be established along the desired direction. Currently, there are two different methods to realize this: (1) constant heat flux, e.g. the Jund and Julien algorithm,³⁵ or the Muller-Plathe algorithm,³⁶ in which the heat current or flux is an input parameter and the resulting temperature gradient is calculated; (2) constant temperature gradient, i.e., the heat source and heat sink are connected to constant temperature thermostats (thus, the temperature gradient is known in advance) and the resulting heat flux is calculated. In our simulation, we adopted the second method because of the fact that for a constant heat flux method the temperature difference in the model system cannot be easily estimated, and the heat flux parameters must usually be tried several times to achieve an appropriate temperature difference. To establish a temperature gradient along the longitudinal direction, we set another 5 nm long region next to the “rigid” wall as a heat source and heat sink. The temperature gradient was realized using Nosé-Hoover thermostats to maintain the temperature of the heat source and heat sink at 320 K and 280 K, respectively. To calculate the heat flux along the *y* (longitudinal) direction, we recorded the input and output energies for the heat source and heat sink at each time step, and the averaged heat power divided by the cross-sectional area was considered to be the heat flux. Because the energy that is added to the heat source of silicene may flow into the substrate, in order to distinguish the input and output energies for the heat source and heat sink, and thus calculate the heat flux that actually flows through the silicene, we set up four thermostats with two on each end, i.e. we applied separate thermostats to silicene and to the substrate.

To verify that the heat flux calculated by the Nosé-Hoover thermostat is the real heat energy carried by the silicene, we compared the heat flux with that calculated later by the polarization method, which does not have the potential problem of interfacial heat energy change because each term is defined onto a single atom. We found that the results obtained by these two methods are consistent with each other. Therefore, we believe that the heat flux calculated using the input and output energies for the heat source and heat sink is reliable. The thickness of silicene was chosen as 4.2 Å in calculating the cross-sectional area.¹⁸

The thermal conductivity of silicene from the NEMD is calculated by Fourier's law

$$\kappa_{\text{NEMD}} = -\frac{J_L}{\partial T/\partial y}, \quad (2)$$

where J_L is the averaged heat flux in the longitudinal (*y*) direction and $\partial T/\partial y$ is the temperature gradient determined from a linear fitting of the time-averaged temperature profile along the longitudinal direction. We did not observe a noticeable nonlinear temperature profile, due to the small temperature difference in our system (see a typical temperature profile in the bottom panel of Fig. 1); therefore, we used all the temperature data to calculate the temperature gradient. A typical heat-source heat-sink run took about 2 ns to establish a steady heat flow, and additional 2–6 ns to average the temperature profile and heat flux, depending on the system size and interfacial interaction strength.

The length dependence of the thermal conductivity of silicene supported on different substrates is presented in Fig. 2(a). We also show the thermal conductivity of free standing silicene for comparison. The reason we used different scaling factors ($\chi = 10$ for 6H-SiC and $\chi = 5$ for 3C-SiC) is that $\chi = 10$ will lead to an unstable structure of silicene supported on the 3C-SiC substrate, which may be due to the lattice mismatch between the supported silicene and the 3C-SiC substrate, and the large interfacial interaction. It should be emphasized that using different values of χ does not influence the main statement and conclusion in the paper. We see that when the silicene length is short (less than 50 nm), the thermal conductivity values of free standing silicene and the silicene supported on the 6H-SiC substrate are close to each other, while the thermal conductivity of the silicene supported on the 3C-SiC substrate is slightly smaller. With increasing silicene length, the thermal conductivity of silicene supported on the 6H-SiC substrate increases considerably faster than those of both free standing silicene and the silicene supported on the 3C-SiC substrate, which have very similar speeds of thermal conductivity increase. Nevertheless, all three cases converge to a specific value when the length reaches several hundred nanometers. We fitted the NEMD data points at longer lengths (150–600 nm) using a linear function³⁷

$$\frac{1}{\kappa} = \frac{1}{\kappa_\infty} \left(\frac{l}{L_y} + 1 \right), \quad (3)$$

Fig. 2 (a) Length dependence of the thermal conductivity of free standing silicene (black squares), silicene supported on 6H-SiC (red circles, $\chi = 10$) and 3C-SiC (blue triangles, $\chi = 5$). (b) The corresponding linear relationship of $1/\kappa$ and $1/L_y$ with longitudinal (y) lengths of 150 nm, 300 nm and 600 nm. The scaling factors are $\chi = 10$ and $\chi = 5$ for 6H-SiC and 3C-SiC, respectively.

where κ_∞ is the thermal conductivity of an infinitely long silicene and l is the effective phonon mean free path in silicene. The $1/\kappa$ - $1/L_y$ dependence is shown in Fig. 2(b). The converged thermal conductivity of the supported silicene on the 6H-SiC substrate was found to be $21.32 \text{ W m}^{-1} \text{ K}^{-1}$ for infinitely long supported silicene, with a phonon mean free path of 101.6 nm, which is significantly higher than that for free standing silicene ($10.97 \text{ W m}^{-1} \text{ K}^{-1}$ with a phonon mean free path of 29.3 nm). In contrast, the converged thermal conductivity of silicene supported on the 3C-SiC substrate ($8.49 \text{ W m}^{-1} \text{ K}^{-1}$ with phonon mean free path of 27.1 nm) is considerably lower as compared to the free standing silicene. This new phenomenon is counter-intuitive in that the substrate has a bilateral effect on the phonon transport of silicene; the thermal conductivity of silicene can be either enhanced or suppressed by choosing a different substrate, which is fundamentally different from supported graphene, in which the substrate has always been found to have a negative effect on the

thermal transport of graphene, as is well documented in the literature.^{22–27} It is worth pointing out that, although it is still under heavy debate,^{38,39} previous literature has studied the origin of the linear relation of $1/\kappa$ and $1/L$,⁴⁰ in which it is clearly stated that the only requirement for the linear extrapolation procedure is that the system size should be comparable to the longest mean-free paths of the phonons that dominate the thermal transport.

First-principles calculations have shown that the largest phonon mean free path for silicene is about 24 nm (see details in ref. 19), and the system sizes we used for the linear extrapolation procedure in this paper range from 150 nm to 600 nm, which are considerably larger than the largest mean free path in silicene. Moreover, our classical MD simulations (see later for spectral energy density analysis) yielded the longest phonon mean free paths of 13.8 nm for free standing silicene and 92.3 nm and 11.2 nm for silicene supported on the 6H-SiC and 3C-SiC substrates, respectively. Again, the system sizes used for linear extrapolation fulfill the requirement of the linear fitting.

We have calculated the size effects for the thermal conductivity of both silicene and the substrate (not shown for brevity). It seems that for the 3C-SiC substrate, which has lower thermal conductivity, the supported silicene also has lower thermal conductivity. However, we also noticed that for the 6H-SiC substrate, the thermal conductivity of silicene is finally considerably higher than that of the substrate. Moreover, we ran additional simulations with fixed (frozen) 6H-SiC substrates, in which the thermal transport property of the substrate is no longer relevant to the thermal transport of silicene. The calculated thermal conductivity of supported silicene with a length of 80 nm and $\chi = 10$ is $13.30 \pm 2.06 \text{ W m}^{-1} \text{ K}^{-1}$, which is even larger than that for silicene supported on a movable substrate, which has a value of $10.76 \pm 0.55 \text{ W m}^{-1} \text{ K}^{-1}$. The results suggest that suppressing the out-of-plane vibrations of the substrates can significantly enhance the thermal conductivity of the supported silicene. The thermal conductivity of silicene supported on frozen 6H-SiC substrate shows similar trends to the case of the movable substrate; *i.e.*, the 6H-SiC substrate enhances the thermal conductivity of silicene. Therefore, we believe that the bilateral effect is mainly due to the match with the substrate structure instead of the thermal conductivity of the substrate (as revealed later). Moreover, we attempted to mimic a semi-infinite substrate in the simulation; therefore, we chose a substrate thickness such that the bottom layer is below the cut-off of the interatomic potential adopted here. Different substrate thicknesses in the NEMD simulation could give slightly different results due to the size effect of the NEMD simulation. However, because it is out of the scope of this work, we did not further investigate the thickness effect of the substrate.

We then studied the effect of interfacial interaction strength on the thermal conductivity of the supported silicene; the length of the model system studied here was fixed as 300 nm. The results are reported in Fig. 3(a). The trend is very clear that as the interfacial interaction strength increases, the

Fig. 3 Effect of interfacial interaction strength on the (a) thermal conductivity and (b) buckling distance of the supported silicene on the 6H-SiC (black squares) and 3C-SiC (red circles) substrates. The silicene length is 300 nm for all cases.

6H-SiC substrate considerably facilitates the thermal transport of silicene, while the 3C-SiC substrate more severely hinders its heat conduction. Again, it can be seen that SiC substrates with different surface crystal planes can dramatically change the intrinsic thermal conductivity of silicene, especially in a bilateral manner. We also show the effect of interfacial interaction strength on the average buckling distance of the supported silicene in Fig. 3(b), from which we can see that with increasing interfacial interaction strength, the buckling distance of the supported silicene decreases for both the 6H-SiC and 3C-SiC substrates. Compared to the 3C-SiC substrate, the 6H-SiC substrate has an even larger effect on the buckling distance of the supported silicene.

To understand this intriguing phenomenon, we first quantified the relative contributions of the lattice vibrations in the x , y , and z directions to the total heat flux of the supported silicene, using the NEMD-based method we proposed recently⁴¹

$$J_{A \rightarrow B, \alpha} = -\frac{1}{2S} \sum_{i \in A} \sum_{j \in B} F_{ij\alpha} (\nu_{i\alpha} + \nu_{j\alpha}), \quad (4)$$

where α is the x , y , or z direction, A and B are the left and right side of a virtual interface located at the middle of silicene in the y (heat flux) direction, $J_{A \rightarrow B, \alpha}$ is the heat flux from A to B due to lattice vibrations in the α direction, S is the cross-section area, $F_{ij\alpha}$ is the α component of the force acting on atom i due to atom j , and $\nu_{i\alpha}$ is the α component of the velocity of atom i . Details of calculating eqn (4) in the form of three-body potential can be found in ref. 41. Although simple, this approach has been successfully used for studying phonon transport in different nanostructures, and thermal transport across interfaces.^{18,42–44} Fig. 4 shows the relative contributions to the total heat flux from the lattice vibrations in the x , y , and z directions, corresponding to the in-plane transverse, longitudinal, and out-of-plane flexural modes, respectively. We first notice that the in-plane longitudinal modes contribute the most to the total heat flux for silicene supported on both substrates, while the out-of-plane flexural modes contribute little to the heat transfer. This mechanism is the same as that for free standing silicene,^{18,19} but is the opposite of that for graphene. The dominant role of the in-plane longitudinal modes in free standing and supported silicene originates from the unique low buckled structure of the silicene. The general understanding for phonon transport in supported graphene in the literature is that the out-of-plane flexural modes, which dominate the thermal transport in free standing graphene, are strongly suppressed; thus, the thermal conductivity of supported graphene is dramatically reduced compared with the free standing case.^{22–27} From Fig. 4 we also see that, with increasing interfacial interaction strength, for silicene supported on the 6H-SiC substrate the contributions from both the longitudinal and transverse modes continuously increase, while for silicene supported on the 3C-SiC substrate, these

Fig. 4 Relative contribution (percentage) to the total heat flux from vibrations in the x (transverse), y (longitudinal), and z (out-of-plane) directions as a function of interfacial interaction strength for the supported silicene on 6H-SiC (filled symbols) and 3C-SiC (open symbols) substrates. The zero interfacial interaction strength corresponds to the case of free standing silicene.

contributions greatly decrease. For both substrates, the contribution from the out-of-plane flexural modes does not change at all, which can be understood in terms of the constraints of the out-of-plane movement due to the presence of the substrate. Therefore, we know that the significant increase in the thermal conductivity of silicene supported on the 6H-SiC substrate, presented in Fig. 2(a), mainly stems from the large enhancement of the in-plane longitudinal and transverse modes, and the majority of the affected in-plane modes are anticipated to be acoustic, as we see below. For silicene supported on the 3C-SiC substrate, the thermal conductivity reduction mainly originates from the suppression of the in-plane longitudinal modes, but the major affected longitudinal modes are optic (see later).

In order to gain more insight into the mechanism of the bilateral substrate effect on the thermal conductivity of silicene, we investigated the mode dependent thermal conductivity of the supported silicene, which can be derived from the phonon Boltzmann transport equation (BTE) under the relaxation time approximation⁴⁵

$$\kappa_{\alpha} = \sum_{\vec{k}} \sum_{\nu} c_{\text{ph}} \nu_{g,\alpha}^2(\vec{k}, \mu) \tau(\vec{k}, \mu), \quad (5)$$

where $\vec{k}$ is the wave vector in the first Brillouin zone, μ is the phonon branch, κ_{α} denotes the thermal conductivity in the α direction, c_{ph} is phonon volumetric specific heat, $\nu_{g,\alpha}$ is α component of the phonon group velocity, and τ is the phonon lifetime (relaxation time). For a classical system, the phonon volumetric specific heat can be defined as follows:

$$c_{\text{ph}} = \frac{k_{\text{B}}}{V}, \quad (6)$$

where k_{B} is the Boltzmann constant, and V is the system volume. To obtain the phonon lifetime, we carried out phonon spectral energy density (SED) analysis.^{46,47} First, the phonon normal modes can be obtained by the following equation:⁴⁸

$$\dot{Q}(\vec{k}, \mu, t) = \sum_{jl} \sqrt{\frac{m_j}{N}} \vec{v}_{jl}(t) \cdot \vec{e}_j^*(\vec{k}, \mu) \exp(-2\pi i \vec{k} \cdot \vec{r}_l). \quad (7)$$

Second, the spectral energy density can be calculated by the following equation:⁴⁶

$$\Phi(\vec{k}, \mu, f) = \left| \int \dot{Q}(\vec{k}, \mu, t) \exp(-2\pi i f t) dt \right|^2, \quad (8)$$

and the phonon lifetime can be obtained by fitting the Lorentzian function as follows:⁴⁹

$$\Phi(\vec{k}, \mu, f) = \frac{I}{1 + \left[\frac{2\pi(f - f_0)}{\gamma} \right]^2}, \quad (9)$$

where I is the peak magnitude, f_0 is the frequency at the peak center, and γ is the half-width at half-maximum. Finally, the phonon lifetime is defined as follows:

$$\tau = \frac{1}{2\gamma}. \quad (10)$$

The phonon spectral energy densities of silicene in different cases are compared in Fig. 5. To obtain a better display resolution of the SED for the case of supported silicene, we used a model system with $6.6 \text{ nm} \times 82.14 \text{ nm}$ for the x and y directions, and retained the same size in the z direction as in the NEMD simulation. The 1000 sets of atomic velocities required for SED calculation were obtained by outputting the velocities every 200 timesteps during the 20 ps simulation run in the NVE ensemble. However, for the SED calculation in Fig. 6 and 7 (see the text below), due to the fact that Lorentzian fitting is needed for the phonon lifetime, 1000 sets of atomic velocities are not nearly enough; therefore, we reduced the size of the model system in the x and y directions to be $6.76 \text{ nm} \times 5.85 \text{ nm}$, and increased the number of sets of velocities to be 100 000, which is sufficiently high for phonon

Fig. 5 Phonon spectral energy densities of (a) free standing silicene and supported silicene on the (b) 6H-SiC and (c) 3C-SiC substrates. For supported silicene, the interfacial interaction strength is 5 times larger than the original value ($\chi = 5$). The unit for the phonon spectral energy density is eV.

Fig. 6 Comparison of frequency dependent phonon lifetimes between free standing silicene and supported silicene with an interfacial interaction strength of 5 ($\chi = 5$).

Fig. 7 The accumulative thermal conductivity as a function of frequency for free standing and supported silicene with interfacial interaction strength of 5 ($\chi = 5$).

lifetime fitting.⁵⁰ The 100 000 sets of atomic velocities required by the SED calculation for Fig. 6 and 7 were obtained by outputting the velocities every 250 timesteps during the 2.5 ns simulation run in the NVE ensemble. As evidenced in Fig. 5(a) (free standing silicene) and 5(b) (silicene supported on the 6H-SiC substrate), with strong interfacial interaction between the silicene and the 6H-SiC substrate ($\chi = 5$), the phonon SED with frequencies lower than 5 THz becomes considerably clearer compared to free standing silicene, suggesting reduced phonon scattering and enhanced thermal conductivity. Unlike graphene, in which the in-plane C–C interaction is extremely strong, the interaction between the Si atoms in silicene is weaker. As a result, the normal modes of the supported silicene structure are actually modified by the interfacial interaction of the substrate. This leads to the difference between the phonon dispersion of free standing silicene and supported silicene; moreover, this also partially explains why the thermal conductivity of supported silicene is modified. The very unclear phonon SED in Fig. 5(c) (supported silicene on the 3C-SiC substrate), as compared with the free standing case, indicates strong phonon scattering at the interface and thermal conductivity reduction, which may be due to the large structure mismatch between silicene (honeycomb lattice) and the 3C-SiC surface (f.c.c. like structure), as shown in the top panel of Fig. 1.

We have investigated the size effect⁵¹ of the thermal conductivity of free standing silicene for SED calculations with a sample size of $n \times n \times 1$, where n ranges from 4 to 12. We found that the size effect is minimal. Therefore, for our SED calculation, and also considering lattice mismatch, we only considered the size of $10 \times 15 \times 1$ unit cells (similar to $12 \times 12 \times 1$) of silicene as a model system. The frequency dependent phonon lifetimes of free standing and supported silicene are compared in Fig. 6. It can be clearly seen that for silicene sup-

ported on the 6H-SiC substrate, the lifetime of phonons with frequencies less than 5 THz is significantly enhanced compared with free standing silicene, while the lifetime of high frequency phonons is slightly reduced. From the dispersion curves (Fig. 5), we see that 5 THz is the gap between the acoustic transverse modes and the optical flexural modes. This indicates that the phonons that have longer lifetimes when supported on the 6H-SiC substrate are purely acoustic, which is consistent with the findings in Fig. 4. The longer lifetime of the acoustic phonons is also in line with Fig. 2(b), in which the phonon mean free path of silicene supported on 6H-SiC is found to be largely enhanced compared with free standing silicene (101.6 nm vs. 29.3 nm). The slight decrease in the lifetime of phonons above 5 THz for the case of silicene supported on the 6H-SiC substrate can be attributed to the scattering between the acoustic longitudinal modes and the high frequency optical modes. In contrast, for silicene supported on the 3C-SiC substrate, the phonon lifetime is reduced for almost the entire frequency range, especially for the phonons with frequencies higher than 3 THz; *i.e.*, the major affected phonons are optic, which is again consistent with Fig. 4 and 5.

In Fig. 7, we show the accumulative thermal conductivity as a function of frequency for the free standing and supported silicene calculated by eqn (5). In the case of silicene supported on the 6H-SiC substrate, the accumulative thermal conductivity first sharply increases with frequencies up to 5 THz, and then increases at a considerably slower pace (almost the same slope as free standing silicene). Comparing with Fig. 4, we know that the steep increase before 5 THz originates from the large enhancement in the lifetime of the acoustic phonons, and the same increase in slope after 5 THz originates from the slightly changed lifetime and the minor contribution of optical phonons to the overall heat conduction. Fig. 7 also provides direct evidence that the acoustic phonons below 5 THz dominate the phonon transport of silicene when supported on the 6H-SiC substrate, which is consistent with the previous phonon polarization analysis presented in Fig. 4. In the case of silicene supported on the 3C-SiC substrate, the accumulative thermal conductivity is almost the same as that for free standing silicene for low frequency phonons (less than 3 THz). After that, it starts to deviate, and the accumulative thermal conductivity of the supported silicene is considerably lower than that of free standing silicene for the rest of the frequency range. Again, this is consistent with previous results (Fig. 4 and 5), which demonstrates that almost all the phonons are influenced (suppressed) by the substrate. It is worth pointing out that there is a difference in the absolute values of thermal conductivity between the SED calculation and the NEMD simulation. This difference is actually a general problem, which is similar to the thermal conductivity discrepancy between Green-Kubo MD (EMD) and NEMD. Because the general trend presented in this paper is more relevant, we are more concerned about the mechanism revealed by the SED calculation than the absolute values of thermal conductivity.

In summary, we have studied the effect of substrates on the thermal transport of two-dimensional Si (silicene) by performing nonequilibrium molecular dynamics simulations. A counter-intuitive phenomenon, in which the thermal conductivity of silicene can be either enhanced or suppressed by changing the surface crystal plane of the substrate, has been observed. The phenomenon presented herein is fundamentally different from the behavior of supported graphene, which has been well documented in literature, where the thermal conductivity is always reduced upon the addition of substrate. The underlying physics of the new phenomenon for supported silicene has been investigated and presented by performing phonon polarization and spectral energy density analysis. Both the methods yield the consistent mechanism that the bilateral effect of the 6H-SiC and 3C-SiC substrates on the thermal conductivity of silicene stems from the different impacts on the phonons induced by the substrate: the dramatic increase (about 2 times larger) in the thermal conductivity of silicene supported on the 6H-SiC substrate is due to the augmented lifetime of the majority of the acoustic phonons, while the significant reduction in the thermal conductivity of silicene supported on the 3C-SiC substrate results from the depression in the lifetime of almost the entire phonon spectrum. This bilateral effect may be correlated with the structure mismatch between the honeycomb silicene and the surface crystal plane of the substrates: the 6H-SiC has a similar honeycomb lattice on the surface, leading to less lattice mismatch between the silicene and the substrate, while the 3C-SiC has a very different f.c.c.-like surface structure, resulting in a large structure mismatch. We anticipate that our results could generate great interest in exploring the thermal transport properties of other two-dimensional materials supported on various substrates. Our findings also provide a useful guide for modulating the thermal transport properties of two-dimensional Si by choosing different substrates, and may be of use in tuning the electronic and optical properties of silicene for electronic, thermoelectric, photovoltaic, and opto-electronic applications.

Acknowledgements

This work is funded by the Excellence Initiative of the German federal and state governments through ERS interdisciplinary Seed Fund Projects (Project no. OPSF274). X. Z. would like to thank Prof. A. J. H. McGaughey and Dr J. M. Larkin for helpful discussions about the phonon spectral energy density calculation. H.B. would like to acknowledge the support by the National Natural Science Foundation of China (no. 51306111) and Shanghai Municipal Natural Science Foundation (no. 13ZR1456000). Simulations were performed with computing resources granted by the Jülich Aachen Research Alliance-High Performance Computing (JARA-HPC) from RWTH Aachen University under Project No. jara0073.

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