ABSTRACT: Silicon is one of the most frequently used chemical elements of the periodic table in nanotechnology (Goodilin et al., ACS Nano 2019, 13, 10879–10886). Two-dimensional silicene, a silicon analogue of graphene, has been readily obtained to make field-effect transistors since 2015 (Tao et al., Nat. Nanotechnol. 2015, 10, 227; Tsai et al., Nat. Commun. 2013, 4, 1500). Recently, as new members of the silicene family, penta-silicene and its nanoribbon have been experimentally grown on a Ag(110) surface with exotic electronic properties (Cerda et al., Nat. Commun. 2016, 7, 13076; Sheng et al., Nano Lett. 2018, 18, 2937–2942). However, the thermoelectric performance of penta-silicene has not been so far studied, which would hinder its potential applications of electric generation from waste heat and solid-state Peltier coolers. Based on the Boltzmann transport theory and \textit{ab initio} calculations, we find that penta-silicene shows remarkable room-temperature figures of merit \( ZT \) of 3.4 and 3.0 at the reachable hole and electron concentrations, respectively. We attribute this high \( ZT \) to the superior “pudding-mold” electronic band structure and ultralow lattice thermal conductivity. The discovery provides new insight into the transport property of pentagonal nanostructures and highlights the potential applications of thermoelectric materials at room temperature.

KEYWORDS: \textit{ab initio} calculations, penta-silicene, “pudding-mold” electronic structure, figure of merit, thermoelectric property

INTRODUCTION

The thermoelectric effect directly converts waste heat to electrical energy. Its efficiency is defined by a dimensionless figure of merit \( ZT \), written as \( ZT = S^2\sigma T/(\kappa_e + \kappa_L) \) in which \( S, \sigma, \kappa_e, \kappa_L \) are the Seebeck coefficient, electrical conductivity, electronic thermal conductivity, and lattice thermal conductivity, respectively. Since \( S, \sigma, \kappa_e \) are closely entangled with each other, it is challenging to increase the numerator and decrease the denominator concurrently, gaining a high \( ZT \). Explicitly, an average \( ZT \) larger than 2 would make thermoelectric materials without toxic substances attractive and competitive when compared with other types of energy conversion.\(^7\) Furthermore, taking into account the application in daily life, near-room-temperature thermoelectric materials with high \( ZT \) are desirably needed.

A reduced \( \kappa_L \) can improve the thermoelectric efficiency, \( ZT \).\(^8\) One can use resonant bonding\(^9\) and lone electron pairs\(^10\) to reduce \( \kappa_L \). Besides, the power factor \( S^2\sigma \) can be augmented by electronic band engineering\(^{11-13}\) and the quantum confinement effect.\(^14\) Furthermore, two-dimensional (2D) materials have inherent advantages to moderate the contradiction between \( S \) and \( \sigma \) due to the tunable electronic band gap, resulting in a high power factor. This is much simpler than in the case of bulk materials. In the case of 2D materials, one has great potential to break the complicated relationship between \( S \) and \( \sigma \) due to the quantum confinement effect. This argument was first given by pioneer Mildred Dresselhaus.\(^14\) She also pointed out that one of the advantages of 2D layered materials is that one can actually engineer the band gap. In 2D, one can...
simply change the number of layers or apply stress/strain to modify the band gap or even tune the chemical bond to modify the electronic band gap.\textsuperscript{14}

In 2014, a theoretical work predicted a new 2D carbon allotrope called penta-graphene with favorable stability\textsuperscript{15} whose prototype was first proposed in iron-based materials with exotic magnetic frustration.\textsuperscript{16} Afterward, the pentagonal system has attracted much attention, such as unexpected thermal conductivity\textsuperscript{17–19} and seamless electrical contacts.\textsuperscript{20} Recently, a stable penta-silicene was found by reducing the Coulomb interaction of silicon dimers.\textsuperscript{21} They also reported that it has an ultrahigh Curie temperature of 1190 K. However, the thermoelectric performance of penta-silicene is still lacking.

In this study, we explore the thermoelectric property of penta-silicene based on the Boltzmann transport theory and \textit{ab initio} calculations. It has good thermal, dynamical, and mechanical stability compared with many typical 2D materials. We find that penta-silicene has a nearly direct band gap of 0.68 eV at the DFT-HSE06 level. Lattice thermal conductivities of penta-silicene have values of 1.66 and 1.29 W/mK along \textit{x}- and \textit{y}-axes, respectively. At room temperature, penta-silicene shows maximum figures of merit \textit{ZT} of 3.4 and 3.0 at the reachable hole and electron concentrations. Our work indicates that penta-silicene is a promising thermoelectric material, especially near room temperature.

\textbf{COMPUTATIONAL METHODS}

We perform DFT calculations using the projector-augmented-wave (PAW) method\textsuperscript{22,23}, Perdew–Burke–Ernzerhof (PBE),\textsuperscript{24} and hybrid exchange-correlation HSE06 functional\textsuperscript{25,26} with a default mixing parameter value \(\alpha = 0.25\) in the VASP code.\textsuperscript{27–29} Plane waves with a 550 eV kinetic cutoff energy are used. The vacuum distance between the neighboring layer is set to be 20 Å removing the nonphysical long-range electrostatic interaction. The ionic Hellmann–Feynman forces in each atom and total energy are converged to 10\(^{-4}\) eV/Å and 10\(^{-4}\) eV in the structure optimization and band calculation. The Brillouin zone is sampled by uniform 21 \(\times\) 21 \(\times\) 1. The electronic transport properties are calculated using the electronic Boltzmann transport theory implemented in BoltzTraP.\textsuperscript{30} In the phonon calculation, we used a 5 \(\times\) 5 \(\times\) 1 supercell and 2 \(\times\) 2 \(\times\) 1 k-point sampling to compute the second- and third-order force constants. To solve the phonon Boltzmann transport equation, we adopted a 101 \(\times\) 101 \(\times\) 1 \(\Gamma\)-centered q-grid. We also have tested the convergence of lattice thermal conductivity with respect to the cutoff radius, as shown in the Supporting Information. The linearized phonon Boltzmann transport equation is solved by ShengBTE\textsuperscript{31} via a full iteration.

\textbf{RESULTS}

\textbf{Crystal Structure.} The optimized monolayer penta-silicene is shown in Figure 1a,b. There are six atoms in the primitive cell indicated by blue shading. From the top view, penta-silicene is the same as penta-graphene.\textsuperscript{15} However, penta-silicene has a little distortion compared with penta-graphene.\textsuperscript{31} This is due to the tilting of silicon dimers in the penta-silicene in order to reduce the strong Coulomb repulsion and stabilize the crystal structure. It means that one cannot obtain penta-silicene by simple element substitution. One should break the symmetry by moving one of the atoms in order to further lower the energy and reach a local minimum potential profile. The symmetry becomes \(P2_1\) (space group no. 4) from \(P4_2/m\) (space group no. 113). The optimized lattice constants of penta-silicene and penta-graphene, shown in Table 1, are \(a = b = 3.58\) Å and 3.64 Å, respectively, which are in good agreement with previous results.\textsuperscript{15,21} It is reasonable to the augment of atomic size in the same main group IV. Intrinsically, the buckling distance also increases from 1.21 to 2.44 Å from penta-graphene to penta-silicene. The cohesive energy can be calculated by \(E_c = (n \times E_{Sl} - E_o)/n\) in which \(E_{Sl}\) and \(E_{o}\) are the energy of single silicon atom, the energy of the whole system at the equilibrium state, and the number of atoms in the system. The calculated \(E_c\) of penta-graphene and penta-silicene are 7.08 and 3.92 eV/atom. Note that, in the experiment, \(E_c\) of the experimentally accessible silicene (hexagonal symmetry with two atoms in the primitive cell) and phosphorene, suggesting a robust chemical environment bond to maintain the stability of penta-silicene.

In 3D materials, the elastic tensor is a \(6 \times 6\) tensor with 36 number of tensor elements. By considering the symmetry of the crystal structure, the \(6 \times 6\) tensor can be further simplified according to the specific crystal systems. There are seven crystal systems in solid. The higher the symmetry of the crystal system, the smaller the number of independent tensor elements. For 2D materials, the elastic tensor is a \(3 \times 3\) tensor. To be specific, the mechanical property has a close relationship with phonon modes on the crystal momentum near the center of the Brillouin zone.\textsuperscript{36} For penta-silicene, there are three independent elastic components, which are \(C_{11}\), \(C_{12}\), and \(C_{66}\). Note that the value of \(C_{66}\) is equal to the shear modulus \(G\). The calculated mechanical data of penta-silicene is shown in Table 1. The elastic constants of any stable 2D materials must satisfy \(C_{11}C_{22} - C_{12}^2 > 0\) and \(C_{66} > 0\). From the table, it can be found that penta-silicene is mechanically stable. Furthermore, the value of \(C_{12}\) is \(-46.88\) GPa, indicating a negative in-plane Poisson’s ratio that is defined as\textsuperscript{37} \(\nu_{xy} = \frac{C_{12}}{C_{11}}\).

For penta-graphene and penta-silicene, \(C_{11} = C_{22}\) and \(C_{12} = 0, C_{22} = C_{11}\). For penta-graphene and penta-silicene, \(C_{11} = C_{22}\) and \(C_{12} = 0, C_{22} = C_{11}\). Of penta-silicene is smaller than those of Si-\(\text{Cmma}\) of and Si-\(\text{Pmma}\),\textsuperscript{38} indicating a more flexible mechanical

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{image.png}
\caption{(a, b) Top and side views of the atomic structure of the monolayer penta-silicene in a \(3 \times 3\) supercell. (c) Electronic band structure of penta-silicene using the DFT-PBE (black) and DFT-HSE06 (red) functionals. (d) Electronic density of states (DOS) at the HSE06 level. The indirect fundamental band gaps are marked by the green (PBE) and orange (HSE06) arrows in (c). The Fermi levels are set to zero. The sum of the intrinsic thickness \(d\) and two van der Waals radii of the outermost atom is defined as the effective thickness \(h\). The primitive cell is indicated by blue shading in (a). Four hole pockets in valence bands around the Fermi level are labeled by different colors and numbers (VBM, VB2, VB3, and VB4). VBM denotes the valence band maximum. In the first Brillouin zone, the high symmetry \(k\) points are: \(\Gamma(0\ 0\ 0), X(1/2\ 0\ 0), S(1/2\ 1/2\ 0)\), and \(Y(0\ 1/2\ 0)\), respectively.}
\end{figure}
properties than other silicon allotropes. The calculated $\nu$ of penta-graphene and penta-silicene are $-0.09$ and $-0.55$. The value of $\nu$ in penta-silicene is 5 times larger than that in penta-graphene. This mechanical property of the negative Poisson’s ratio is highly desirable for shock absorption in transistors.37,39

### Electronic Band Structure
The electronic band structure of penta-silicene is shown in Figure 1c,d. At the PBE level (black), the indirect band gap indicated by the green arrow is 0.28 eV. Since the fundamental band gap is usually underestimated in DFT-PBE calculations, we also calculate it using the HSE06 functional (red). Overall, the entire energy bands are almost unchanged except for the shift up of the conduction bands and the shift down of the valence bands. Interestingly, the HSE06 band shows a nearly direct band gap of 0.68 eV indicated by the orange arrow. This change from the indirect-to-direct band gap would significantly enhance the optical absorbance.40 Some top valence bands of monolayer penta-silicene around the Fermi level not only are quite close but also are degenerate energetically. The conduction bands around the Fermi level have no similar behavior. We marked the “mountain peaks” of valence bands by different colors and numbers (VBM, VB2, VB3, and VB4). As a matter of fact, these degenerate valence bands will significantly enhance DOS and further Seebeck coefficient41,42 that directly enters the final figure of merit ZT. Furthermore, since the valence bands are highly degenerate, while conduction bands are nondegenerate, this leads to an asymmetric DOS in Figure 1d. This physical picture is known as “pudding-mold” and desirably required to achieve a large ZT.11 We will further discuss it in the following.

### Electronic Transport Properties
In order to obtain the electronic transport properties, such as Seebeck coefficient $S$, electrical conductivity $\sigma$, and electronic thermal conductivity $\kappa$, one has to compute the following quantities based on the Boltzmann transport theory, written as a function of the tensor $K_{\alpha \beta}^{i}$:

$$K_{\alpha \beta}^{i} = \frac{2}{(2\pi)^{3}} \sum_{i} \int \frac{d^{3}k}{\omega_{i}} \epsilon_{i}(k) \left[ \partial \mu \left( k, T, \epsilon_{i} \right) \right]$$

$$\sigma = e^{3} K_{0}$$

$$S = \frac{1}{eT} K_{0}^{-1}$$

### Table 1. Calculated Physical Properties of Penta-Graphene and Penta-Silicene

<table>
<thead>
<tr>
<th>materials</th>
<th>$a_{1}$(Å)</th>
<th>$d$(Å)</th>
<th>$h$(Å)</th>
<th>$E_{c}$(eV/atom)</th>
<th>$C_{11}$(GPa)</th>
<th>$C_{12}$(GPa)</th>
<th>$G$(GPa)</th>
<th>$\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>penta-Gr</td>
<td>3.64</td>
<td>1.21</td>
<td>4.61</td>
<td>7.08</td>
<td>584.34</td>
<td>-46.88</td>
<td>328.94</td>
<td>-0.09</td>
</tr>
<tr>
<td>penta-Si</td>
<td>5.58</td>
<td>2.44</td>
<td>6.64</td>
<td>3.92</td>
<td>43.13</td>
<td>-23.56</td>
<td>30.31</td>
<td>-0.55</td>
</tr>
</tbody>
</table>

$\bar{a}_{1}$(Å) is the lattice constant. $d$ and $h$ are the intrinsic buckling distance and effective thickness, respectively. $E_{c}$ is the cohesive energy per atom. $C_{ij}$ is the elastic modulus tensor. $G$ and $\nu$ are the shear modulus and Poisson’s ratio, respectively.

![Figure 2](https://example.com/figure2.png)

Figure 2. Calculated temperature-dependent electronic transport coefficients. (a, b) Seebeck coefficient $S$ and (c, d) electrical conductivity $\sigma$ as a function of temperature and carrier concentration (holes and electrons) for x- and y-axis at 300 and 600 K.
$$\kappa_e = \frac{1}{T} (K_2 - K_0^2 K_0^{-1})$$

in which 2 is for the spin degeneracy, \(v_i(k)\) is the electron group velocity of the wave vector \(k\) and band index \(i\), \(\varepsilon_i\), \(\mu_i\), and \(\tau_i(k)\) are electronic energy, chemical potential, and electronic relaxation time. Alternatively, \(\kappa_e\) can also be calculated through the Wiedemann–Franz law

$$\kappa_e \sigma = LT$$

where \(L\) is a constant called the Lorenz number with a value of 2.4 \times 10^{-8} \text{ W} \Omega \text{ K}^{-2}. The calculated \(\kappa_e\) from eqs 4 and 5 are the same for semiconductors, which has been verified by many previous works.\(^{43-45}\)

Here, we consider two temperatures (300 and 600 K) in the following calculations. The calculated \(S\) and \(\sigma\) are shown in Figure 2. For both p-type and n-type doping, \(S\) first increases (absolute value) at low carrier concentrations \(n < 10^{12} \text{ cm}^{-2}\) and then linearly decreases at high carrier concentrations \(10^{12} \text{ cm}^{-2} < n < 10^{14} \text{ cm}^{-2}\). According to the Mahan–Sofo theory, \(S\) for degenerate 2D semiconductors can be written as

$$S_{2D} = \frac{2\pi^3 k_B^2 T^2}{3h^2 n^3} m_d^*$$

where \(h\), \(n\), and \(m_d^*\) are the Planck constant, carrier concentration, and DOS effective mass around \(E_F\). Since electrons of 2D materials only have freedom in the plane, \(S_{2D}\) is quite different from \(S_{3D} = \frac{2\pi^3 \hbar^2 T}{3\pi^2} \times \left(\frac{2}{3}\right)^{2/3} \times m_d^*\) in bulk materials.\(^{42}\) Hence, there is a competition relation between \(n\) and \(m_d^*\). For high concentrations, our calculated \(S_{2D}\) of penta-silicene is inversely proportional to \(n\), which is in good agreement with the Mahan–Sofo theory. For low concen-
See the natural text in the main body of the document.
40.23 mW/mK² at 5.09 × 10¹³ cm⁻² concentration along the x- and y-axes, respectively. Similarly, maximum PF for n-type doping are 61.75 and 39.22 mW/mK² at 1.55 × 10¹³ cm⁻² concentration along both axes at the same temperature. Such PF values are quite larger than those of 2D tellurium (57.3 mW/mK²)⁴² and 2D SnSe (57.3 mW/mK²).⁴⁷

A good thermoelectric material should satisfy that the distribution of electronic energy carriers at the Fermi level is as narrow as possible, as well as high carrier velocity according to the Mahan’s guideline.⁵² Subsequently, researchers find an effective approach to enhance the Seebeck coefficient S and electrical conductivity σ simultaneously, where the electronic bands around E_F contain both flat and dispersive bands in the dependent momentum space. It is known as a “pudding-mold” band structure.⁵³,⁵⁴ Flat bands increase the DOS and dispersive bands induce high carrier velocities. It has been used to explain many prominent thermoelectric performances, such as Na₃CoO₂,⁵³ SnSe,⁵⁵ PbTe¹, and tellurium.⁴₂ The ultrahigh PF of penta-silicene is derived from four hole pockets and relatively flat bands with the same spirit of “pudding-mold” shown in Figure 2c.d.

**Lattice Thermal Conductivity.** Maybe the lattice thermal conductivity κ_L is the only parameter that can be tuned independently. The calculated phonon transport property of penta-silicene is shown in Figure 4. The phonon dispersion in Figure 4a is free from imaginary numbers, indicating a strong dynamical stability of penta-silicene. The sound velocity is defined as \( v = \frac{d\omega}{dk} \bigg|_{k=0} \). The calculated v of acoustic phonon modes TA and LA are shown in Table 3 (ZA mode is a quadratic function of the wave vector). More details about this parabolic ZA mode can be found in the Supporting Information. \( v_{TA} \) are 3.99 and 4.70 km/s along the x- and y-axes, respectively. \( v_{LA} \) is larger than \( v_{TA} \), having values of 4.77 and 5.54 km/s along the x- and y-axes, respectively. κ_L as a function of temperature is shown in Figure 4b. At room temperature, κ_L of penta-silicene are 1.66 and 1.29 W/mK along x- and y-axes, respectively. There are two types of scatterings of phonon transport. One is the Normal process and the other one is the Umklapp (U) process. The latter is the only contributor to the final thermal resistance. The touchstone to explore the role of the U process is to study κ_L as a function of temperature. If κ_L \( \propto \frac{1}{T^2} \) the U process dominates the heat transport in this material. Figure 4b of penta-silicene shows a good example of this type in heat transport behavior.

According to the Slack model, a small Θ_D generally means a small κ_L since acoustic phonons are the main carrier in heat transport. The definition is \( \Theta_D = h\omega_{max}/k_B \) in which \( \omega_{max} \) is the maximum frequency of the acoustic phonon branches. The calculated Θ_D of penta-silicene is shown in Table 3. The largest Θ_D has a value of 131.51 K along the x-axis. This value is about one-fifth that of penta-graphene (Θ_D = 692 K).⁵⁶ What is more, the frequency-resolved κ_L of penta-silicene further confirms this discussion. Phonon vibrations below 50 cm⁻¹ contribute most to the final κ_L and heat transport whether it is the x-axis or the y-axis. Phonon relaxation time in Figure 4d also verifies this fact. In the three branches of acoustic phonons, the LA branch has the largest phonon relaxation time compared with the ZA and TA modes. The ultralow κ_L of penta-silicene originates from the weak phonon harmonic interaction and strong anharmonic scattering.¹⁹,⁵⁷,⁵⁸ We hope that this low κ_L would induce a high figure of merit ZT of penta-silicene.

**Figure of Merit ZT.** Based on the above results of electronic and phonon transport properties, one can evaluate the value of merit ZT written as

\[
ZT = \frac{S^2\sigma}{\kappa_L + \kappa_F}T
\]

The calculated ZT of penta-silicene for both p-type and n-type are shown in Figure 5. Interestingly, due to the high PF and low κ_F, penta-silicene shows a large ZT (＞2) at room temperature for both x- and y-axes. Specifically, maximum ZT_p (for the hole) has values of 3.43 and 2.24 at 3.42 × 10¹² and 4.60 × 10¹² cm⁻² concentrations along x- and y-axes at room temperature, respectively. Similarly, maximum ZT_n (for the electron) has values of 2.18 and 3.04 at 2.51 × 10¹² and 1.85 × 10¹² cm⁻² along x- and y-axes at 300 K. In a graphene-based field-effect transistor, a doping level up to 4 × 10¹⁴ cm⁻² for both electrons and holes has been reached by electrical gating⁵⁹ and ionic liquid injection.⁶⁰ Due to the portability of the experimental technique, 2D materials, like graphene, MoS₂, and black phosphorus, generally can reach 4 × 10¹⁴ cm⁻² for both electron and hole doping level. Note that our carrier concentrations (＜4 × 10¹⁴ cm⁻²) all are reachable in these current experimental technique. Therefore, our result indicates that monolayer penta-silicene is a promising thermoelectric material.

![Figure 4a](image1.png)

**Figure 4a.** A comparison of carrier concentration vs. the calculated electrical conductivity for both p-type and n-type penta-silicene. The calculated PF for n-type is 42 and 2D SnSe (57.3 mW/mK²).⁴⁷

![Figure 4b](image2.png)

**Figure 4b.** The calculated frequency-resolved phonon relaxation time in Figure 4d also verifies this fact. In the three branches of acoustic phonons, the LA branch has the largest phonon relaxation time compared with the ZA and TA modes. The ultralow κ_L of penta-silicene originates from the weak phonon harmonic interaction and strong anharmonic scattering.¹⁹,⁵⁷,⁵⁸ We hope that this low κ_L would induce a high figure of merit ZT of penta-silicene.

**Figure 5.** Calculated figure of merit ZT of (a) p-type and (b) n-type penta-silicene as a function of the carrier concentration along x- and y-axes at 300 and 600 K.
**CONCLUSIONS AND DISCUSSION**

According to eq 8, the figure of merit ZT is closely related to the temperature. Generally, ZT increases when temperature increases, such as SnSe with a ZT of 2.6 ± 0.3 at 923 K.55 and PbTe–PbS pseudo-binary with a ZT of 2.3 at 923 K.62 Taking into account the application in daily life, near-room-temperature thermoelectric materials with high ZT are desirable. There is no doubt that B₄I₄–Te₆–based thermoelectric materials still dominate around room temperature. However, the tellurium element has very low reserves on earth and much expensive. How to find inexpensive thermoelectric material that works efficiently at room temperature is still an open question.1–3 Very recently, some researchers have made progress in this direction. For example, Mg,Bi₃ alloy has a ZT of 0.9 at 350 K.63 Penta-silicene with a ZT of 3.43 probably enriches the room-temperature thermoelectric materials. Besides, how to manipulate defects, lattice symmetry, spin, and electron–phonon coupling to further enhance room-temperature ZT is one of the cutting edges in the thermoelectric field.

For 2D materials, stability is the most important before property. As a matter of fact, metastable phases are quite common in condensed matter. Materials science overwhelmingly deals with metastable states. Besides penta-silicene, many simple light-element compounds including high hydrocarbons, nitrogen oxides, hydrides, carbides, carbon monoxide (CO), alcohols, and glycerin are also metastable at ambient conditions. Nevertheless, the ubiquitous metastable phases do not produce a bad effect on their vast and tremendous applications in modern industrial societies and our daily life. The world has been varied and diverse due to the fact that the metastable states provide the complexity of structures and energy transformation. Furthermore, previous works have successfully obtained penta-silicene nanoribbon on Ag(110) with exotic electronic properties.4–6,21 At the energy level, the cohesive energy $E_c$ of penta-silicene is 3.92 eV/atom that is comparable with the 3.71 eV/atom23 of silicene (hexagonal symmetry with two atoms in the primitive cell) and 3.61 eV/atom34,35 of black phosphorene. Note that above two metastable 2D materials, at present, can be easily obtained in experiment based on the advanced experimental technique such as creating a complex chemical environment and variable substrate effect. Besides, we also calculate other two allotropes of penta-silicene. There are Si-Cmma and Si-Pmma.38 The calculated $E_c$ of Si-Cmma and Si-Pmma are 4.17 and 4.18 eV/atom, relatively more stable than penta-silicene.

Moreover, we offer three very promising experimental approaches to make freestanding penta-silicene potentially. Besides, these methods also have great potential for other 2D materials. “Geometrical frustration” was first raised by Joel Therrien who are synthesizing the penta-graphene and other freestanding carbon rings, such as the U-carbon.65 As far as we can see, penta-silicene has no counterpart in the corresponding bulk material. This fact is quite different from graphene and graphite. Crystalline oxide perovskites, like penta-silicene, also cannot be obtained by mechanical exfoliation. However, monolayer freestanding crystalline oxide perovskites have been grown by “reactive molecular beam epitaxy”.64 Besides, freestanding monolayer amorphous carbon has successfully been created by the “laser-assisted chemical vapor deposition” method.65 This monolayer amorphous carbon contains five-, six-, seven-, and eight-membered carbon rings. Note that penta-silicene only consists of five-membered silicon rings. Encouraged by these above advanced technologies in the experimental cutting edge, we conclude that monolayer free-standing penta-silicene and other novel nanostructures can also be obtained on the near horizon.

Sometimes, the figure of merit ZT based on the mobility $\mu$ in eq 7 is a little overestimated since acoustic phonon is not the only factor to impact the $\mu$ that determines the final ZT. As we mentioned before, nonpolar optical phonons and ionized impurities also influence $\mu$. Generally, the impact of these two factors can be neglected and the role of longitudinal acoustic phonons is dominant.12,51,66,67 Given that realistic calculation of couplings between nonpolar optical phonons and electrons, ionized impurities and electrons are beyond our current computing capabilities, and they are interesting open questions that deserve further exploration.

The DP theory is based on the rigid band approximation. Surprisingly, this approximation works well for most cases when the electronic bands around the Fermi level are not highly degenerate.42,68 Besides, VASP, Quantum ESPRESSO, and BoltzTraP softwares,27–30 to name a few, also can add electrons into or remove electrons from the system through a compensating uniform charge background of opposite sign to maintain charge neutrality, which verifies the correctness of this approximation additionally.

The DP theory has been widely used and has been successful in calculating the intrinsic (freestanding and defect-free) mobility, which can be found everywhere. Certainly, almost any theoretical model has assumptions, either large or small, such as the famous density functional theory, Dulong–Petit law (high temperature), and even Newton’s laws of motion (inertial system). The DP theory is also included. As a matter of fact, in the DP theory, only the longitudinal-acoustic phonon is considered without any dispersion and the electron–phonon matrix is expressed by the DP constant and the elastic constant that are described in the eq 7. The optical phonon scatterings are absent in the DP theory. However, DP theory’s results are qualitatively and even quantitatively reasonable in many cases compared with the full evaluation of electron–phonon coupling.69 Since this calculation is far beyond our current computational capabilities, hence, we suggest leaving the $e$–$\mu$ coupling as an open question, which should be explored further.

How a 2D functional material, like our penta-silicene, is to be used in bulk devices? There are four options to integrate bulk materials with 2D materials for physical coupling and applications.70 On the one hand, one can construct 2D materials on 3D materials (2D-on-3D) heterostructures. The technique methods are van der Waals epitaxy (vdWE), wet transfer, and the metal-induced quasi-dry transfer process. On the other hand, the realization of 3D-to-2D heterostructures is still at a premature stage. However, the relevant experiment is growing fast, which has significantly broadened the material beyond conventional 3D material-based heterostructures.

In summary, we have calculated the thermoelectric performance of monolayer penta-silicene by first-principles. It has good thermal, dynamical, and mechanical stability compared with many other typical 2D materials, such as hexagonal silicon and black phosphorus. Lattice thermal conductivities of penta-silicene have values of 1.66 and 1.29 W/mK along x- and y-axes, respectively. Superior electronic properties originate from the “pudding-mold-like” shape of valence bands around the Fermi level. Ultralow thermal conductivity and high power
factor collaboratively lead to an ultrahigh ZT of penta-silicene. At room temperature, maximum ZT has values of 3.43 and 3.04 for hole doping and electron doping, respectively. Our work has indicated that penta-silicene is a promising thermoelectric material, especially at near room temperature. The layer-dependent thermoelectric property of penta-silicene deserves more follow up study in the future.

■ ASSOCIATED CONTENT

 Supporting Information

 The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsami.9b21076.

 Room-temperature lattice thermal conductivity of penta-silicene as a function of the cutoff for the interaction range of anharmonic force constants and phonon dispersion superposed on the spectra from the continuum theory (PDF)

 ■ AUTHOR INFORMATION

 Corresponding Author

 Zhibin Gao — Department of Physics, National University of Singapore, Singapore 117551, Republic of Singapore; orcid.org/0000-0002-6843-381X; Email: zhibin.gao@nus.edu.sg

 Author

 Jian-Sheng Wang — Department of Physics, National University of Singapore, Singapore 117551, Republic of Singapore

 Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.9b21076

 Notes

 The authors declare no competing financial interest.

 ■ ACKNOWLEDGMENTS

 The authors are grateful to Wu Li for the kind guidance on calculation of lattice thermal conductivity. We acknowledge Jinnyang Xi for many fruitful discussions and kind help. We acknowledge the kind help. We acknowledge the support from MOE tier 1 funding of NUS Faculty of Science, Singapore (grant no. R-144-000-402-114).

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