Weak interaction between germanene and GaAs(0001) by H intercalation: A route to exfoliation

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Epitaxial germanene on a semiconducting GaAs(0001) substrate is studied by ab initio calculations. The germanene-substrate interaction is found to be strong for direct contact but can be substantially reduced by H intercalation at the interface. Our results indicate that it is energetically possible to take the germanene off the GaAs(0001) substrate. While mounted on the substrate, the electronic structure shows a distinct Dirac cone shift above the Fermi energy with a splitting of 175 meV. On the other hand, we find for a free standing sheet a band gap of 24 meV, which is due to the intrinsic spin orbit coupling.

Epitaxial growth of bulk Ge on GaAs(100) has been demonstrated experimentally, which can be of interest for metal oxide semiconductor field effect transistors. In addition, growth of GaAs on Ge has been verified experimentally. For these reasons, we study in the following germanene on a GaAs(0001) substrate. We will demonstrate that germanene in fact can be grown on as well as taken off this substrate, and we will address its electronic properties with and without substrate, taking into account the spin orbit coupling.

Our calculations are based on density functional theory, using the Quantum-ESPRESSO code. Ultrasoft pseudopotentials are employed together with the generalized gradient approximation in the Perdew, Burke, and Ernzerhof parametrisation. The van der Waals interaction is taken into account by means of dispersion corrections. Moreover, a plane wave cutoff energy of 816 eV and a Monkhorst-Pack k-mesh (8 × 8 × 1 for the structure optimization and 16 × 16 × 1 for the calculation of the electronic properties) are used. The in-plane lattice parameter of the supercell is based on the bulk GaAs value, amounting to 2 × 3.91 Å, and a vacuum slab of 16 Å thickness is considered in the out-of-plane direction to avoid artificial interaction due to the periodic boundary conditions. The atomic positions are relaxed until an energy convergence of 10⁻⁶ eV and a force convergence of 3 × 10⁻⁴ eV/Å are reached. The supercell contains a 2 × 2 germanene layer with 8 Ge atoms on top of a Ga-terminated 2 × 2 GaAs(0001) slab with 12 Ga atoms and 12 As atoms, giving rise to a lattice mismatch of 3.6%. The dangling bonds on the bottom of the GaAs(0001) slab are saturated by pseudo-H atoms.

Since for the prototypical two-dimensional honeycomb material graphene both band gap opening and mass production are challenging problems from a practical point of view, search for other materials with similar or even better properties becomes eminent. In this context, the isostructural honeycomb networks of Si and Ge atoms, silicene, and germanene have been put forward as potential alternatives. However, these materials require a substrate, which makes accurate measurements of their properties difficult, in particular on metallic substrates. It remains unclear how the strong interaction with the substrate could be reduced. Growth on less interacting substrates, such as semiconductors, would be highly beneficial. C, Si, and Ge belong to the same group in the periodic table, but the ionic radius of C is much smaller than that of Si and Ge. This is an important difference since a larger ionic radius promotes $sp^3$ hybridization as compared to the $sp^2$ hybridization of graphene. The mixed $sp^2$ and $sp^3$ hybridizations in silicene and germanene result in prominent bucklings of 0.46 Å and 0.68 Å, which pave the way to electrically tunable band gaps and thus represent a huge advantage over classical graphene.

The first principles calculations of germanene in Refs. 4–6 have resulted in metallic characters because the spin orbit coupling has not been taken into account. Under biaxial compressive strain the linear energy dispersion at the K and K' points is maintained. In addition, the Fermi velocity of $1.7 \times 10^6$ m/s, which is comparable to that of graphene ($1 \times 10^6$ m/s (Ref. 7)) and silicene ($1.3 \times 10^6$ m/s (Ref. 8)), does hardly depend on the strain. In general, the intrinsic spin orbit coupling is stronger for Ge (46.3 meV) than for C (1.3 μeV) and Si (4 meV). For this reason and due to the enhanced buckling of the honeycomb network, as compared to silicene, germanene has been proposed to host a quantum spin hall effect with a sizable band gap at the Dirac point.

Hence, germanene is particularly promising for spintronics devices. Recently, the electronic properties of germanene with chemisorbed F, Cl, Br, and I have been studied by first principles calculations.11 While the intrinsic band gap is found to be enhanced under absorption of Cl, Br, and I (to 69 meV, 237 meV, and 162 meV, respectively), F absorption results in a metallic state due to significant structural modifications.

As a consequence of the significant three-dimensional bonding in bulk Ge (despite the graphite-like structure), which is due to the $sp^3$ hybridization, a substantial amount of energy is required to separate neighboring Ge layers.12 In contrast to graphene/graphite, exfoliation of germanene from bulk Ge thus is not possible. On the other hand, it is also an open question whether germanene can be grown on any kind of substrate and, in a second step, can be taken off this substrate to obtain a free standing sheet. However, epitaxial growth of bulk Ge on GaAs(100) has been demonstrated experimentally, which can be of interest for metal oxide semiconductor field effect transistors.13 In addition, growth of GaAs on Ge has been verified experimentally.14 For these reasons, we study in the following germanene on a GaAs(0001) substrate. We will demonstrate that germanene in fact can be grown on as well as taken off this substrate, and we will address its electronic properties with and without substrate, taking into account the spin orbit coupling.

Our calculations are based on density functional theory, using the Quantum-ESPRESSO code.15 Ultrasoft pseudopotentials are employed together with the generalized gradient approximation in the Perdew, Burke, and Ernzerhof parametrisation.16 The van der Waals interaction is taken into account by means of dispersion corrections.17,18 Moreover, a plane wave cutoff energy of 816 eV and a Monkhorst-Pack k-mesh (8 × 8 × 1 for the structure optimization and 16 × 16 × 1 for the calculation of the electronic properties) are used. The in-plane lattice parameter of the supercell is based on the bulk GaAs value, amounting to 2 × 3.91 Å, and a vacuum slab of 16 Å thickness is considered in the out-of-plane direction to avoid artificial interaction due to the periodic boundary conditions. The atomic positions are relaxed until an energy convergence of 10⁻⁶ eV and a force convergence of 3 × 10⁻⁴ eV/Å are reached. The supercell contains a 2 × 2 germanene layer with 8 Ge atoms on top of a Ga-terminated 2 × 2 GaAs(0001) slab with 12 Ga atoms and 12 As atoms, giving rise to a lattice mismatch of 3.6%. The dangling bonds on the bottom of the GaAs(0001) slab are saturated by pseudo-H atoms.
As-terminated GaAs(0001) results in rather strong structural distortions and thus is not promising for our purposes. We focus on germanene on Ga-terminated GaAs(0001), see Fig. 1, considering two configurations: In the case of Fig. 1(a) the germanene lies directly on top of the topmost Ga atoms. Here the buckling is found to be substantially larger (0.75–0.80 Å) than reported for pristine germanene (0.68 Å (Ref. 2)), due to the interaction with the substrate. We obtain a significant elongation of the Ge-Ge bonds by about 2% (see Table I). In addition, the bond angle between neighboring Ge atoms amounts to 109°–110°, which reflects the role of the sp^3 hybridization in germanene. In pristine germanene the corresponding value is 112.3°.11 In the case of Fig. 1(b) the dangling Ga bonds towards the germanene are saturated by H atoms. This results in covalent bonds between the Ga and H atoms with a bond length of 1.57 Å. We note that H intercalation in the case of GaAs(0001) has been carried out previously in a chemical vapor deposition reactor with an ultra-pure atmosphere of molecular H2,20 which is a technique similar to H etching and H passivation of SiC surfaces.21 The development morphology of the graphene after H intercalation has been studied by angular resolved photoelectron spectroscopy, low energy electron diffraction, and microscopy. Importantly, the experimental procedure for hydrogenation of GaAs(0001) is well understood and well controlled. Typically, a 13.56-MHz hydrogen plasma is applied in a quartz tube at a pressure of 1 mbar and a temperature of 250°C to 300°C for 1 h.22–24 In Ref. 25 a three-step procedure was employed, consisting of cleaning at 400°C for 30 min, annealing at 600°C for 15 min, and cooling to 100°C for 90 min, all performed under atomic hydrogen flux.

In our calculations for germanene on GaAs(0001) we observe a buckling magnitude of 0.71–0.72 Å with an bonding angle close to 111°. These values are very similar to those obtained for pristine germanene, except for the Ge-Ge bond, which is found to be about 1% longer. Still, the findings clearly point to a much weaker interaction between the substrate and the germanene as compared to the case without H intercalation. The charge density isosurfaces included in Fig. 1(a) demonstrate a huge amount of charge redistribution in the area between the germanene and the top atomic layer of the substrate. This fact indicates that the electronic states of the germanene are strongly affected by the substrate, which we will discuss again later in terms of binding energies. On the other hand, we find essentially no charge redistribution in the case of H intercalation (see Fig. 1(b)), reflecting a weak influence of the substrate on the germanene. In graphene H intercalation leads to a decoupling of the buffer C layer from the substrate and monolayer graphene is formed as a result.20 This procedure is known as epitaxial growth of graphene on SiC(0001). A similar decoupling of germanene from an appropriate substrate by H intercalation seems tempting.

It is an essential question for practical purposes whether germanene can be separated from the substrate on that it is grown. To address this problem, we calculate the binding energy \( E_b = E_{\text{combined}} - E_{\text{GaAs}} - E_{\text{Ge}} \) between germanene and the GaAs(0001) substrate. Here, \( E_{\text{combined}} \) is the total energy of the combined system, \( E_{\text{GaAs}} \) that of the GaAs(0001) substrate, and \( E_{\text{Ge}} \) that of the germanene under strain, i.e., using the GaAs(0001) lattice constant. We obtain values of 568 meV and 69 meV (per Ge atom) for the configurations of Figs. 1(a) and 1(b), respectively. Germanene without H passivated dangling Ga bonds, thus, is found to be substantially bound to the substrate, making it virtually impossible to exfoliate a free standing sheet. However, our results demonstrate that H intercalation strongly reduces the interaction with the substrate. A binding energy of only 69 meV per Ge atom indicates that in this configuration the germanene can be separated from the substrate. Experimental data for the binding energy between the atomic sheets (graphene sheets) in graphite range from 47 to 57 meV,26 reflecting the weak bonding between the atomic layers in graphite. Besides graphite, graphene also has been exfoliated successfully from SiC(0001). In this case the bonding to the substrate is much stronger than the interlayer interaction in graphite due to its ionic nature. As a consequence, we can expect that germanene can be taken off a GaAs(0001) substrate after H intercalation although Ge-Ge bonds are weaker than C-C bonds.

The electronic band structure of free-standing germanene is shown in Fig. 2 as obtained by calculations (a) without and (b) including spin orbit coupling. We find a metallic behavior with a linear energy dispersion at the K point, consistent with previous reports.27–29 Similar to graphene and silicene, the \( \pi \) and \( \pi^* \) bands forming the Dirac cone are due to

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**TABLE I. Selected bond lengths, bond angle between neighboring Ge atoms, buckling, and binding energy.**

<table>
<thead>
<tr>
<th></th>
<th>Ge-Ge (Å)</th>
<th>Ga-H (Å)</th>
<th>Bond angle (deg)</th>
<th>Buckling (Å)</th>
<th>( E_b ) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>2.43</td>
<td>—</td>
<td>109 to 110</td>
<td>0.75 to 0.80</td>
<td>568</td>
</tr>
<tr>
<td>(b)</td>
<td>2.41</td>
<td>1.57</td>
<td>111</td>
<td>0.71 to 0.72</td>
<td>69</td>
</tr>
</tbody>
</table>
interaction of the Ge \( p_z \) orbitals. However, for germanene we obtain a substantial band gap of 24 meV, see the zoomed area in Fig. 2(b), when the intrinsic spin orbit coupling is taken into account. These results agree well with Refs. 9 and 10. Clearly, spin orbit coupling thus plays an important role in germanene and cannot be neglected. As a consequence of the intrinsic band gap, germanene becomes interesting for applications in electronic devices. Moreover, an external electric field can be used to enhance the magnitude of the band gap because it breaks the sublattice symmetry,\(^1,^2\) as previously observed in silicene. To check whether the Dirac cone of free standing germanene remains intact for interaction with the GaAs(0001) substrate, we plot a spin-cone of free standing germanene remains intact for in-

FIG. 2. Band structures of free standing germanene (a) without and (b) with SOC.

The shift comes along with a band splitting that gives rise to a gap of about 175 meV, reflecting the interaction with the substrate breaks the sublattice symmetry of the germanene structure. A similar breaking of the sublattice symmetry has been observed for silicene and cannot be neglected. As a consequence of the same (buckled) layer.

FIG. 3. Band structure of germanene on GaAs(0001) with partial densities of states: Ge atom on top of H, Ga atom bound to H atom, and As atom in the same (buckled) layer.

modified by adatoms.\(^2^7\) We note that application of an appropriate back voltage will bring the Dirac cone back to the Fermi energy and therefore result in a semiconducting state, which can be interesting for radio frequency circuits. Coming back to Fig. 3, the remainder of the Dirac cone is dominated by the Ge \( p_z \) orbitals, as in free standing germanene, with minor contributions of the Ge \( p_x \) and \( p_y \) orbitals. As to be expected, contributions from the substrate are essentially negligible.

We have presented a structural analysis, results on the chemical bonding, and insight into the electronic properties of germanene on GaAs(0001). Our results point at a substantial bonding between the germanene and the substrate when they are in direct contact. On the other hand, intercalation of H atoms to saturate the dangling Ga bonds strongly reduces the interaction. Therefore, the combination of a GaAs(0001) substrate with H intercalation could be a feasible route to free standing germanene sheets by exfoliation. The mechanism of the H intercalation can be expected to be similar to the established H intercalation of graphene on SiC(0001). Therefore, this procedure should not pose a relevant obstacle on the way to free standing germanene, in particular, since the H passivation of GaAs(0001) is a well understood and controlled process. The electronic structure of germanene while attached to the substrate exhibits the remainder of a Dirac cone, which is splitted by a 175 meV gap and shifted above the Fermi energy by 267 meV. For free standing germanene we observe in the vicinity of the K point a linear dispersion that is almost symmetric around the Fermi energy and therefore result in a semiconducting state.

FIG. 4. Interrelation between the Brillouin zones of (black full lines) 1 \( \times \) 1 and (red dashed lines) 2 \( \times \) 2 germanene cells.