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Adsorption-enhanced spin–orbit coupling of buckled honeycomb silicon

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HIGHLIGHTS

- The buckled silicon structure can be stabilized by atomic adsorption.
- Atomic adsorption can enhance the spin–orbit coupling in silicon structures.
- Half-saturated buckled silicon with hydrogen is magnetic.

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ABSTRACT

We have studied the electronic structures of quasi-two-dimensional buckled honeycomb silicon (BHS) saturated by atomic hydrogen and fluorine by means of first-principles calculations. The graphene-like hexagonal silicon with chair configurations can be stabilized by atomic hydrogen and fluorine adsorption. Together with a magnetic ground state, large spin–orbit coupling (SOC) of BHS saturated by hydrogen on either side (Semi-H-BHS) indicated by the band splitting of σ bond at Γ point in the Brillouin zone is attributed to the intermixing between the density of states of hydrogen atoms and π bonds of unpassivated Si_2 around the Fermi level. The Zeeman spin splitting is most likely caused by the internal electric field induced by asymmetric charge transfer.

1. Introduction

When the size of a crystal decreases to nanometer scale from a three-dimensional periodic structure to a lower-dimensional one, there often accompanies the appearance of novel exotic solid-state properties. For example, two-dimensional graphene, a single layer of graphite, has received much research interest since its successful fabrication due to the novel physical properties and great potential applications for future electronic devices [1]. Graphene exhibits behaviors of massless Dirac fermion in the range of low excitation energy due to the touching bands at the K points [2]. Graphene is predicted to not only have very high mobility of charge carriers in the order of magnitude of $10^5\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$ even at room temperature [3,4], but also the mobility of charge carrier shows weak dependence on the carrier concentration and temperature [5]. Furthermore, graphene is considered to be an ideal material for spintronics devices due to the weak relativistic effect of intrinsic spin–orbit coupling (SOC) [6,7]. It was demonstrated that the spin-current injection and detection in graphene can be achieved with very large spin coherence length [6,8]. However, due to the very weak intrinsic SOC in the order of magnitude of 10^{-3} meV, the quantum spin Hall effect is only favored at ultra-low temperature [9,10]. The substrate and the transverse electric fields may have significant influence on the electronic band structure of graphene when taking SOC into account [11–16]. In particular, the effect of impurities in graphene was predicted to induce a large spin–orbit interaction which is comparable to that found in other carbon based materials, due to the rehybridization of sp^3 bonding within graphene [17].

In analogy with graphene, silicene, a single layer of hexagonal silicon network is predicted to have exotic electronic properties [18,19] and its quasi-two-dimensional fractional network was detected on metal substrates by scanning tunnelling microscopy (STM) experiment [20–22]. Like graphene, the charge carrier of pure hexagonal silicon matrix have features of a Dirac fermion [19,21]. However the two-dimensional graphene-like silicon

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structure is most probably a metastable material [18]. And the modification of electronic structures of silicene upon external adsorption is still lacking. In this work, we present results of the electronic structure calculations of buckled honeycomb silicon (BHS) passivated by hydrogen and fluorinate atoms using first-principles approaches. The semi- or fully passivated BHS by hydrogen and fluorine atoms is very similar to recently reported graphone and graphane, both of which display chair conformations [23,24]. Of particular interest is the effect associated with the inclusion of SOC for BHS, which is found to induce large spin–orbit coupling by partial hydrogen adsorption and large Zeeman splitting due to asymmetric charge density redistribution. The increased SOC of silicene by hydrogen adsorption, which relates closely to the application of quantum Hall effect in silicene [25], is also discussed.

2. Computational details

The first-principles density functional theory (DFT) calculations were performed by Vienna Ab-initio Simulation Package (VASP) [26] based on projector augmented wave (PAW) method [27] for the electron–ion interactions, Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) for the exchange-correlation functional [28], and plane wave basis sets with a kinetic energy cutoff of 400 eV. Structural optimizations were performed until the residual forces on all the atoms are smaller than 0.01 eV/Å. For Brillouin-zone integrations, *K* points mesh of 12 × 12 × 1 and 18 × 18 × 1 were used for structural optimization and total energy calculations respectively. The equilibrium cell volumes were obtained by fitting energy-volume curves based on Murnaghan equation of state through a series of calculations [29], where the atomic positions, lattice vectors, and cell angles were allowed to relax, while the total volume was held constant for each system. This approach can avoid the Pulay stress and changes in basis sets accompanying volume changes in plane wave calculations. The fully relativistic calculations as implemented in VASP have been successfully applied to the small band gap problem of lead chalcogenides and the ferroelectricity of spiral magnets [30–32]. The band structures for the studied systems after including the SOC interactions is calculated without symmetry restriction.

It is a well-known fact that the fundamental band gaps in semiconductors can be systematically and underestimated by GGA approximation because the quasiparticle corrections are not included. However the indeed gap opening is independent on the applied approximations with respect to the case of gap closing. Here we present the possibility that the spin degeneracy in the graphene-like silicon structures can be lifted under external atomic adsorption. Our conclusion would remain valid irrespective of the presence of the minor quantities of spin splitting in the studied systems.

3. Results and discussion

Fig. 1 shows the top and side views of optimized structure of Full-H-BHS schematically, which is fully saturated BHS by hydrogen atoms in analogy with graphane [23]. The BHS structure with partial hydrogen saturation in analogy with graphone is represented by Semi-H-BHS (not shown here) [24]. This naming convention also applies to fluorine saturation. H-F-BHS stands for one case where H and F atoms are attached to Si_1 and Si_2 atoms alternatively on opposite side of the BHS (see Fig. 1a). The structural parameters of fully or partially saturated BHS are listed in Table 1. To evaluate the relative stability of BHS passivated by hydrogen and fluorine atoms, we calculated the binding energies of the optimized structures. The binding energy is defined as [23,33]

$$E_b = \left(2E_{Si} + \sum_i N_i E_i - E_{BHS}\right) \Big/ \left(2 + \sum_i N_i\right) \quad (1)$$

where E_{Si} is the binding energy per atom of bulk silicon, E_i the binding energy of per hydrogen and fluorine atom in gas state, E_{BHS} the energy of partially or fully saturated BHS. Positive (negative) value corresponds to stable (unstable) state. As presented in Table 1, the calculated binding energies of the studied BHS are all positive, indicating that all the studied BHS structures are stable. The studied structures should be stabilized by the buckling, which have double and single sp^3 hybridization for the cases of full and half adsorption respectively. Moreover, fluorine atom adsorption can increase the stability of BHS, which should be due to the strong electron affinity of fluorine. Our results can be substantiated by the recently detected monolayer silicon in STM experiments [20]. In addition, attempts in synthesizing single-crystal

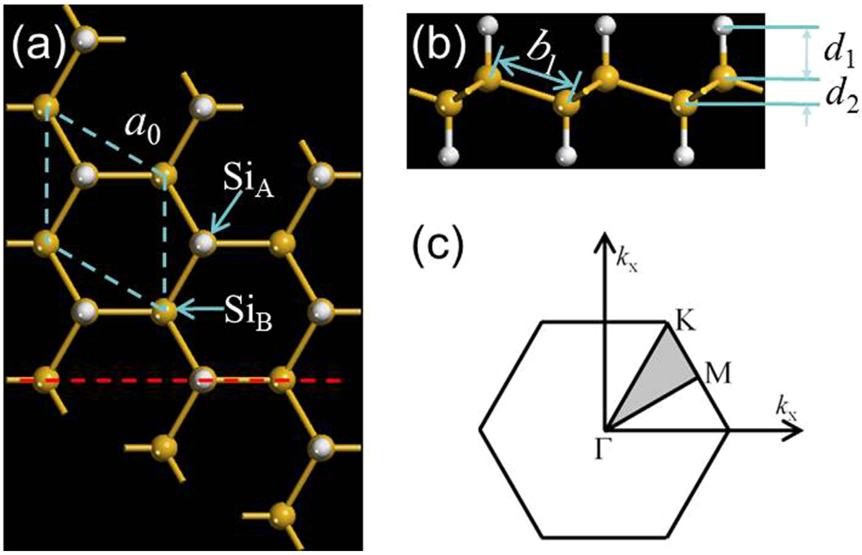

Fig. 1. Top (a) and side (b) view of optimized configuration of Full-H-BHS. The silicon and hydrogen atoms corresponding to yellow and white balls are clearly distinguished. (c) Schematic of Brillouin zone of BHS. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)