Interpenetrating silicene networks: A topological nodal-line semimetal with potential as an anode material for sodium ion batteries

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(Received 24 April 2018; revised manuscript received 3 July 2018; published 27 August 2018)

Motivated by the novel properties of topological nodal-line semimetal and its compatibility with the well-developed Si-based semiconductor technology, we propose a three-dimensional all-silicon topological nodal-line semimetal composed of interpenetrating silicene networks (ISN). Using state-of-the-art first-principles calculations and the cluster expansion method, we find the ISN structure to be dynamically, thermally, and mechanically stable. In addition, it exhibits linearly dispersive band crossings along two perpendicular high-symmetry directions due to the band inversion and shows two nontrivial nodal lines, traversing in the Brillouin zone near the Fermi level. Furthermore, ISN has the potential as an anode material for sodium-ion batteries with an extremely low diffusion energy barrier and a small volume change during the charging/discharging process, which would lead to a high rate and stable cycling performance.

DOI: 10.1103/PhysRevMaterials.2.084201

I. INTRODUCTION

Due to their fascinating physical properties and potential for applications as electronic devices, three-dimensional (3D) topological semimetals (TSMs) have received a great deal of attention [1]. Extensive studies have been carried out to search for novel TSM structures [2–5]. Among these, carbon-based TSMs are of special interest as shown in Mackay-Terrones crystal [6], body-centered orthorhombic [7], Weyl-surface semimetallic 3D graphene networks [8], body-centered tetragonal C16 [9], and nodal-net semimetallic modified body-centered tetragonal C4 [10]. The wealth of topological semimetallic carbon allotropes can be attributed to the bonding flexibility and negligible spin-orbit coupling (SOC) of carbon. The former helps to satisfy the structural symmetry that is required to protect the semimetal state, and the latter is needed to preserve the semimetal state in the presence of SOC.

Although carbon and silicon belong to the same group in the periodic table, silicon behaves differently from carbon. For example, carbon can form single, double, and triple bonds with themselves as well as with other atoms. As a result, carbon exhibits very rich structures such as graphite, diamond, fullerenes [11], nanotubes [12], graphene [13], and penta-graphene [14]; all display diverse properties ranging from semiconductor to semimetal, metal, and superconductor. In contrast, larger number of core electrons in Si makes it much more difficult for two Si atoms to form double or triple bonds. Consequently, Si prefers to form multidirectional single bonds (sp3), making it difficult to form fullerene cages [15], carbonlike nanotube [16], and structures like penta-graphene [17]. Interestingly, in some cases Si does behave like carbon.

For instance, the two-dimensional (2D) structures of carbon (graphene) and silicon (silicene) have honeycomblike structures and exhibit Dirac cones in their electronic states. Thus, silicene can be thought of as an analog of graphene, and hence a 2D Dirac material. Then, an intriguing question arises: Can we find a Si analog for 3D topological nodal-line semimetal? Currently, there are no studies to address this question.

Due to the compatibility with the well-developed Si-based semiconductor industry, it is highly desirable to explore 3D silicon allotropes that exhibit features of topological nodal-line semimetal. In this work, we have explored this question by considering a 3D interpenetrating silicene network (ISN), which is the analog of interpenetrating graphene network. Note that the latter has been found to be a stable topological nodal-line semimetal [18,19]. We show that ISN is a stable topological nodal-line semimetal with two mirror-inversion nodal lines in its Brillouin zone (BZ), exhibiting an almost flat band localized at the surface, leading to a high surface density of states (DOS) at the Fermi level. Furthermore, we explore the potential of ISN as an anode material for Na ion batteries because of its regularly distributed channels for ion transport and intrinsic high conductivity for electron transport [20]. We find that the ISN has an extremely low diffusion energy barrier for Na ion and small volume changes during charging and discharging operation.

II. METHODS

All calculations are performed using density-functional theory implemented in the Vienna Ab initio Simulation Package (VASP) [21]. The projector-augmented wave [22] method with a kinetic energy cutoff of 400 eV is used to describe the electron-ion interactions. The exchange-correlation interactions are treated using the Perdew-Burke-Erzerhof (PBE) functional within the generalized gradient approximation [23].
The first BZ is sampled by a $k$-point mesh with a grid density of $2\pi \times 0.02 \, \text{Å}^{-1}$ using the Monkhorst-Pack scheme [24]. The structure relaxations are carried out without symmetric constraint using the conjugated gradient method with the convergence thresholds of $1 \times 10^{-6}$ eV and 0.001 eV/Å for total energy and force components, respectively. The phonon spectrum is calculated using the finite displacement method as implemented in the PHONOPY code [25]. \textit{Ab initio} molecular-dynamics (AIMD) simulation is performed using the canonical ensemble with the Nosé-Hoover heat bath scheme [26] (300 K) in a $2 \times 2 \times 4$ supercell. The band symmetric representations and slice band structures are calculated with the help of the QUANTUM ESPRESSO [27] and the WANNIER TOOLS package [28], respectively. The diffusion energy barriers for Na ions and the charge population analysis are calculated by using the climbing-image nudged elastic band (CI-NEB) method [29,30] and Bader charge [31,32].

We use the cluster expansion (CE) method to accurately determine the stable intermediate configurations at various Na concentrations, based on which the Na$_x$-ISN system is treated as an alloy and configurational energy is described. We represent each possible Na cation site $i$ with an occupation variable $\sigma_i$, which takes the value 1 if a cation resides at that site and $-1$ if a vacancy is at that site. The configuration-dependent Hamiltonian is mapped onto a generalized Ising Hamiltonian:

$$E(\sigma) = J_0 + \sum_i J_i \sigma_i + \sum_{j<i} J_{ij} \sigma_i \sigma_j + \sum_{k<j<i} J_{ijk} \sigma_i \sigma_j \sigma_k + \cdots$$

and

$$E(\sigma) = J_0 + \sum_{\alpha} J_\alpha \varphi_\alpha,$$

where the subscripts $i$, $j$, and $k$ range over all occupation sites, $\varphi_\alpha$ is the product of occupation variables $\sigma_i$, $\sigma_j$, $\sigma_k$ that form a cluster configuration $\alpha$, which can be a single point, a pair cluster, a triplet cluster, etc. $J_\alpha$ is the corresponding effective cluster interactions, which is obtained by fitting these to the first-principles calculated energies of selected configurations. The quality of the fitted CE is measured by the cross-validation score, and the fitting process is performed by using Alloy Theoretic Automated Toolkit (ATAT) code [33].

### III. RESULTS AND DISCUSSION

#### A. Structure and stability

As shown in Fig. 1(a), ISN can be viewed as a structure constructed by two sets of interlocking silicene sheets, which share zigzag atomic linkages along the $c$ axis. ISN possesses the nonsymmorphic $D_{2d}^{27}$ space-group symmetry (No. 63, Cmcm) and has a 12-atom unit cell with the lattice parameters for its unit cell $a = 8.88 \, \text{Å}$, $b = 9.99 \, \text{Å}$, and $c = 3.85 \, \text{Å}$, occupying two nonequivalent Wyckoff positions of $8g$ (0.2799, 0.8032, 0.75) and $4c$ (0.5, 0.0680, 0.25), denoted by Si1 (colored blue in Fig. 1) and Si2 (colored brown in Fig. 1), respectively. Fig. 1 also shows that SI1 is threefold coordinated, and Si2 is fourfold coordinated. The bond lengths of Si1-Si1 and Si2-Si2 are 2.26 and 2.36 Å, similar to that of silicene (2.24 Å) and cubic-diamond silicon (2.35 Å), respectively, suggesting that the bonding character of ISN shares some features with 3D diamond silicon and 2D silicene. The primitive cell of ISN is shown in Fig. 1(b), which contains six silicon atoms. Furthermore, ISN has squarelike one-dimensional (1D) nanotube channels along the $c$ direction and the side length of the square tubes is around 6.68 Å, leading to a low mass density (1.63 g/cm$^3$), which is noticeably smaller than those of the cubic-diamond silicon (2.38 g/cm$^3$) [34] and the clathrate Si$_{24}$ (2.17 g/cm$^3$) [35]. Moreover, the nanopores could accommodate large atom species such as sodium (Na), potassium atoms (K), or H$_2$ molecules, implying potential applications of ISN in the fields of rechargeable batteries, gas storage, or catalysts.

To assess the structural stability of ISN, we first calculate its phonon band structure, and DOS. The results are plotted in Fig. 2(a), where no imaginary modes are found in the whole BZ, suggesting that ISN is dynamically stable. Furthermore, to examine the thermal stability, AIMD simulation is carried out by constructing a $2 \times 2 \times 4$ supercell containing 96 atoms. The result of simulation at temperature 300 K is plotted in Fig. S1 in Supplemental Material [36], which shows us that the skeleton of ISN remains almost intact without any apparent distortion after being heated at 300 K for 5 ps and total energy only fluctuates around a constant value, confirming that ISN is thermally stable at room temperature.

To examine the mechanical stability of ISN, we calculate the independent elastic constants under small lattice distortion. The calculated results, which satisfy the Born-Huang criteria of orthorhombic lattice [37], are listed in Table S1:

$$
\begin{align*}
C_{11} &> 0, & C_{11}C_{22} &> C_{12}^2, \\
C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 &> 0 \\
C_{44} &> 0, & C_{55} &> 0, & C_{66} &> 0.
\end{align*}
$$

Thus, the ISN structure is mechanically stable. In addition, according to Voigt-Reuss-Hill approximation [38], the bulk modulus ($B$), shear modulus ($G$), and Young’s modulus ($E$) of ISN are calculated to be 51.90, 20.12, and 48.07 GPa, respectively. These values are significantly smaller than those of diamond silicon and hP12-Si [34], which can be attributed...
to the porous structure and low mass density of ISN. Pugh proposed the ratio of shear-to-bulk modulus ($G/B$) as a criterion to evaluate the brittle character of the material [39]. If $G/B < 0.57$, the material behaves in a ductile manner, otherwise in a brittle manner. In our case, the $G/B$ of ISN is 0.42, suggesting that ISN is ductile and external strain can be applied to it easily.

**B. Electronic properties**

In Fig. 3(a), the electronic band structure of ISN at the PBE level indicates that ISN is a semimetal with linear band crossing near the Fermi energy along the $\Gamma$-$Z$ and $T$-$Y$ high-symmetry lines. In addition, as shown in Fig. 3(b), the linear dispersion gives rise to a vanishingly small DOS around the Fermi level, and the partial density of states (PDOS) projected to nonequivalent atomic orbitals indicates that the bands near the Fermi level mainly originate from the $p_x$ or $p_y$ orbitals of the four peripheral three-coordinated Si atoms. Recognizing that the PBE functional usually underestimates the band gap of materials, the more accurate Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional is used to recalculate the band structure of ISN. As presented in Fig. 3(c), the semimetallic band structure of ISN is preserved at the HSE06 level.

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**FIG. 2.** (a) Phonon dispersions and corresponding total frequency density of states of ISN. (b) BZ of ISN with high-symmetry points and paths.

**FIG. 3.** (a) Band structure of ISN. The different symmetry representations $A_1$, $B_2$, $B_1$, $A_2$ are highlighted in red, blue, magenta, and green, respectively. (b) Partial density of states projected to nonequivalent atomic orbitals. (c) The high-symmetry $k$-point path in the BZ. (d) Band crossing of the two bands near the Fermi level nodal line (in purple) in the $k_a = k_b$ plane. (e) Nodal lines inside the ($\bar{1}10$) mirror-invariant plane [blue plane in (c)] of the BZ. The color bar indicates the energy difference between conduction band and valence band at each $k$ point.
The colored band structure of Fig. 3(a) shows the details of band symmetry for the two crossing bands along different high-symmetry paths. In ISN, both the conduction band (CB) and valence band (VB) along the high-symmetry $\Gamma$-$Z$ and $T$-$Y$ lines belong to the same point group ($C_{2v}$), but differ in their symmetric representations. Along the $\Gamma$-$Z$ path, the CB and the VB have the irreducible representations $A_1$ (red, symmetric with respect to all the operators) and $B_2$ (blue, antisymmetric with respect to the operators $C_{2v}$ and $\sigma_{v(z)}$), respectively. However, their energy ordering exchanges after the intersection, leading to the so-called band inversion, which is one of the key ingredients in topological semimetals. The band crossing along the high-symmetry line $T$-$Y$ is similar. When including the SOC effect in the first-principles calculation, gaps of around 17 and 12 meV open up at the crossing points along the $\Gamma$-$Z$ and $T$-$Y$ lines, making ISN a 3D weak topological insulator. The two crossing bands in the $T$-$Z$ and $Z$-$0$ plane of BZ are minimal volumetric change.

Because of the natural abundance, lower cost, environment-friendly nature, and chemical similarity with Li [40,41], Na ion battery is an attractive alternative to Li ion battery for energy storage applications. Among the several anode materials that have been studied for Na ion batteries [42,43], silicon-based anodes are more desirable materials due to their high abundance and low cost [44,45]. Unfortunately, crystalline Si, which exhibits large capacity in Li ion batteries, is not suitable for Na ion batteries [46,47]. In addition, amorphous Si can accommodate Na atoms and deliver a high specific capacity but suffers from substantial volume expansion and slow Na kinetics [48]. In this respect, finding novel crystal silicon structures that have sufficient space to accommodate Na ions and allow rapid ion insertion/extraction is urgent and of great practical significance. Considering the relatively high porosity and intrinsic metallicity, we expect that ISN could be a promising silicon-based anode material for Na ion batteries. To examine this possibility, we systematically investigated the binding and diffusion behavior of Na as well as the theoretical capacity, average potential, and volume change during the ion-insertion process. We find ISN to be an effective anode material for Na ion batteries with high rate capacity and minimal volumetric change.

First, we calculate the binding energy $E_b$ of a single Na atom using a $2 \times 2 \times 4$ supercell of ISN, in order to avoid interaction between the adsorbed atoms,

$$E_b = E_{Na-\text{ISN}} - E_{\text{ISN}} - \mu_{Na},$$

where $E_{Na-\text{ISN}}$ is the total energy of ISN after Na insertion, $E_{\text{ISN}}$ is the energy of the pristine ISN structure, and $\mu_{Na}$ represents the energy per Na atom in bulk sodium metal; negative $E_b$ indicates an exothermic reaction. According to the structural symmetry shown in Fig. 5(a), three possible binding sites are considered. Here, the top site (T) is above the Si atom on zigzag atomic chain, the bridge site (B) is above the middle of the Si–Si bond in the zigzag atomic chain, and the hollow site (H) is above the center of the Si six-membered ring. After full optimizations, we find that the T site is energetically the most preferable binding site for Na atom with a binding energy of 1.37 eV. Furthermore, Bader charge analysis shows that the Na atom donates almost its entire valence electron (0.81 e$^-$) to the ISN framework, leading to a strong ionic interaction between the Na cation and ISN. Besides, the top and side views of the fully sodiated geometry of ISN are displayed in Fig. S6. The stoichiometric formula of maximum Na-intercalated ISN is Na$_{36}$ and the corresponding theoretical specific capacity is 159.5 mAh/g. While this is smaller than that of hard carbon (230 mAh/g) [49], it is the same as that of the open-cage allotrope Si$_{124}$ [45] and larger.
than that of 1T-MoS2 (86 mAh/g) \[50\] (Table I). Bader charge analysis demonstrates that 0.77 e\(^{-}\) per Na atom is transferred to the ISN matrices, slightly smaller than that of the dilute case.

The diffusion behavior of Na cations in ISN is also calculated using the CI-NEB method. As presented in Fig. 5(b), the diffusion pathway along the channel connecting the most stable adsorption T site with its neighbor is considered due to the restriction of the 1D-channel structure. The corresponding diffusion energy profile is shown in Fig. 5(c). The energy barrier for Na atoms along the 1D tunnel is only 5.2 meV, which can be attributed to the large channel size (6.68 Å) and the flat energy landscape along the pathway resulting from the delocalized electrons along the zigzag Si chains. The calculated barrier energy is more than one order of magnitude smaller than that of black phosphorus (0.18 eV) \[53\], 1T-MoS2 (0.28 eV) \[50\], and even significantly smaller than that of 2D silicene (0.16 eV) \[51\], indicating a high rate capability of ISN for Na ion batteries (Table I).

Open-circuit voltage profile is another crucial parameter to assess the performance of the anode materials. For ISN, the charge/discharge process complies with the following half-cell reaction vs Na/Na\(^{+}\):

\[
(x_2 - x_1)Na^{+} + (x_2 - x_1)e^- + Na_{x_1} - ISN \leftrightarrow Na_{x_2} - ISN.
\]

When volume, pressure, and entropy effects are neglected, the average voltage of Na\(_x\)-ISN in the concentration range of \(x_1 < x < x_2\) can be estimated by calculating the energy difference as follows:

\[
V \approx \frac{E_{Na_{x_1} - ISN} - E_{Na_{x_2} - ISN} + (x_2 - x_1)\mu_{Na}}{(x_2 - x_1)},
\]

where \(E_{Na_{x_1} - ISN}\), \(E_{Na_{x_2} - ISN}\), and \(\mu_{Na}\) are the total energy of Na\(_{x_1}\)-ISN, Na\(_{x_2}\)-ISN, and per Na atom in bulk metallic sodium, respectively. Therefore, it is necessary to determine the stable intermediate geometries in order to accurately calculate the step voltage. To this end, CE method is applied and the Hamiltonian of Na\(_{x}\)-ISN is constructed by fitting to the first-principles calculated energies of 123 configurations with varying Na concentrations. The cross-validation score of the CE fitting is 10 meV, small enough to guarantee the accuracy of CE Hamiltonian prediction of intermediate configurations of Na\(_x\)-ISN. As the results presented in Fig. 6(a) show, there are three stable intermediate geometries at various Na concentrations (0.125, 0.6, and 0.8). The corresponding structures are displayed in Fig. S7. Next, we calculate the step open-circuit voltage profile based on Eq. (5). The result is plotted in Fig. 6(b). There are two prominent regions of voltage plateau, separated by a drop from 1.41 to 1.29 V at the concentration of 0.6, which results from the increasing repulsive interaction between the Na ions when \(x > 0.6\). Besides, the voltage remains positive throughout the whole process, suggesting that half-cell reaction can go on spontaneously to reach the final phase (NaSi\(_6\)). Thus, ISN performs as an

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specific capacity, mAh/g</th>
<th>Diffusion barrier, eV</th>
<th>Open-circuit voltage, V</th>
<th>Volume change, %</th>
<th>Electronic band</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISN</td>
<td>159.5</td>
<td>0.005</td>
<td>1.35</td>
<td>2.80</td>
<td>Topological nodal line</td>
</tr>
<tr>
<td>1T-MoS(_2) [50]</td>
<td>86</td>
<td>0.280</td>
<td>1.25</td>
<td>27.5</td>
<td>Metal</td>
</tr>
<tr>
<td>2H-MoS(_2) [50]</td>
<td>146</td>
<td>0.680</td>
<td>0.75</td>
<td>27.1</td>
<td>Semiconductor</td>
</tr>
<tr>
<td>Si(_2z) [45]</td>
<td>159</td>
<td>0.683</td>
<td>0.30</td>
<td>2.30</td>
<td>Metal</td>
</tr>
<tr>
<td>Amorphous-Si [48]</td>
<td>957</td>
<td>0.310</td>
<td>–</td>
<td>227</td>
<td>Semiconductor</td>
</tr>
<tr>
<td>Silicene [51]</td>
<td>954</td>
<td>0.160</td>
<td>0.3-0.5</td>
<td>–</td>
<td>Dirac semimetal</td>
</tr>
<tr>
<td>Na(_{x_1})Ti(<em>2)O(</em>{15}) [52]</td>
<td>64.6</td>
<td>–</td>
<td>1.0</td>
<td>5.4</td>
<td>Semiconductor</td>
</tr>
</tbody>
</table>
FIG. 6. (a) Formation energies predicted by CE method for various Na concentrations for three stable intermediate phases. (b) The corresponding voltage profile.

anode with a fully reversible capacity of 159.5 mAh/g. The corresponding average voltage, by numerically averaging the voltage profile at the whole region, is 1.35 V, which is larger than that of Na$_{2+x}$Ti$_7$O$_{15}$ (1 V) [52], and comparable to that of 1T-MoS$_2$ (1.25 V) [50] (Table I). In addition, the DOS of these Nax-ISN structures (see Fig. S8) suggests that the metallicity is maintained and a good electrical conductivity is ensured during the sodiation/desodiation process, which is promising for anode materials. Moreover, compared with the pristine ISN structure, there are negligible changes in the silicon framework of intermediate stable Na-inserted structures, resulting in a slight volume change of less than 2.8%, which is significantly smaller than that of sodium-silicon alloy anode. This indicates that ISN can accommodate Na ions reversibly, with an excellent cycling stability.

IV. SUMMARY

To summarize, we have proposed an all-silicon topological semimetal composed of interpenetrating silicene networks. We have carefully confirmed the dynamical, thermal, and mechanical stabilities of ISN by first-principles calculations. Electronic structure calculations demonstrate that ISN possesses a nontrivial topological nodal line in the BZ, protected by time reversal and inversion symmetry. PDOS clearly reveals that the linear crossing bands near the Fermi level originate from the $p_x$ or $p_y$ orbitals of the four peripheral three-coordinated silicon atoms. Moreover, there exists a flat band, localized around the Fermi level, when the bulk nodal line is projected onto a surface. In addition to its topological properties, ISN is a promising anode material for Na ion batteries with a reversible capacity of 159.5 mAh/g. Although ISN sacrifices the energy density to some extent, its relatively high storage voltage of 1.35 V, intrinsic metallic property along with extremely low barrier energy of 5.2 meV, and negligible volume change make it a promising candidate for Na ion battery anode. Furthermore, considering the recent successful synthesis of porous silicon structure by introducing Na atoms to modulate the porosity in high pressure [35], we may expect that the proposed ISN in this study could also be realized in a similar fashion. In this sense, our study opens a research direction in topological 3D silicon structures, enriching the structure diversity and providing clues for finding Si-based materials for high-performance Na ion batteries.

ACKNOWLEDGMENTS

This work is partially supported by grants from the National Key Research and Development Program of China (Grant 2016YFB0100200), and from the National Natural Science Foundation of China (Grants No. 21573008 and No. 21773003). P.J. acknowledge support by the US DOE, Office of Basic Energy Sciences, Division of Material Sciences and Engineering under Award No. DE-FG02-96ER45579. The calculations are supported by High-performance Computing Platform of Peking University.
