

van der Waals Heteroepitaxy of Germanene Islands on Graphite

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Supporting Information

ABSTRACT: We fabricated flat, two-dimensional germanium sheets showing a honeycomb lattice that matches that of germanene by depositing submonolayers of Ge on graphite at room temperature and subsequent annealing to 350 °C. Scanning tunneling microscopy shows that the germanene islands have a small buckling with no atomic reconstruction and does not give any hints for alloy formation and hybridization with the substrate. Our density functional theory calculations of the structural properties agree well with our experimental findings and indicate that the germanene sheet interacts only weakly with the substrate underneath. Our band structure calculations confirm that the Dirac cone of free-standing germanene is preserved for layers supported on graphite. The germanene islands show a small but characteristic charge transfer with the graphite substrate which is predicted by our ab initio simulations in excellent agreement with scanning tunneling spectroscopy measurements.



he discovery of graphene, a single layer of sp² hybridized carbon atoms, ignited a cornucopia of new fundamental physics and applied research.¹ The observation that a single free-standing sheet of atoms is stable, apparently contradicting the Mermin and Wagner theorem,² has been justified by anharmonic coupling between stretching and bending modes^{3,4} resulting in intrinsic corrugations of the layer. Graphene has outstanding properties, such as the Dirac-cone-shaped energy band and the high carrier mobility,⁵ but it is also gapless, and this severe drawback makes it useless for field-effect applications. The most obvious alternatives to graphene are "graphene-like" materials made of the group IV elements, i.e., silicon and germanium.^{6,7} Silicene and germanene share several peculiar properties of graphene. They are Dirac materials in which electrons near the K and K' points of the Brillouin zone behave as relativistic massless particles because of the linear dispersion around the Fermi level.^{7,8} The velocity of charge carriers is also comparable to that in graphene and estimated to be of the order of $10^5 - 10^6$ m/s.^{7,9} On the other hand, silicene and germanene show peculiar physical properties which make them better suited than graphene in the race for ultimate thickness scaling of nanoelectronic devices. First of all, they offer perfect compatibility with the current Si-based technology of semiconductor processing. More importantly, the structure of silicene and germanene is more flexible than that of graphene because of the absence of strong π -bonds enforcing planarity. The larger buckling, as well as the resulting larger spin-orbit coupling, make it easier to create a bandgap in Si and Ge twodimensional (2D) crystals without degrading their electronic properties.^{10,11}

However, there are still several obstacles that must be overcome for the practical applications of silicene and germanene in microelectronic devices. To date, these materials have been almost exclusively grown on metallic substrates.^{12–20} On metals, their 2D Dirac character is, in most cases, either altered or completely destroyed because of hybridization of the relevant electronic states near the Fermi level with electronic states of the metallic substrates.²¹ The first sign of these processes is the observation of complicated surface reconstructions superimposed to the honeycomb structure. In addition, fabrication of functional electronic devices necessarily requires nonmetallic supports.²² One possibility is introducing a buffer layer for decoupling the 2D adlayer from the metal substrate, as has been recently proposed for germanene/AlN/ Ag(111)²³ even though no direct scanning tunneling microscopy (STM) imaging of the honeycomb lattice was obtained in this case. The other option is to directly use a nonmetallic substrate. To date, however, reports on the successful growth of silicene and germanene on nonmetallic substrates are rather scarce. Indeed, for silicene the only attempt was done by using exfoliated flakes of MoS₂ on which a highly buckled Si honeycomb lattice was evidenced.²⁴ However, the buckling was so high (~ 2 Å) that it is difficult to claim the existence of a 2D silicene layer in this case. As concerns germanene, a single report 25 on the growth of germanene on

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MoS₂ has appeared while our Letter was under review. Among nonmetallic templates, highly oriented pyrolytic graphite (HOPG) is a promising substrate having the same lattice symmetry as germanene. Moreover, graphite is chemically inert, and this is expected to avoid alloy formation, i.e., the intermixing of Si/Ge and C atoms²⁶ which can easily occur on metallic substrates. Indeed, the deposition of Si adlayers on graphite indicates an alloy-free creation of silicene.²⁷ In the past, germanium substrates were demonstrated to be suitable templates for graphene growth.^{28,29} Here, we reverse the epitaxial relation and report on the growth of Ge on graphite resulting in 2D islands showing a honeycomb lattice with a periodicity matching that of germanene. The thickness of the islands is compatible with a single germanene layer bonded by van der Waals interaction to the graphite surface. The structural parameters nicely match our ab initio calculations which, in turn, reveal the presence of a Dirac cone in the band structure due to germanene. The germanene islands exhibit a characteristic charge transfer with the HOPG substrate which is evidenced by both simulation and scanning tunneling spectroscopy (STS).

We first characterize the surface of the graphite substrates used for the growth of germanene. Figure 1 shows atomicresolution STM images of the bare graphite surface prior to Ge deposition. In panels a and b, we observe the well-known triangular lattice of graphite with a periodicity of about 0.25



Figure 1. Atomic-resolution STM images of the bare graphite surface used as a template for germanene growth: (a, b) triangular lattice; (c) honeycomb lattice ($V_{\rm bias}$ = -106 mV; I= 2.1 nA). On the images, ball-and-stick models showing the triangular and the honeycomb lattices are superimposed as a guide for the eye.

nm, matching well the second-neighbor distance of C atoms. The triangular lattice stems from the electronic interaction of the surface graphene layer and the underlying layers: for the A-B stacking of graphite, there is a lower electronic density of states for carbon atoms that are situated directly above a carbon atom in the underlying layer because of the π -state interaction between the two carbon atoms.^{30,31} This suggests that the whole honeycomb lattice can be imaged if the coupling between the layers is reduced. It has actually been demonstrated that the STM tip can lift the surface layer enough to make this happen.^{32*} An example is reported in Figure 1c which shows a honeycomb lattice with a firstneighbor distance of about 0.14 nm, as expected for a graphene layer. A ball-and-stick model, in which the atoms belonging to the two triangular sublattices of the honeycomb are displayed in different colors, is also shown. Despite sharing a honeycomb structure, the lattice constant of graphite is markedly smaller (about 38%) than that expected for germanene; consequently, the two lattices can be unequivocally distinguished by STM. The difference in the relative size is evident from the schematic illustration of the germanene-graphite system reported in Figure 2a,b. Such a lattice mismatch, which would be giant for



Figure 2. Schematics showing the top (a) and side (b) views of the $(2\sqrt{3} \times 2\sqrt{3})$ germanene/ $(\sqrt{31} \times \sqrt{31})$ graphite system with 21° rotation between the surfaces based on DFT calculations. Ge atoms have a residual buckling (Δ) of 0.7 Å and a distance (d) of 3.2 Å from the graphite substrate. Orange and gray balls represent germanium and carbon atoms, respectively.

classical epitaxial growth based on covalent bonding, is easy to handle in van der Waals heteroepitaxy because of the weakly bound heterojunction.^{33,34}

Indeed, in line with the early work of Cai et al.,³⁵ our firstprinciples calculations performed in the framework of density functional theory (DFT) (see Methods) show that the van der Waals interaction is responsible for the bonding of the germanene layer to the graphite substrate. Eventual covalent

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bonding between the Ge and C atoms is ruled out by the search for the minimum-energy structure (see movie in the Supporting Information). The weak bonding to the substrate allows for an out-of-plane buckling and in-plane misorientation of the germanene layer with respect to the graphite substrate, enabling a partial relief of the misfit strain of the system. As a consequence of the weak interaction, our simulations show multiple configurations having similar stability which could coexist at finite temperatures. The binding energy per Ge atom, defined as $E_{\rm b} = (E_{\rm Ge/HOPG} - N_{\rm Ge} \times E_{\rm Ge} - N_{\rm C} \times E_{\rm C})/n_{\rm Ge}$, where $E_{\rm Ge/HOPG}$ is the total energy in the supercell Ge/HOPG; $N_{\rm Ge}$ × $E_{\rm Ge}$ and $N_{\rm C} \times E_{\rm C}$ are the total energies in the monolayer germanene and graphite unit cells, respectively; and n_{Ge} is the number of germanium atoms in the Ge/HOPG supercell, shows a maximum difference in E_b for the different configurations investigated to be about 40 meV. The structural parameters are then defined by averaging over the configurations, with the uncertainty being the statistical dispersion. From DFT, the relaxed germanene structure has a Ge bond length of (2.45 \pm 0.07) Å with a buckling of (0.69 \pm 0.07) Å, and its distance to the top layer of graphite is (3.28 ± 0.04) Å.

Figure 3a shows a typical nanometer-sized island grown on top of graphite after the deposition of a nominal coverage of 0.2 monolayers (ML) of Ge at room temperature and subsequent annealing to 350 °C. The height profile across the edge of the sheet (inset of Figure 3a) indicates that the distance of the overlayer from the substrate is (3.0 ± 0.2) Å, a value compatible with the expected separation of a germanene layer grown on graphite. On the islands, high-resolution imaging of the germanene honeycomb lattice is obtained (Figure 3b) and both triangular sublattices of the honeycomb are resolved. This is noteworthy because in the other reports on the growth of silicene and germanene on insulating substrates the honeycomb lattice was often imaged only in part.^{24,25} The periodicity of the structure shows a first-neighbor separation of (2.5 ± 0.2) Å and a second-nearest distance of (4.2 ± 0.3) Å. These values closely match those expected for a germanene layer. Also, the lattice does not lie perfectly flat on the substrate but shows a residual buckling of about 0.7 Å. In contrast to metal-supported germanene, we do not observe any atomic reconstruction, suggesting that the properties of free-suspended germanene are preserved on graphite. The absence of atomic reconstruction is confirmed by the simulated STM image of germanene on graphite shown in Figure 3c. In addition to the 2D germanene island, a small three-dimensional (3D) Ge cluster is visible in Figure 3a. This confirms the existence of a competition between perfect 2D growth driven by van der Waals interaction and the onset of 3D growth.³⁵ As a larger amount of Ge is deposited (0.7 ML) (Figure 3d), the germanene patches follow the underlying graphite layers as does a carpet, confirming that the formation of the 2D sheets is driven by Ge. The density and size of germanene islands increase, although uncovered substrate areas are still visible between the islands.

Figure 4a shows the calculated electronic band structure of the germanene/HOPG heterosystem along the line paths M– K, K– Γ , and Γ –M of the Brillouin zone. An enlarged picture in the vicinity of the Fermi level is displayed in Figure 4b. To facilitate the comprehension of the band structure of the heterosystem, the contributions of germanene (Ge) and graphite (C) to the bands are shown in green and red, respectively. In agreement with the results of Cai et al.,³⁵ we find that the Dirac cone of germanene supported on graphene is mapped to Γ . Note that in the free-standing case, the Dirac



Figure 3. STM images showing 2D islands formed after Ge deposition at room temperature and subsequent annealing to 350 °C. Panel b shows an enlarged view of the honeycomb lattice of the 2D islands. The nominal Ge coverage is 0.2 ML in panels a and b and 0.7 ML in panel d. In the inset of panel a, the height profile taken along the green line in the image is shown. A 3D Ge cluster is also visible in the top part of the image in panel a. (c) Simulated STM image of germanene/ graphite having the same size as in panel b and recorded with the same scanning parameters but at 0 K. The Ge atoms in the honeycomb arrangement are highlighted by a ball-and-stick model. In panel d, the edges of the islands are highlighted. The STM scan parameters are $V_{\text{bias}} = -980 \text{ mV}$ and I = 1.0 nA for panels a and d and $V_{\text{bias}} = -860 \text{ mV}$ and I = 0.88 nA for panel b.

cone of germanene is at the K/K' point. The Dirac cone of bare graphene is at K/K' as well. When the germanene–graphene



Figure 4. (a, b) Electronic band structure of germanene/HOPG by DFT calculation. Projected bands of Ge and C are highlighted in green and red, respectively. Panel b shows a blow-up close to the Fermi level. The linearly dispersing bands of germanene around the Γ -Dirac point are highlighted by thin dashed lines. (c) Calculated total DOS for germanene on graphite. (d, e) Normalized differential tunneling conductance (V/I)dI/dV obtained by STS at room temperature: (d) on top of a germanene island; (e) on the HOPG substrate (main panel), on a Ge 3D cluster (inset). In contrast to clusters, germanene shows a finite DOS at the Fermi level. The axis labels of the inset are the same as for the main panel. Each experimental curve is an average of 10 acquisitions.

system is built, the Brillouin zones of both graphene and germanene are rotated one with respect to the other. Hence, the K point of germanene falls onto the Γ point of the Brillouin zone of the germanene-graphene system. Thin dashed lines are also added as a guide to the eye to highlight the linearity of the electronic bands of germanene at the Γ point. When germanene is paired up to an inert substrate like graphite, the van der Waals interaction at the interface breaks the sublattice symmetry in germanene and opens a small band gap. We find that the band gap of germanene supported on HOPG is about 80 meV, larger than the free-standing germanene value of 24 meV.³⁶ The difference is due to two distinctive origins for the gap opening in both cases. For the free-standing layer, the gap is induced only by effective spin-orbit coupling (SOC), whereas in our case, it is directly caused by the broken symmetry at the interface driven by the van der Waals interaction between germanene and graphene layers. In particular, the charge transfer at the interface builds up an interlayer potential difference, i.e., the two sublattices of germanene feel different Coulomb fields, and this results in a charge redistribution leading to the opening of a gap.³⁷ The Fermi level crosses the Dirac cone, promoting an electron transfer between germanene and graphene layers which shifts the Dirac cone of germanene about 0.1 eV above the Fermi

level. It is interesting to note that similar light doping effects have already been found for the inverse epitaxy, e.g., graphene/ germanium²⁹ or observed for graphene coupled to silicon islands.²⁶ The shift is also clearly visible from the calculated total electronic density of states (DOS) (Figure 4c) and can be used as a fingerprint of germanene compared to HOPG. We therefore compared STS spectra taken on top of a germanene island (Figure 4d) with that on the bare substrate Figure 4e. As expected, both curves reveal a metallic character with a finite DOS close to the Fermi level. Recently, the metallic behavior of the silicene I/V curve has been exploited for realizing a fieldeffect transistor (FET) based on ambipolar charge transport effects.²² However, while the STS curve for HOPG has a minimum at the Fermi level, the germanene curve is shifted toward the empty states, well-matching the results of our calculations. Besides topography, this electronic fingerprint clearly distinguishes germanene from the graphite substrate. Conversely, STS curves taken on 3D clusters (inset of Figure 4e) show the absence of electronic states at the Fermi level, confirming that 3D Ge nanoislands are semiconducting.³⁸

In conclusion, flat 2D sheets showing a honeycomb lattice matching that of germanene are grown by deposition of submonolayers of Ge on graphite at room temperature followed by annealing to 350 °C. The overlayers show a

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small buckling and no atomic reconstruction suggesting the absence of any alloy formation and hybridization with the substrate. Ab initio calculations indicate that the Dirac cone of free-standing germanene is preserved for layers supported on HOPG. Compared to the substrate, the islands show a characteristic charge transfer which is predicted by simulations and observed in STS spectroscopy. Because very large graphene wafers are routinely produced, the growth process can easily be scaled-up and opens interesting opportunities for fabricating functional electronic devices based on germanene.

METHODS

Experiments were performed in an ultrahigh vacuum (UHV) environment at a base pressure $p < 4 \times 10^{-11}$ mbar. Graphite substrates were thoroughly outgassed in UHV for several hours at 400 °C. Ge was deposited at room temperature using an *e*-beam evaporator at a rate of 0.07 ML per minute. After Ge deposition, samples were annealed to 350 °C for 10 min. The growth was monitored in situ by scanning tunneling microscopy (Omicron-STM) using W tips at room temperature with the Z-feedback off. Lattice parameters were obtained by analyzing the STM images with the *Lattice* tool of WsXM software.

Ab initio electronic structure and total energy calculations have been performed using the Vienna Ab-initio Simulation Package (VASP-5.3.5).^{39,40} The calculations are based on DFT and the projector-augmented wave (PAW) representations.⁴ The exchange-correlation interaction is treated with the generalized gradient approximation (GGA) parametrized by the Perdew-Burke-Ernzerhof (PBE) formula.⁴² To correctly describe the van der Waals interactions resulting from dynamical correlations between fluctuating charge distributions, the van der Waals correction to the GGA calculations is included by using the D2 method of Grimme.⁴³ The wave functions are expanded in plane waves up to a kinetic energy cutoff of 400 eV. For Brillouin zone integrations, a Γ -centered k-point mesh of size $4 \times 4 \times 1$ was used for the geometry optimizations and of size $11 \times 11 \times 1$ for the density of states computations. The optimization of the atomic positions is performed via the conjugate-gradient method with the maximal force equal to 0.01 eV Å⁻¹. The convergence criterion of the total energy for self-consistent field calculations was chosen to be 10^{-4} eV. The graphite substrate is modeled by a four-layer slab in an ABAB stacking of graphene layers with periodic boundary conditions in three dimensions and keeping the bottom two layers fixed at the optimized bulk values. Two neighboring slabs are separated by a vacuum space of about 15 Å along the z-direction that is perpendicular to the surface to avoid interactions between the different slabs. For establishing the calculation models for germanene/HOPG structure and to minimize the lattice mismatch between the two lattices, different configurations have been investigated. Several models have been created by combining different supercells of germanene and graphite with a rotation angle between the two surfaces. The simulated STM image was obtained using the constant current mode based on calculated partial charge densities and at a temperature of 0 K.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b01284.

Movie showing the relaxation process of the germanene/ HOPG system. A germanene layer on top of the graphite structure, with germanium and carbon atoms that were artificially covalently bonded at the beginning of the simulation, is subject to full relaxation. The germanene and graphite layers move apart and become stable with an interlayer distance of about 3.3 Å, corresponding to the van der Waals distance. (AVI)

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Notes

The authors declare no competing financial interest.

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