Engineering magnetism and electronic properties of silicene by changing adsorption coverage

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ABSTRACT

Electronic and magnetic properties of silicene functionalized by H, C, and F atoms at different coverages are studied based on density functional theory. For H and F adatoms, the most stable adsorption sites are top sites. The situation is different for C adatom, and its most preferable adsorption site is valley site. Among the three kinds of adatoms, the magnetism can always be induced by H adsorption, while spin polarization is triggered only in silicene with low C concentration. The F adsorption mainly changes sites of Fermi level. The various band structures of metal, spin gapless semiconductor, and semiconductor can be obtained.

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1. Introduction

The investigation of two-dimensional (2D) crystals has been undergoing a rapid development since the famed isolation of graphene [1]. Silicene, the silicon counterpart of graphene, has been successfully synthesized by several groups [2–4]. In contrast to the planar sheet of graphene, silicene has a buckled sheet with the two sublattices not in the same plane [5]. Due to its exotic electronic structure and promising applications in nanoelectronics, silicene has attracted many scientific researchers in recent years [6–9]. Moreover, the compatibility of silicene with current silicon-based electronic technology is also an important factor that it is investigated widely. Similar to the case of graphene, the exotic features such as linear energy dispersion and massless Dirac fermions are still kept in silicene [5]. On the other hand, the buckled structures of silicene produce different electronic circumstances from graphene, and some new properties can be found in silicene. For instance, the buckled structure of silicene strengthens the hybridization between σ orbital and π orbital, which makes its surface reactivity higher than that of graphene [10]. Therefore, compared to graphene, the metal adatoms can be more strongly bound to silicene [11–14]. In addition, the quantum spin Hall effect can be realized in silicene, which makes it become an ideal material to build spintronics devices [15,16].

For 2D materials, tunable electronic properties are crucial for their applications [17–19]. Relative to graphene, the simpler techniques to engineer the band gaps may become available for those 2D materials with buckled structures [20,21]. Strain engineering has been viewed as an appropriate method for 2D materials. In contrast to bulk materials, the reduced-dimensional structures can sustain much larger strains [22–24]. Both biaxial and uniaxial stains can influence the electronic properties of silicene. The biaxial tensile strain could weaken Si-Si bonds and induce hole doping in silicene, and the uniaxial tensional strain could result in a small energy band gap at K points [25]. The band gap could also be opened through applying an electric field perpendicular to the plane of silicene [26]. The electronic properties of silicene on different substrates have also been investigated widely [6]. Kaloni et al. reviewed the latest developments of silicene and germanene on various substrates in a recent review article [27]. A superlattice of silicene and hexagonal boron nitride has been investigated by Kaloni et al. They found the Dirac cone of silicene could be preserved in this superlattice due to the wide band gap of hexagonal boron nitride [28]. The similar scenario can take place for silicene on hydrogenated Si-terminated SiC(0001) surface. However, the metallic property could be obtained if silicene is placed on hydrogenated C-terminated SiC(0001) surface [29]. Through angular-resolved photoemission spectroscopy and scanning tunneling spectroscopy, Vogt et al. [4] and Chen et al. [30] suggested Diracfermions still existed in silicene even if it was placed on Ag(111) surface. However, the theoretical results of Wang and Cheng indicated that the linear dispersions observed by the above mentioned two groups
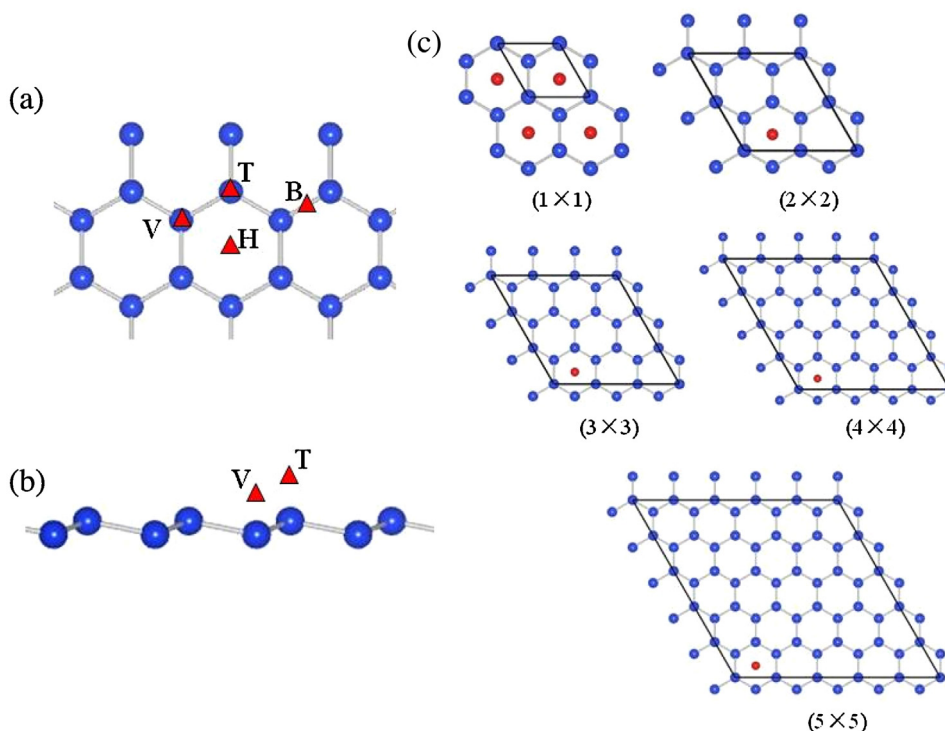
Fig. 1. The top view (a) and side view (b) of considered adsorption sites on silicene. The symbols 'T', 'V', 'H', and 'B' express top, valley, hollow, and bridge sites, respectively. (c) (1×1)–(5×5) silicene supercell with an adatom on the hollow site.

came from the Ag substrate and not from silicene, which meant the disappearance of Dirac cone in silicene on Ag(111) [31]. The further investigations need be done.

The chemical functionalization of silicene with different atoms can also produce exotic properties. Zhang et al. found the abundant topological states could be obtained in silicene adsorbed with $4d$ transition metal atoms [32]. The adsorption of $3d$ transition metal atoms on silicene has also been investigated systematically, and substantial spin polarization could be caused by transition metal decoration [33]. Furthermore, Mn-decorated silicene and Co-decorated silicene were paid more attentions. The magnetism of Mn-decorated silicene could still be maintained even if this system was placed on hexagonal boron nitride [34]. The quantum anomalous Hall effect was found in Co-adsorbed silicene [33]. Except transition metal atoms, the small organic molecules could also be used as decoration to engineer electronic properties of silicene [35].

In the investigations on 2D materials, hydrogenation has been considered to be a feasible method to adjust their properties due to its fine reversibility and nice controllability. Both full hydrogenated and semihydrogenated silicene have been investigated in recent years, and the electronic structures and magnetic properties are dramatically affected by hydrogenation [36,37]. Moreover, the investigation on half-fluorinated silicene showed the arrangement of the doped F atoms had significant influence on the electronic structures of silicene [38]. However, the influence of the different adatoms concentration on electronic structures of silicene was still unexplored in these reports. In Ref. [29], the property of silicene obviously changed when it is placed on C-terminated SiC(0001) surface. Based on this result, the investigation on C adsorption on silicene is very necessary. In this work, the adsorption of H, C, and F atoms on silicene with variable concentration is explored within the framework of density functional theory. The results suggest the coverage densities do not affect the most stable adsorption sites, which only depend on the adatoms species. The abundant electronic and magnetic properties can be obtained in silicene with H, C, and F adsorption. The mechanism of multiple phase transitions is analyzed based on partial densities of states and band structures.

2. Method and models

The electronic structures of silicene adsorbed with H, C, and F atoms are studied with projector augmented wave formalism based on density functional theory, as implemented in the Vienna *ab initio* simulation program (VASP) [39,40]. The Perdew-Burke-Ernzerhof (PBE) gradient approximation is used to describe the exchange and correlation functional [41]. Since the PBE exchange correlation often underestimates the band gap, the more accurate hybrid functional (HSE06) [42] was also used to correct the PBE results. The valence electrons are described by a plane wave basis set with an energy cutoff of 500 eV. For each system, four different adsorption positions are considered, *i.e.*, hollow site (above the center of hexagonal), top site (on top of the upper silicon atoms), valley site (on top of the lower silicon atoms), bridge site (on top of the Si—Si bond), for which the abbreviations 'H', 'T', 'V' and 'B' are used, as illustrated in Fig. 1(a) and (b). To simulate the different adsorption coverage, both unitcell and supercell models is used, which consists of an $(n \times n, n = 1, 2, 3, 4, 5)$ primitive silicene cell and an adatom, as shown in Fig. 1(c). The vacuum thickness along the z axis is no less than 15 Å to avoid artifacts due to periodic boundary conductions. All models are constructed based on the calculated lattice constant for (1×1) unitcell of 3.82 Å and the buckling distance 0.44 Å, which are in good agreement with previous theoretical values [5]. It is known that the adsorption of the large coverage is likely to change the lattice constants, which will affect the band structures of 2D materials [43,44]. Thus, the lattice constants were relaxed for those systems with large coverage (1×1) and $2 \times 2)$. The results suggested the variation of lattice constants was less than 1.5%, which hardly affect the electronic structures of silicene with large coverage. For geometry optimization, the internal coordinates are allowed to relax with the fixed lattice constants until the Hellmann-Feynman forces are less than 0.01 eV/Å. The convergence threshold for energy