Nonmetallic substrates for growth of silicene: an \textit{ab initio} prediction

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Abstract

By means of first-principles calculations we predict the stability of silicene layers as buckled honeycomb lattices on Cl-passivated \text{Si(1\,1\,1)} and clean \text{CaF}_2(1\,1\,1) surfaces. The van der Waals interaction between silicene and the inert substrate stabilizes the adsorbate system while not destroying the Si \text{p}_z-derived linear bands forming Dirac cones at the Brillouin zone corners. Only small gaps of about 3 and 52 meV are opened.

Keywords: silicene, first principles calculations, Cl-passivated \text{Si(1\,1\,1)} surface, \text{CaF}_2(1\,1\,1) surface, Dirac cones

(Some figures may appear in colour only in the online journal)

1. Introduction

The graphene-like allotrope of silicon, silicene, represents a buckled two-dimensional (2D) honeycomb lattice \cite{1}. Despite the partly sp\textsuperscript{3} bonding, the theory predicts Dirac cones at the corner points \text{K} and \text{K}' of the 2D hexagonal Brillouin zone (BZ) for freestanding silicene sheets. The accompanying massless Dirac fermions in the low-energy regime provide unique electronic, IR-optical, and transport properties \cite{2--5}. In contrast to other novel 2D materials, silicene can be ideally used in current Si-based device technologies.

The major problem of the application of silicene is its preparation. Recently, the epitaxial growth of silicene on metallic and halfmetallic substrates such as \text{Ag(1\,1\,1)} \cite{6--9}, \text{ZrB}_2 \cite{10}, and \text{Ir(1\,1\,1)} \cite{11} has been reported. Theory predicts the use of hydrogen-passivated \text{Si(1\,1\,1)} and \text{Ge(1\,1\,1)} substrates because of their lattice match \cite{12}. For deposition of silicene on \text{Ag(1\,1\,1)}, two ARPES experiments \cite{6,9} but also the mapping of differential conductance \cite{8} have been claimed to confirm Si \text{p}_z-based conical linear bands. Recently, Dirac cones have been reported for bilayer silicene on \text{Ag(1\,1\,1)} \cite{13}. However, theoretical studies based on the density functional theory (DFT) showed the absence of Si-derived conical linear bands for the mostly studied 3 × 3 silicene on \text{Ag(1\,1\,1)}4 × 4 adsorbate system. The origin of these conical linear bands is traced back to the interaction of silicene with the silver substrate \cite{14--16}. Si-based Dirac cones are the subject of an ongoing controversial discussion \cite{8,14--19}.

In this paper, we investigate, by means of parameter-free DFT calculations, silicene deposited on two novel substrates, Cl-passivated \text{Si(1\,1\,1)}1 × 1 and clean \text{CaF}_2(1\,1\,1)1 × 1 surfaces, as indicated in figure 1: (i) The substrates possess a fundamental gap. (ii) The silicene and their surface lattices are nearly commensurable. (iii) The chemical interaction between silicene and the substrates should be weak because of the absence of dangling bonds. We especially study the bonding, energetic, structural, and resulting electronic properties of the Si overlayers.

2. Methods

The structural optimization and total-energy calculations are performed within the DFT as implemented in the Vienna \textit{Ab-initio} Simulation Package (VASP) \cite{20}. The van der Waals (vdW) interaction is included according to Dion \textit{et al} \cite{21}. The correlation taken in local density approximation (LDA) is corrected by a nonlocal correction that accounts for dispersion forces. The exchange functional in generalized gradient approximation (GGA) is used in the version

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as Dirac cones. demonstrate the appearance of characteristic features such as Dirac cones. The distance \( D \) between the bottom silicene atom and the Cl\(^-\) or F\(^-\) ion layer characterizes the adsorbate substrate interaction. Parameters of the resulting 2D band structure of silicene near a \( K \) or \( K' \) point, the Fermi velocity \( v_F \) and the energy gap \( E_g \) are also listed. In addition, the energy shift of the Dirac point with respect to the Fermi level \( E_{\text{Dirac}} \) is given.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Freestanding</th>
<th>Cl/Si(111)1×1</th>
<th>CaF(_2)(111)1×1</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a (\text{Å}) )</td>
<td>3.857</td>
<td>3.861</td>
<td>3.878</td>
</tr>
<tr>
<td>( \Delta (\text{Å}) )</td>
<td>0.480</td>
<td>0.490</td>
<td>0.431</td>
</tr>
<tr>
<td>( D (\text{Å}) )</td>
<td>3.12</td>
<td>2.70</td>
<td></td>
</tr>
<tr>
<td>( v_F (10^3 \text{ m s}^{-1}) )</td>
<td>0.53</td>
<td>0.48</td>
<td>0.49</td>
</tr>
<tr>
<td>( E_g (\text{meV}) )</td>
<td>3</td>
<td>3</td>
<td>52</td>
</tr>
<tr>
<td>( E_{\text{Dirac}} (\text{eV}) )</td>
<td>0</td>
<td>0.21</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 1. Silicene adsorbed on (a) Cl-passivated Si(111)1×1 and (b) clean CaF\(_2\)(111)1×1 surface. Si atoms: blue, Cl: green, Ca: yellow, F: red.

Table 1. Lattice constant \( a \) and buckling amplitude \( \Delta \) of freestanding and adsorbed silicene from total-energy DFT calculations including vdW. The distance \( D \) between the bottom silicene atom and the Cl\(^-\) or F\(^-\) ion layer characterizes the adsorbate substrate interaction. Parameters of the resulting 2D band structure of silicene near a \( K \) or \( K' \) point, the Fermi velocity \( v_F \) and the energy gap \( E_g \) are also listed. In addition, the energy shift of the Dirac point with respect to the Fermi level \( E_{\text{Dirac}} \) is given.

The Cl-passivated Si(111)1×1 and the CaF\(_2\)(111)1×1 surfaces are simulated by repeated symmetric slabs of 18 and 24 atomic layers respectively. In the Si case both sides are covered by chlorine. In the CaF\(_2\)(111) slabs, fluorine layers form the surface. Additionally, on each slab surface one silicene sheet is adsorbed. The vacuum between two slabs is chosen to be 20 Å. The slightly biaxially strained silicene, the chlorine layer, and the uppermost atomic layers in the slab are allowed to relax using a conjugate-gradient algorithm until the Hellmann–Feynman forces are below 0.01 meV Å\(^{-1}\). The BZ of the resulting superlattice structure is sampled with a 16 × 16 × 1 k-point grid. Many different starting geometries with different displacements of the strained silicene overlayer relative to positions of the Cl\(^-\) or F\(^-\) surface atoms are investigated.

3. The substrates

Upon reaction of Cl atoms with the cleavage Si(111)7×7 surface and subsequent repeated annealing, the favorable bulk like 1×1 surface [25] appears. A stable monolayer of Cl\(^-\) ions covers the Si(111)1×1 surface with almost Si\(^+\) ions in the topmost atomic layer, even when the sample is held at 550°C. The projected fundamental gap with a minimum value of 1.1 eV is free of surface states. The Cl/Si(111)1×1 surface is indeed passivated, while the 2D hexagonal symmetry of the uppermost Si layer is conserved. The Si(111)1×1 surface is perfectly lattice-matched to the Bravais lattice of the 1×1 silicene sheet with a deviation of only 0.1% (see theoretical lattice constants in table 1).
The natural cleavage CaF$_2$(111)1 × 1 surface is terminated by a complete triple layer of F$^-$–Ca$^{2+}$–F$^-$ monoatomic layers with a topmost F$^-$ layer for electrostatic reasons [26]. The latter one consists of a trigonal arrangement of F$^-$ ions spaced by 3.878 Å (see table 1), that leads to a lattice mismatch to silicene of 0.5%. Calculations show that such a small tensile strain does not destroy the Dirac cones. Because of the inertness of the CaF$_2$(111) surface, it is suggested as a convenient substrate for a van der Waals epitaxy of almost strain-free overlayers [27]. The completely filled outermost electron shell of the F$^-$ ions makes the uppermost surface triple layer inert. The silicene atoms should not chemically react with an intact triple-layer surface, similar to the behavior of oxygen atoms [28].

The results for a F$^-$-terminated CaF$_2$(111)1 × 1 substrate are rather similar. However, as a consequence of the slightly increased biaxial strain, the buckling amplitude of silicene is reduced (see table 1). The distance $D = 2.70$ Å between overlayer and substrate is somewhat smaller than in the Cl/Si(111)1 × 1 case but still indicates an influence of the vdW bonding.

To investigate the influence of the 1 × 1 unit-cell constraint, we have also studied 3 × 3 lateral unit cells for both substrates, Cl/Si(111) and CaF$_2$(111). Despite significant initial displacements, the silicon overlayers relax back into the silicene geometry optimized within 1 × 1 cells. This result supports the statement of a stable configuration.

The band structures of the silicene-covered (a) Cl-passivated Si(111)1 × 1 surface and (b) CaF$_2$(111) substrate are displayed in figure 3. The regions of the dense slab bands mainly indicate the projected bulk (a) Si or (b) CaF$_2$ band structures. The striking differences in the chemical bonding of the substrates are indicated by the completely different band width and energy gaps. The gaps are free of surface states. Only in the pockets of the projected valence bands do such states associated with Cl–Si bonds appear near $K$ and $M$. The electronic-structure modifications, due to the silicene overlayer, are indicated by additional bands whose chemical nature has been determined by projections onto the silicene atoms. As a consequence of the weak vdW bonding one observes the almost unchanged band structure of freestanding silicene. This is especially true for the Dirac cones around $K$ within the fundamental gaps. The corresponding band states are still derived mainly from Si $p_z$ orbitals.

The weak vdW bonding only slightly modifies the bands near the Fermi energy and a $K$ point. The Fermi velocities of the Dirac cones are conserved (see table 1). In the case of the Cl/Si(111) substrate, practically no gap is opened. Only the Fermi level is shifted by 0.2 eV toward lower energies, i.e., holes are created in the $\pi$-state-derived cone. The projected bulk conduction band minima near $M$ indicate a small electron transfer into the substrate. On CaF$_2$(111) the silicene overlayer opens a small gap between the $\pi^*$ and $\pi$ cones. The Fermi energy remains in the gap center.
5. Conclusions

Summarizing, by means of first-principles calculations we have shown that the CI-passivation of Si(1 1 1) and the cleavage of CaF$_2$ lead to inert surfaces formed by halogen ions Cl$^-$ or F$^-$ with completely filled valence shells on top. The silicene with a buckling similar to the freestanding 2D system forms a vdW-bonded adsorbate. The outstanding properties known for freestanding silicene are preserved for the slab system, because of the weak bond. We suggest intensive experimental studies of the deposition of silicene on the two investigated substrates. In contrast to the silicene/Ag(1 1 1) adsorbate system with strong chemical bonds, the electronic structure of silicene should be detectable within the fundamental gaps of the studied substrates.

Acknowledgments

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