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Asymmetric functionalization as a promising route to open the band gap of silicene: A theoretical prediction

Nan Wang [b], Hao Guo [c], Yue-jie Liu [a], Jing-xiang Zhao [a,b,*], Qing-hai Cai [a,b], Xuan-zhang Wang [a]

[a] Key Laboratory of Photonic and Electronic Bandgap Materials, Ministry of Education, Harbin Normal University, Harbin 150025, China
[b] College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150025, China
[c] College of Education of Heilongjiang, Harbin 150080, China

HIGHLIGHTS

- We study the effects of the functionalization of graphene with a series of functional groups on the properties of silicenes.
- We find that all functionalized silicenes can be energetically stable.
- It is found that the band gap of silicenes can be tuned by the kinds and coverages of the adsorbed functional groups.

GRAPHICAL ABSTRACT

The band gap of silicene nanosheet can be opened by the asymmetric functionalization with X/Y groups.
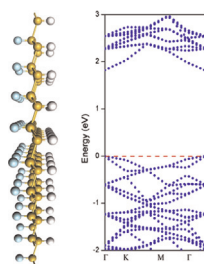
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ABSTRACT

Recent studies have suggested that chemical functionalization is a promising avenue to tailor the band gap of silicene, which plays an important role on widening its application. Here, we propose a new route to functionalize silicene, that is asymmetrically modification of silicene (Janus silicene or X–silicene–Y), which is produced by co-grafting of two different groups (X and Y) on both sides of silicene. By performing density functional theory (DFT) calculations, we demonstrate the stability and electronic properties of X–silicene–Y sheets. The results indicate that chemical functionalization on one side can greatly enhance the chemical reactivity of the opposite side, suggesting the communication between the two adsorbed groups and enhancing the stability of the hybrids. Compared to the pristine silicene with a zero band gap, X–silicene–Y sheets exhibit semiconducting nature with a non-zero band gap, which is dependent on the coverage of X/Y. Our results provide a novel and effective method to engineer the band gap of silicene, which would be useful to design novel silicene-based devices with multiple functions.

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1. Introduction

Silicene [1], a single atomic layer silicon atoms material, has attracted great attention due to its intriguing electronic properties [1–4] and the compatibility with mature Si-based electronics that are similar to but richer than those of graphene. Moreover, they are advantageous to carbon based nanostructures, as they can be expected to be compatible with the existing semiconductor industry. It is observed that the electronic band structure of silicene shows a linear dispersion around the Dirac point, like graphene, and hence is a candidate for applications in nanotechnology. Experimentally, epitaxial silicene has been successfully grown on

* Corresponding author at: College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150025, China.
E-mail address: xjz_hmily@163.com (J.-x. Zhao).

some metal substrates, such as Ag [5–9], Ir [10], and ZrB$_2$ [11], although the free-standing silicene sheets have not been achieved so far. This opens a new path for novel nanomaterials that have the potential to bypass some of the obstacles existing in the usage of graphene.

Similar to graphene, the feasibility of employing silicene for various electronics applications is dependent largely on the realization of controlling its electronic properties by chemical functionalization [12]. Earlier efforts on graphene suggest that its band gap can be modified by some chemical adsorbates, e.g., H [13–15], F [16–18], and O [19–21] groups. Interestingly, Liu et al. synthesized an asymmetrically modified graphene (Janus graphene) recently, in which two distinct and different functionalities are attached to the both sides of graphene [22]. The innovative study is exciting because Janus-type covalent functionalization of graphene has obvious advantage in obtaining a ubiquitous and tunable band gap, as compared with the symmetrical chemical modification [22]. Firstly, the Janus-type covalent modification with any combination of H, F, Cl, and Br in asymmetric modification always results in a semiconducting graphene [22], whereas the band gap opening in symmetrically modified graphenes is sensitively determined by geometries and symmetries of the systems. Secondly, Janus composites with two different components divided on the same object have wide potential applications in many fields, such as solid emulsion stabilizers, sensors, optical probes, and self-propellers [23]. Motivated by the effectiveness of asymmetrical functonalization in modifying the electronic properties of graphene and the potential applications of Janus nanomaterials, we feel that the asymmetrical modification of silicene is highly desirable. Although considerable efforts have been made on the exploration of electronic properties of silicene by chemical fucntionalization [24–44], we note that there is no prior report on the asymmetrical functionalization of silicene to the best of our knowledge. In the present work, we thus perform density functional theory (DFT) calculations to explore the structural stability and electronic properties of the asymmetrically functionalized silicene by various groups (X–silicene–Y). Our results would be helpful to provide a theoretical guidance to engineer the band gap of silicene and thus broaden its potential applications.

2. Methods and models

All the computations were performed with density functional theory (DFT), which was implemented in DMol^3 code [45,46]. The generalized gradient approximation (GGA) was treated by the Perdew–Burke–Ernzerhof functional [47]. All-electron calculations were carried out with the double numerical basis sets plus the polarization functional (DNP), which are comparable to the Gaussian 6–31G(d,p) basis set in size and quality and have excellent consistency with experiments. The convergence tolerance of energy is 10^{-5} au, the maximum force and displacement are 0.002 Ha/Å and 0.005 Å, respectively, for the geometry optimization. To ensure high-quality results, the real-space global orbital cutoff radius was set to be 4.60 Å. The Brillouin zone was sampled by $3 \times 3 \times 1$ k–points according to the test. All structures were fully relaxed without any symmetry constraints. To study the interaction of the silicene with various adsorbates, we employ a supercell consisting of a 5×5 supercell of silicene that contains 50 Si atoms. There is a vacuum layer of 20 Å along the vertical direction to silicene slab to avoid the interactions between the adjacent images. The charge transfer was calculated according to Hirschfeld method [48].

3. Results and discussion

Before discussing the binding strength of various adsorbates on silicene, we will briefly describe the structure and property of pristine silicene. The equilibrium structure for pristine silicene is shown in Fig. 1a. Our values for Si–Si bond length, lattice constant, and buckling height are 2.29, 3.88, and 0.46 Å, respectively, which are in good agreement with those of the literature [26,30,31,42,49], validating the accuracy of the employed methods and models in our work. Similar to graphene, silicene is a semimetal with linearly crossing bands at the Fermi level with a zero electronic band gap (Fig. 1b).

Next, we study the asymmetric modification of silicene by various atoms or groups on silicene, leading to the formation of X–silicene–Y sheets. Here, X, Y=H, F, OH, CHO, COOH, CH$_3$O, CN, NH$_2$, and CH$_3$, because they are shown to be effective to modified the
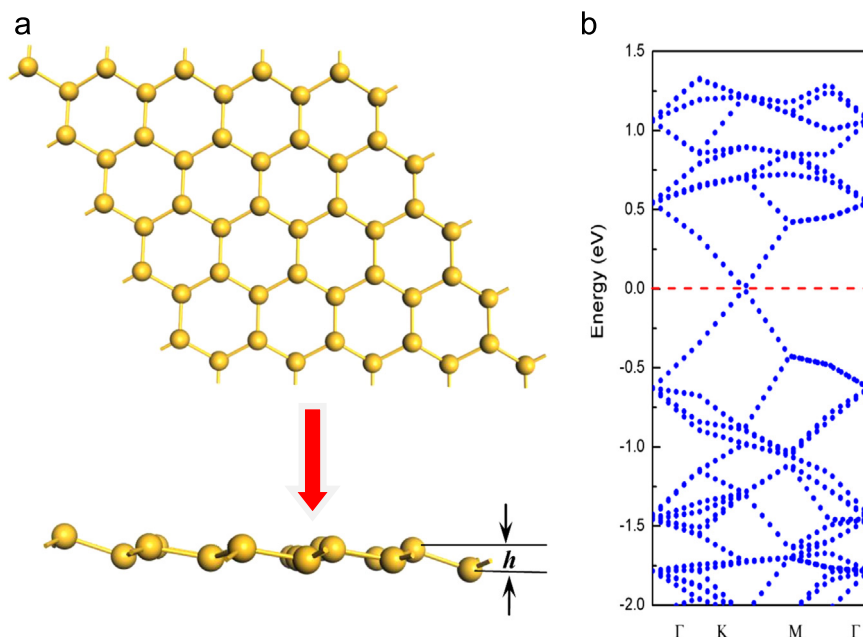

Fig. 1. (a) The most stable structure and (b) the corresponding band structure of pristine silicene. The Fermi level is set as zero in dotted line.