Silicene, an analogue of graphene, was so far predicted to be the only two-dimensional silicon (2D-Si) with massless Dirac fermions. Here we predict a brand new 2D-Si Dirac semimetal, which we name siliconeet $\text{[silik'ni:t]}$. Unexpectedly, it has a much lower energy than silicene and robust direction-dependent Dirac cones with Fermi velocities comparable to those in graphene. Remarkably, its peculiar structure based on pentagonal rings and fivefold coordination plays a critical role in the novel electronic properties. Taking spin-orbit coupling into account, siliconeet can also be recognized as a 2D-topological insulator with a larger nontrivial band gap than silicene.
Atomic positions and lattice constants were optimized using the conjugate gradients (CG) scheme. A kinetic energy cutoff of 600 eV was adopted and the threshold of electronic self-consistency was set as $10^{-8}$ eV. Dense k-point grid ($30 \times 30 \times 1$) was employed for charge density and band structure calculations. Phonon calculations by supercell approach using the Phonopy code [39] and first-principles molecular dynamics simulations under constant temperature and volume (NVT) were performed to examine dynamical stability with respect to infinitesimal and finite distortions.

In this work, many 2D-Si structures were generated. Most structures with low energies have disordered geometries. Interestingly, pentagonal rings could frequently be found among them. Siliceneet, a peculiar 2D-structure containing pentagonal rings, is shown in Fig. 1(a) and 1(b). Its rectangular lattice constants are $a = 5.544$ Å and $b = 4.238$ Å, with a thickness $c = 3.290$ Å. In fact, silicene is also non-planar with a 0.450 Å buckling as discussed above. Silicene’s honeycomb structure has only one independent atomic site and the Si-Si bond length is 2.278 Å. Siliceneet is quite different [Fig. 1(a)], with 2 nonequivalent atoms (Si1 and Si3) and 4 distinct Si-Si bonds with bond lengths of 2.294 Å (Si1-Si2), 2.412 Å (Si2-Si4, Si3-Si5), 2.582 Å (Si2-Si5) and 2.637 Å (Si1-Si3, Si2-Si3), respectively. Siliceneet structure can be considered as an elongated honeycomb silicene with adatoms (top-Si3 and bottom-Si4), as shown in Fig. S1. Its side-view looks like recently reported 2D Dirac $Pmmn$-boron [28], and it also has two sub-lattices (blue top-, bottom-Si atoms and red middle-Si atoms), as shown in Fig. 1(b).

Prior work confirmed that buckled 2D boron structures are usually more stable than planar ones, because $sp^2$-hybridization is hard to achieve, and the same is true for 2D-Si. Total energy calculations show that siliceneet has lower energy than silicene even under external strain up to 8.8%, as shown in Fig. 1(c). The energy difference is as large as 119 meV/atom based on GGA-PBE calculations. Indeed, we see how far siliceneet is from $sp^2$-hybridization: (1) The hypothesis adsorbing atoms on elongated honeycomb silicene, allow a good release of the instability of $sp^2$-like bonding configurations; (2) Si pentagonal rings are formed when adsorbing atoms on the middle sublattice. Strikingly, this peculiar structure with pentagonal rings presents two different coordination numbers, fivefold for the middle and fourfold for the adsorbing surface atoms.

Charge density distributions in Fig. 2(a)-(c), which are projected to different cross-sections around top-Si atoms, further validate its bonding configurations. Obviously, top-Si (Si3 as example) and atoms from the middle sublattice (Si5 as example) have two and three strong covalent bonds in pentagonal rings respectively, as shown in Fig. 2(a). Meanwhile, as depicted in Fig. 2(b) and 2(c), Si3 has obvious charge density overlaps with atoms (Si1 and Si2) in the neighboring pentagonal ring, while Si5 has overlaps with Si2 and Si4. In this way, top- and bottom-Si (Si3 and Si4) present fourfold coordination and middle ones (Si1, Si2, Si5 and Si6) fivefold. Note that stable bulk Si has fourfold coordination [40, 41], while threefold in silicene. Here is the first time to demonstrate fivefold coordination can be formed in periodic 2D-Si structure at normal conditions.

For this peculiar 2D-Si structure with fivefold coordination, we confirmed the dynamical stability by checking its phonon dispersion curves and phonon density of states (PDOS), which show no imaginary frequencies, as presented in Fig. 2(d). To examine its thermal stability,
a 3×3 supercell was built to perform ab initio molecular dynamics simulations. After heating at room temperature (300 K) for 3 ps with a time step of 1 fs, no structural change occurred. We also have verified it using a fixed-cell technique in USPEX with lattice-matching Ag(110) substrate, as shown in Fig. S2. Siliconene is located at the lowest energy region of the structure evolution, which implies the possibility of growing it on Ag(110) substrate. All in all, siliconene can exist with peculiar pentagonal rings, and is much more stable than honeycomb silicene due to the presence of both fivefold and fourfold coordinations.

Siliconene is not only lower in energy than silicene, but also has unique electronic properties. The band structures in Fig. 2(e) show a distorted Dirac cone in the rectangular first BZ. The valence and conduction bands (denoted as bands I and II) meet at the Fermi level and form distorted Dirac cones. The density of states (DOS) is zero at the Fermi level, i.e. siliconene is a semimetal, which further supports the presence of Dirac cones. Fermi velocities ($v_f$) in both $k_x$ and $k_y$ directions were obtained from slopes of the bands at the Dirac point. In the $k_x$ direction, $\frac{\partial E}{\partial k_x} = \pm 34.29$ eVÅ ($v_{f_x} = 8.29 \times 10^5$ m/s); while in the $k_y$ direction, the slope of the bands equals $-3.74$ eVÅ ($v_{f_y} = -0.91 \times 10^5$ m/s) and 18.05 eVÅ ($v_{f_y} = 4.36 \times 10^5$ m/s). Note that $v_{f_x}$ of this direction-dependent Dirac cone is even larger than that of graphene ($v_f = 8.22 \times 10^5$ m/s) [29] based on GGA-PBE results.

To further explore the origin of Dirac bands, orbital-resolved band structures and partial charge density calculations for the two bands near the Fermi level were performed, which are depicted in Fig. 3. It is obvious that they are mainly from the $p_z$ orbitals of the two sublattices. Interestingly, due to tilting of pentagonal rings (about 36° with respect to the $ab$ plane), $p_z$ orbitals also have a tilting angle, as shown in Fig. 3(c) and 3(f). While band-I is mainly composed of $p_z$ orbitals of the middle sublattice, band-II mainly originates from $p_z$ orbitals of surface atoms. Moreover, the dispersion of band-I is much larger than that of band-II near Fermi level, which results in direction-dependent Fermi velocities. Such unique Dirac bands are presented in a more pictorial way in Fig. 4(a), and the corresponding bands along the -Γ−Y−Γ line are depicted in Fig. 4(b). The origin of the direction-dependent Dirac cones, as we have discussed in detail in our recent “phagraphene” work [29], is from the band crossing in the vicinity of the Fermi level: only bands I and II can appear and invert to each other at the Fermi level, Dirac cones are then produced on both sides of the space-symmetric and time-invariant $k$-point Y (or Γ). These features proved to be robust and can be kept under 6% tensile and compressive strain, as shown in Fig. S3.

Another interesting property of graphene and silicene is their topologically nontrivial electronic band structures. Taking spin-orbit coupling (SOC) into account, graphene was proposed to be a 2D topological insulator with a nontrivial bulk band gap and gapless edge states protected by time-reversal symmetry and responsible for the QSH effect [4]. However, the weak SOC of carbon and planar configuration of graphene lead to an unobservable...
nonzero topological invariant \( Z^2 \) (see Table S1). Using the strategy proposed by Fu et al. [42], the topological invariant of siliceneet is determined to be \( Z^2 = 1 \), which can be ascribed to the band inversion near the \( Y \) point [Fig. 4(a)]. Moreover, the SOC gap of siliceneet, 2.58 meV [Fig. 4(b)], is much larger than that of silicene, due to the lower symmetry of its unique buckled configuration with fivefold and fourfold coordinations. The energetic preferability and appreciable nontrivial band gap superior to silicene make siliceneet a promising candidate for realizing the QSH effect.

In conclusion, based on systematic evolutionary structure searching, we predict the stable 2D-Si Dirac allotrope named siliceneet. Its peculiar pentagonal rings and unique fivefold coordination are demonstrated to play a critical role in the novel electronic properties. Its direction-dependent Dirac cones are further confirmed to be a 2D topological insulator with an appreciable bandgap induced by spin-orbit coupling. In future, it may become a potential candidate to be integrated in Si-based electronic technology. Our findings not only extend the family of Dirac semimetals, but also clarify the structural stability for 2D forms of silicon.

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