Full Length Article

The intriguing electronic and optical properties modulation of hydrogen and fluorine codecorated silicene layers

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ABSTRACT

First-principles calculations based on density-functional theory reveal some superior physical properties of hydrogen and fluorine co-decorated silicene (HSiF) monolayer and bilayer. Our simulated results reveal that the HSiF monolayer is a large direct band gap semiconductor greatly differing from the gapless semi-metallic silicene. There exists strong interlayer coupling in HSiF bilayer, leading to the good stabilities of HSiF bilayer even beyond bilayer graphene. The proposed HSiF bilayer exhibits a moderate direct band gap of 0.296 eV which is much lower than that of HSiF monolayer. Encouragingly, HSiF layers all have a direct band gap nature, irrespective of stacking pattern, thickness and external electric fields, which is an advantage over MoS$_2$ layers. Furthermore, an out-of-plane electric field has an evident impact on the band structures of the HSiF monolayer and bilayer. Especially, the band gap of HSiF bilayer can be effectively tuned by external electric field, even a semiconductor–metal transition occurs. More importantly, the HSiF bilayer exhibits a significant improved visible light adsorption peak with respect to that of HSiF monolayer, and the superior optical properties is robust, independent of stacking pattern. The complete electron-hole separation also enhances the photocatalytic efficiency of HSiF bilayer. In a word, the moderate band gap, effective band gap modification by external electric field, robust direct band gap nature, suitable band edge positions, electron-hole separation, and fascinating visible light adsorption, which enable HSiF bilayer to have great potential applications in the field of solar energy conversion, high performance photocatalysis and nanoelectronic devices, and we call for more concern over this kind of 2D Janus materials which possesses excellent properties.

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1. Introduction

Very recently, silicene, an analogue to graphene, has attracted increasing attention for its exceptional electronic properties. In experiments, silicene has already successfully deposited on several metallic substrates, including Ag, Ir, Au and ZrB$_2$ substrates [1–3,4–6]. Silicene shows the most outstanding properties similar to those of graphene such as high carrier mobility [7], ferromagnetism [8], half-metallic [9], quantum hall effect [10] and a topological insulator [11]. However, similar to graphene, the linearly dispersing π and π* bands crossing the Fermi level at the K point of the Brillouin zone leading to a gapless nature. The absence of band gap gives rise to its poor performance in the FET applications. Thus, the key to develop silicene-based electronics for practical applications urgently lies in opening a tunable band gap of it. To this end, many strategies have been proposed for engineering the gap of silicene, such as fabrication of silicene nanoribbons [12–15], applying strain [16–18] or bias voltage [19,20], substrate induction [21–24] and chemical functionalization [25–27]. To our best knowledge, the Si atoms in silicene are unsaturated with the existence of two dangling bonding in each Si atom which results in the high surface reactivity of silicene. Therefore, the adsorption of foreign atoms to saturate the unsaturated Si atoms is an effective way to stabilize the reactive surface of silicene.

Hydrogenation and fluorination belong to a unique strategy of chemical functionalization which are common choices for tailoring the properties of 2D materials such as graphene [28–32], h-BN [33–35], SiC [36] and silicene [37,38]. Most interestingly, silicane,

Table 1

Optimized lattice parameters (a is equal to b), bond lengths, and buckling parameter (h) in Å. Bond angles (θ) are shown in degree. Binding energy (E_b) and formation energy (E_f) are shown in eV/atom. E_g represents band gap in eV.

	a	Si-Si	Si-H	Si-F	h	$\theta_{Si-Si-Si}$	$\theta_{H-Si-Si}$	$\theta_{F-Si-Si}$	E_b	E_f	E_g
Silicene	7.70	2.27	–	–	0.47	115.76	–	–	–	–	0
HSiF monolayer	7.77	2.36	1.50	1.63	0.72	111.19	107.69	107.69	−2.01	−1.55	1.68

the fully hydrogenated silicene, has already been synthesized in experiment [39]. What's more, recently, by exposing high-purity H_2 gas onto a silicene sheet on Ag (111) substrate, one-sided hydrogenated silicene has been obtained [40]. Whereas, Hydrogen and fluorine co-decorated silicene monolayer (HSiF monolayer) has yet to be realized in experiment. Fortunately, density functional theory (DFT) calculations can be used to predict the physical properties of materials very well. Many theoretical works have been conducted focusing on piezoelectric properties of hydrofluorinated graphene bilayer [41], monolayer halogenated graphene [42], and semihydrogenated graphene [43,44]. The piezoelectric properties of hydrogen and fluorine co-decorated silicene monolayer also has been theoretically studied [45]. As we know, silicene and graphene are not intrinsically piezoelectric because of the existence of centrosymmetry and complete hydrogenation or fluorination still preserves the centrosymmetry of graphene and silicene. However, semihydrogenation or hydrogen and fluorine co-decoration breaks the inversion symmetry and induces a dipole moment into the sheet, thus, piezoelectricity has been engineered on those structure, their semimetal and nonmagnetic natures will be substituted by semiconductor and magnetic characterstics make them unprecedented potentials for the piezoelectric devices as well as nanoelectronic devices. The rearcheres have devoted much efforts into the piezoelectric properties of those structurte. However, there is lack of systematic understanding of the electronic and optical properties of those asymmetric chemical modification 2D materials. It is well known that the electronic and optical properties of HSiF layers have remained unexplored so far. Especially, the physical properties of HSiF bilayer are completely unknown. In this work, we take great interest in developing fundamental electronic and atomic level descriptions to explore the electronic and optical properties of HSiF layers by means of density functional theory calculations. Although HSiF monolayer has been theoretically studied to explore its potential application as piezoelectric devices, but it should be noted that the present work represents the first attempt to theoretically compute the important properties of the new category of 2D semiconductor HSiF bilayer. From the stability point of view, since the chair-like configuration is energetically more preferable than other three configurations [45]. Therefore, the chair-like HSiF monolayer is considered in our work.

2. Computational methods

In our work, we performed density functional theory (DFT) implemented in DMOL^3 code [46] of Materials Studio. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional [47] was chosen as the exchange-correlation potential. Furthermore, considering the long-range van der Waals interactions, we employed the DFT-D (D stands for dispersion) method proposed by Grimme [48] through all calculations because the weak interactions are not well described by the standard PBE functional [49–52]. Besides, double numerical atomic orbital plus polarization (DNP) was chosen as the basis set with the global cutoff of 5.0 Å to ensure the high computational quality. We used an adequate number of k-points for geometry optimization, equivalent to $16 \times 16 \times 1$ Monkhorst–Pack sampling, besides, a $20 \times 20 \times 1$ k-mesh was utilized for electronic properties calculations. All of the lattice constants and atom coordinates were

optimized until the maximum force was less than 0.001 a.u. To prevent the spurious interactions between periodic images of the neighboring layers, a vacuum spacing perpendicular to the plane was employed to be larger than ∼20 Å. The Methfessel-Paxton searming value was 0.005 Ha (1 Ha = 27.2114 eV). Moreover, to cancel out the artificial electric field due to the net electric dipole moment that arises in polar surface calculations, a dipole correction [53] is used.

To evaluate the relative stability of the HSiF monolayer in chair configuration, the binding and formation energies of HSiF monolayer were calculated. The binding energy (E_{b1}) per atom is defined as,

$$E_{b1} = (E_{T1} - E_{silicene} - n_H E_H - n_F E_F)/N$$

and the formation energy is expressed as,

$$E_f = [E_{T1} - E_{silicene} - (n_H E_{H2})/2 - (n_F E_{F2})/2]/N$$

E_{T1} and $E_{silicene}$ are the total energy of the optimized system and silicene unit cell respectively, E_H, E_F, E_{H2} and E_{F2} are the total energies for H, F, H2, and F2, respectively, and n_H and n_F are the number of H and F atoms in a unit cell, while N is the total number of atoms in the unit cell.

For the case of HSiF bilayer. Concerning the energetics of it, the binding energy (E_{b2}) per atom is summarized in Table 1 which can be defined as,

$$E_{b2} = (E_{T2} - 2E_{HSiF})/N$$ where E_{T2} and E_{HSiF} represent the total energy of the HSiF bilayer, isolated HSiF monolayer, respectively, and N corresponds to the total atoms number of HSiF monolayer in the unit cell. A negative E_{b2} corresponds to a stable adsorption structure.

3. Results and discussion

3.1. Structure, energetic and electronic properties of HSiF monolayer

We firstly investigated the geometric and electronic properties of single-layer HSiF. Fig. 1(a) presents the optimized structure of chairlike HSiF monolayer in a 2×2 supercell. One unit cell of HSiF monolayer consists of 2 Si atoms, one H atom and one F atoms. The structure parameters of the fully relaxed system are listed in Table 1. For the purpose of a contrast analysis, the structure parameters of silicene were also calculated. The calculated results show that the equivalent lattice parameter of single-layer HSiF is 7.77 Å, with covalent bond lengths of 2.36 Å for Si—Si bond, which are larger than the calculated values of 7.70 Å, 2.27 Å for pristine silicene. Notably, much longer Si-Si bonds occur in the HSiF monolayer due to the formation of complete sp^3 hybridization of Si atoms in H and F codecorated silicene distincting from the mixture of sp^2 and sp^3 hybridization in pristine silicene. The buckling parameter we defined is the distance between two parallel silicon planes, unlike pristine silicene, h = 0.47 Å, the buckling parameter of HSiF monolayer is 0.72 Å apparently larger than that of pristine silicene. Moreover, the bond lengths of Si-H and Si-F we calculated are 1.50 Å and 1.63 Å respectively, in agreement with the other reported values of 1.50 Å and 1.63 Å [45]. Owing to the electronegativity difference between Si, F and H atoms, there are some electrons transferring from Si atoms which are bonded with F atoms to F, H and Si atoms attached H atoms. As a result, the