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Stacking-dependent electronic structure of bilayer silicene

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Bilayer silicene (BLS) is a class of material that possibly holds both topological and superconducting properties; however, its structure is not fully understood. By scanning stacking modes and lattice constants using first principles calculations, several meta-stable configurations are identified, including a slightly faulted-AA packing structure, named slide-2AA. Different from the metallic properties of conventional AA and AB stacking forms, band structure of slide-2AA bilayer presents a sizeable indirect energy gap of $\sim 1.16 \text{ eV}$. A metal-semiconductor phase transition along the sliding pathway with a small energy barrier is also observed, indicating its electronic properties can be easily tuned by applying small shear force along the BLS surface plane. Such unique quantitative relationship of structure and electronic properties has profound implications in nanoelectronics and electromechanical devices. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4870534]

Two-dimensional (2D) materials have drawn great interest since monolayer graphene was isolated in 2004.¹ Recently, the silicon version of graphene, silicene, with oneatom thick honeycomb structure, has been both theoretically predicted²⁻⁵ and experimentally synthesized.⁶⁻⁹ Unlike planar graphene, silicene prefers to be a low-buckled structure, due to partial sp^2 - sp^3 hybridization of silicon atoms rather than complete sp² hybridization. Many charming properties of graphene can also be observed in silicene, including its characteristic Dirac-type electron behavior.^{6,7} Compared to graphene, the manipulation of silicene can be compatible with the existing silicon industry. Furthermore, stronger spinorbit coupling (SOC) enables silicene with a great potential be a 2D topological insulator and yields quantum spin-Hall effect (QSHE).^{4,10,11} However, a sizable band gap, which is extremely important for electronic devices, does not yet exist for free-standing monolayer silicene. Therefore, searching for a feasible way to open up a considerable energy gap is still an urgent challenge.

It is well known that stacking order and interlayer interactions play a decisive role to the properties of multilayer graphene.^{12–14} Similarly, changing the stacking structure may also provide us a simple way to modify the electronic structure of multilayer silicene. Although free-standing monolayer silicene is well studied, configurations and properties of bilayer silicene (BLS) remain unclear.^{15,16} Unlike bilayer graphene, whose most stable structure is AB (Bernal) stacking with van der Waals interlayer interactions, BLS nanosheet has been predicted to have a wide variety of morphologies due to the possible interlayer covalent bonds.^{17–20} For instance, the common used theoretical BLS model also has AB stacking mode with half of the Si atoms connected by interlayer covalent bonds. For example, Yao et al. found this structure holds interesting electronic properties such as chiral superconducting behavior.⁶ In addition, Zeng et al. presented a planar AA stacked configuration with all the Si atoms being fully

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covalent bonded.¹⁷ Morishita *et al.* reported a re-DL-Si structure formed from the reconstruction of two-layer thickness Si (111) surface.¹⁹ Recently, Lian and Ni studied the straininduced phase transition of BLS and discovered an intermediate planar phase at high strain along the silicene surface.²⁰ There also have been a few experimental works reporting the synthesis of silicene multilayers on metal substrate, however, neither the precise atomic structure nor the intrinsic electronic properties has been identified.^{21,22} Although there have been several reports on the different morphologies of BLS, the systematic search for low-lying packing isomers of BLS nanosheets with different packing modes and lattice constants, as well as the corresponding transitions of electronic properties are still lacking.

Here, we report a systematic study of the atomic structures, stabilities, and electronic properties of BLS morphologies employing first-principles calculations within the framework of density functional theory (DFT). By searching the lattice constant and scanning the potential energy surface (PES) versus the relative position between adjacent layers, we have found several meta-stable energy minima previously reported. In particular, a stable packing mode named slide-2AA morphology [Fig. 1(d)], in which silicon atoms in the upper layer are not directly upon the top sites of lower atoms but with slight deviation from the exact AA stacking is identified. Such slide-2AA structure has a comparable binding energy with that of exact AA and AB-stacking BLS structures and exhibits extraordinary stability in molecular dynamics (MD) simulations. More important, a sizable energy gap of 1.16 eV is developed in this structure, while all other BLS morphologies are metallic. The PES shows the sliding barrier from slide-2AA to the AA and AB stacking is small, comparable to the sliding barrier of bilayer graphene, indicating that it is possible to introduce a semiconductor-metal transition for BLS nanosheet by a small shear force. This may have profound implications for developing next-generation microelectromechanical system (MEMS) devices.

As the interlayer interaction plays a central role in determining the stacking configuration of BLS, and conventional generalized gradient approximation (GGA) functional sometimes underestimates the weak dispersion energy, we employ both conventional Perdew-Burke-Ernzerhof (PBE)²³ and van der Waals density functional (vdW-DF), optB86b-vdW,²⁴ to make comparison of the geometries and binding energies. In addition, the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional,^{25,26} HSE06, is further used for calculating the electronic structures. The HSE06 functional is based on a screened Coulomb potential applied to the exchange interaction with the screening parameter of 0.2. The exchange interaction is separated into short-range and long-range parts. The short-range part is defined as the mixing of the short-range Hartree-Fock (25%) and the short-range component of the PBE exchange functional (75%), and the long-range component is the same as standard PBE. Projector-augmented wave (PAW) pseudopotential and plane wave energy cutoff of



FIG. 1. Upper panels: Top views and side views of (3×3) supercell for the four optimized (a) 1AA, (b) 1AB, (c) 2AA, and (d) slide-2AA structures of BLS. Lower panel (e): Binding energies per Si atom (PBE level) vary with lattice constants for AA (blue line) and AB (red line) stacking modes. The labels 1, 2, 3 in blue and red font denote the each three minima found for AA and AB modes, respectively. The binding energy of slide-2AA versus lattice constant (cyan short curve) is also shown.

TABLE I. Calculated structural and energetic parameters of the seven bilayer structures, ideal bulk Si, as well as monolayer LB structures, in which *b*, *d*₁, *d*₂, *h*, Δ , and *E*_c, respectively, correspond to lattice constant, intra-layer nearest neighbor distance, nearest distance between two interlayer atoms, space between two layers, buckling distance, and cohesive energy per Si atom.^a

	b (Å)	$d_1(\text{\AA})$	d_2 (Å)	h (Å)	$\Delta(\text{\AA})$	$E_{\rm c}~({\rm eV})$
1AA	4.14	2.39	2.41	2.41	0.00	4.16
	4.13	2.38	2.41	2.41	0.00	4.27
2AA	3.78	2.36	2.70	2.70	0.90	4.10
	3.76	2.36	2.74	2.74	0.91	4.24
3AA	2.70	2.68	2.80	4.43	2.14	3.99
1AB	3.86	2.32	2.54	3.20	0.66	4.10
	3.84	2.32	2.51	3.19	0.68	4.25
2AB	2.70	2.55	2.39	4.50	2.11	4.00
3AB	3.30	2.43	2.34	3.85	1.51	3.90
Slide-2AA	3.82	2.37	2.47	2.75	0.83	4.12
	3.81	2.35	2.46	2.77	0.84	4.27
Bulk Si	3.87	2.37	2.37	3.16	0.79	4.61
LB	3.87	2.28			0.45	3.97

^aThe data in the lower columns for the same structures are obtained from the vdW-optB86b functional.

400 eV are chosen. A sufficiently large vacuum region of more than 15 Å in the surface normal (z) direction is applied to eliminate interaction between periodic images. The Brillouin zone (BZ) is sampled with a $25 \times 25 \times 1$ Monkhorst-Pack *k*-mesh to relax periodic structures of BLS unit cell, as well as a $45 \times 45 \times 1$ *k*-mesh for electronic structure calculation. In geometry optimizations, the structures are relaxed until the force on each atom is less than 10^{-4} eV/Å to ensure accurate convergence. To confirm the thermodynamic stability of BLS, the Born-Oppenheimer molecular dynamics (BOMD) simulations are also performed at infinite temperatures with a time step of 1.0 fs. A 5×5 supercell containing 100 Si atoms is used as the simulation box, and only Γ point in the BZ is sampled. All the calculations are performed with the Vienna *Ab initio* Simulation Package (VASP).²⁷

As the monolayer 2D silicene has been predicted to have two isomers, high-buckled (HB) and low-buckled (LB) structures with different lattice constants, we first check the possible energy minima of BLS by scanning the 1D PES along the hexagonal lattice constant for both AA and AB stacking modes, as denoted by the blue and red lines in Fig. 1(e). Three local minima can be found in each stacking mode, corresponding to six BLS morphologies, which are simply named by the stacking modes combined with the order of cohesive energies.

All the structural parameters and binding energies of BLS morphologies are listed in Table I. The 3AA and 2AB are two local minima of HB structures, which have the same buckling distance (2.1 Å) and lattice constant (2.7 Å) as the monolayer HB silicene. It is interesting that these two HB bilayers have different nearest interlayer Si-Si distance (2.39 and 2.80 Å for 2AB and 3AA, respectively), indicating the silicon layers of 2AB are covalent bonded to each other, on the other hand, the interlayer interaction in 3AA is non-bonded interaction, as shown in Figs. S1(a) and S1(b).²⁸ Furthermore, intralayer Si-Si bond length in 3AA (2.68 Å) is

also obviously larger than it in 2AB (2.55 Å). However, according to the PBE calculation, these two structures almost have the same binding energy, implying that the stability of BLS nanosheet is not proportional to the coordination number and bond order of Si atoms. As the lattice increases to 3.3 Å, another local minimum of AB-stacking structure called 3AB is found, as shown in Fig. S1(c).²⁸ This structure has lower buckling height (1.51 Å) and much higher energy than 2AB, showing it is not stable. The local minimum with similar lattice constant cannot be found for the AA-stacking BLS.

As the lattice constant increases further to the value of monolayer LB silicene, both stacking modes reach the LB minima, called the 1AB and 2AA, which have much larger binding energies than the HB morphologies. The 1AB structure is the common used BLS model in most of previous calculations. The geometries of 1AB and 2AA are displayed in Figs. 1(b) and 1(c), respectively. The buckling heights of 2AA (0.90 Å) and 1AB (0.66 Å) are slightly greater than it of the free standing LB monolayer silicene (0.4 Å), and more close to the buckling height of ideal bulk Si (0.79 Å), demonstrating the LB bilayer has more sp^3 hybridization character. Similar to the HB structures, the interlayer Si-Si distance of 2AA (2.70 Å) is longer than that of 1AB (2.54 Å), however, these two morphologies almost have the same binding energy, as shown in Fig. 1(e). It is noted the interlayer distances of both 1AB and 2AA are larger than regular Si-Si distance of 2.3 Å, but significantly smaller than the van der Waals diameter of silicon atom (4.2 Å). In addition, the lattice constant of 2AA (3.78 Å) is slightly smaller than that of 1AB (3.86 Å). Continuing to increase lattice constant of AA stacking, the planar BLS morphology, 1AA is found with the double silicon layer fully connected to each other via covalent bonds. This structure is identical to the bilayer silicon sheet discovered by Zeng et al.¹⁷ The interlayer distance of 1AA configuration is 2.41 Å, much smaller than other bilayer structures.

To probe the stability of the three low-lying morphologies, 1AB, 1AA, and 2AA, quantum MD simulations based on PBE functional have been performed for these structures at various temperatures in constant-temperature, constantvolume (NVT) ensembles. For 1AA and 1AB, no apparent structural distortion appearing for 5 ps suggests that these two structures are stable at 100 K. In contrast, obvious interlayer dislocation is found for 2AA at 40K, as a result, a unique structure named silde-2AA, whose upper layer is slightly deviated from the underneath layer, as shown in Figs. 1(d) and S2(a).²⁸ The slide-2AA configuration is maintained for the next 4 ps, presenting the good thermodynamic stability [Fig. S2(b)]. The deviation from the exact AA stacking is 0.66 Å. Such deviation results in a smaller interlayer Si-Si distance of 2.47 Å (2.70 Å in 2AA), and half of atoms in slide-2AA are bonded through interlayer covalent interactions. The silde-2AA structure corresponds to an intermediate configuration between exact AA and AB stacking modes, and its binding energy is comparable to and even lower than that for 1AB and 2AA [blue curve in Fig. 1(e)], indicating the high stability of this structure.

The calculated geometries of all the BLS morphologies based on vdW functional (vdW-optB86b) are in good

agreement with conventional PBE calculations, where the differences of structural parameters are less than 0.3 Å, as listed in Table I. The orders of binding energies based on both functionals are also qualitatively consistent, and the stabilities of slide-2AA and 1AB structures are closer on the vdW-optB86b level. To further study geometric transitions between 1AB, 2AA, and slide-2AA, we explore 2D scanned PES as a function of relative dislocation between two layers of BLS (ΔX , ΔY). The energy contours are displayed in Fig. 2(a). Notice that 2AA, 1AB, and slide-2AA configurations can be achieved by sliding the position of one layer relative to the other layer along the x direction. As demonstrated in Fig. 2(b), the potential energy plotted along the line through these three configurations clearly shows that slide-AA is a deep energy minimum, while 1AB is a shallow minimum and 2AA is actually an energy maximum. The 2AA structure can thus transfer to slide-2AA spontaneously. The interconversion between these three configurations is easily achieved. The energy barrier for transitions between slide-2AA structures and 2AA is 29 meV per Si atom (9.18 meV/Å²), and



FIG. 2. Potential energy (eV/Si atom) surfaces of bilayer silicene sheets depending on the interlayer relative slide distance (ΔX , ΔY) calculated by (a) PBE and (c) vdW-optB86b functional, respectively. The curves of relative binding energy per atom (b), (d) as a functional of ΔX are shown in the corresponding lower panels. Interlayer slide distance (ΔX , ΔY) is defined in the small legend (e).



FIG. 3. Band structures and DOS calculated for (a) 1AA, (b) 1AB, (c) 2AA, and (d) slide-2AA structures obtained from HSE06. The energy gap of slide-2AA is 1.16 eV in HSE06 (0.69 eV in PBE) as shown in (d).

between slide-2AA and 1AB is 25.1 meV/Si, equivalent to 7.95 meV/Å², which is comparable to the maximal stacking fault energy of 7.25 meV/Å² for graphite.²⁹ Energy contours of 2D PES calculated with vdW-optB86b, as well as the corresponding energy lines along the *x* direction also confirm the PBE results, shown in Figs. 2(c) and 2(d).

Besides the great diversity in bilayer silicene geometries, different BLS morphologies also exhibit a variety of distinct electronic properties. We calculated the band structures, as well as the density of states (DOS) of 1AA, 1AB, 2AA, and slide-2AA. Considering the energy gaps are underestimated in PBE functional, band structures and DOS are also calculated using HSE hybrid functional, which reproduces qualitatively PBE results, as shown in Fig. 3. Similar to electronic properties of bilayer graphene, linear dispersion bands at Dirac cone of silicene become parabolic for BLS. Calculations suggest the 1AA, 1AB, and 2AA morphologies have metallic electronic structures; however, the slide-2AA is an intrinsic semiconductor with a significant indirect energy gap of 0.69 eV in PBE. The HSE calculation suggests 1AA has a tiny indirect energy gap of 0.11 eV, implying this morphology should be a semimetal-like material. Furthermore, both the 1AA and 2AA have non-zero direct band gaps of $2.18 \,\text{eV}$ and $0.44 \,\text{eV}$ at Γ point, respectively. As a result, these structures may serve as good light absorber for energy and sensor applications. The energy gap of slide-2AA based on HSE calculation is larger (1.16 eV) than PBE result and is very close to that of bulk silicon (1.1 eV). The 1AB, 2AA, and slide-2AA morphologies have not only low interconversion barriers, but also very different electronic properties, ranging from metallic to semiconducting. Therefore, one can easily modify electronic properties by controlling the interlayer slide of BLS sheet, in order to achieve electronic transitions between metal, semimetal, and semiconducting behaviors.

Using first-principles calculations, we have systematically studied possible stacking configurations and corresponding electronic structures of free-standing bilayer silicene sheet. By changing lattice constants and initial stacking configurations, seven distinct BLS morphologies are found. Among all these morphologies, the stable slide-2AA structure is discovered to have a significant energy gap of 1.16 eV. Other morphologies with a similar lattice constant are all metallic. The energy barrier for transitions between these stacking structures is only 29 meV/Si, which is comparable to the value of weak van der Waals interlayer interaction in graphite. Therefore, a small tangential force could alter the stacking configuration of silicene bilayer, resulting in electronic phase transitions between metal, semimetal, and semiconducting behaviors. The BLS system provides us a rational way to tune the energy gap of ultrathin 2D nanomaterial by controlling the slide distance between two adjacent layers, which might find wide applications in nanoelectronic and electromechanical devices.

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