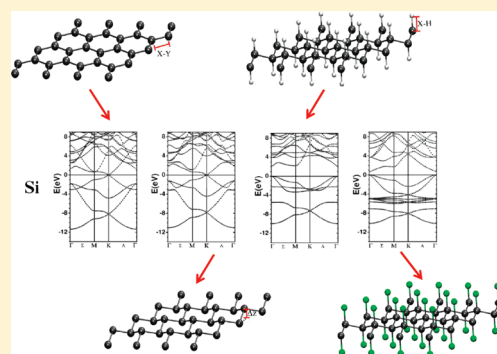


Group IV Graphene- and Graphane-Like Nanosheets

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ABSTRACT: We performed a first-principles investigation on the structural and electronic properties of group IV (C, SiC, Si, Ge, and Sn) graphene-like sheets in flat and buckled configurations and the respective hydrogenated or fluorinated graphane-like ones. The analysis on the energetics, associated with the formation of those structures, showed that fluorinated graphane-like sheets are very stable and should be easily synthesized in the laboratory. We also studied the changes of the properties of the graphene-like sheets as a result of hydrogenation or fluorination. The interatomic distances in those graphane-like sheets are consistent with the respective crystalline ones, a property that may facilitate integration of those sheets within three-dimensional nanodevices.



INTRODUCTION

The properties of graphene, the one-atom-thick sheet with carbon atoms with the sp^2 hybridization, were first discussed in the literature more than 60 years ago.¹ It has been long considered only a theoretical curiosity of impossible experimental realization. This perception changed radically a few years ago, after the separation of graphene sheets with single and multiple layers.^{2–4} Since then, graphene has been intensively investigated, with focus on its physical and chemical properties.⁵ This material carries unique properties that allow one to envision a number of potential applications, such as chemical sensors,^{6,7} nanoelectronic devices,⁸ or hydrogen storage systems.⁹

Graphene could be considered as a prototypical material to study the properties of other two-dimensional nanosystems. Recently, several two-dimensional structures have been explored in the literature. For example, graphane, a fully hydrogenated graphene sheet with all carbon atoms in the sp^3 hybridization, has been proposed by theoretical investigations¹⁰ and was later synthesized.¹¹ Graphene-like sheets, made of silicon carbide,^{12,13} silicon,^{14,15} germanium,^{16,17} boron nitride,^{18,19} and zinc oxide,²⁰ have also been discussed in the literature.

Here, we performed a systematic investigation on the trends in the properties of group IV (C, SiC, Si, Ge, and Sn) graphene-like structures, in flat and buckled configurations, using first-principles total energy calculations. We then observed the modifications on those properties as a result of full coverage of hydrogen and fluorine atoms, to form sp^3 graphane-like structures. We found that hydrogenation and fluorination processes provide structures that were energetically very accessible for all compounds and should be easily synthesized in the laboratory. We also found that all group IV graphene-like structures present null gaps in both flat or buckled configurations, which opened up with hydrogenation or fluorination in most materials. The only exception was the fluorinated graphane-like tin, which, although

tin atoms were 4-fold coordinated, the material presented a null gap. This paper is organized as follows: We first discuss the methodology, then the properties of group IV graphene-like sheets. Finally, we discuss the energetics and resulting physical properties of hydrogenated and fluorinated graphane-like sheets.

METHODOLOGY

The calculations were performed using the Vienna Ab-initio Simulation Package (VASP).²¹ The electronic exchange-correlation potential was described within the density functional theory and the generalized gradient approximation (DFT-GGA).²² The electronic wave functions were described by a projector augmented wave (PAW) method,²³ taking a plane-wave basis set with an energy cutoff of 550 eV. For all calculations, convergence in total energy was set to 0.1 meV/atom between two self-consistent iterations. Configurational optimization was performed by considering relaxation in all atoms, without symmetry constraints, until forces were lower than 3 meV/Å in any atom. The Brillouin zone was sampled by a $15 \times 15 \times 1$ Monkhorst–Pack k -point grid.²⁴ The planar structures were built using periodic boundary conditions with a hexagonal simulation cell. In the direction perpendicular to the sheets (z), we used a lattice parameter of 20 Å, which was large enough to prevent image interactions. Such theoretical framework and convergence criteria have been shown to provide a reliable description of carbon-based nanosystems.^{25,26}

Binding and formation energies for all systems were computed following the same procedure presented elsewhere.¹⁰ The binding energy (E_B) of a certain structure was computed as the difference between the total energy of that stable structure and the total energies of the respective isolated atoms in their neutral

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Table 1. Structural and Electronic Properties of Graphene-Like Sheets (α -XY and β -XY, Respectively, for Flat and Buckled Sheets) and Hydrogenated (XYH₂) or Fluorinated (XYF₂) Graphene-Like Sheets with X = Y = C, Si, Ge, or Sn (or X = C and Y = Si for SiC)^a

	<i>a</i>	<i>d</i> (X–Y)	<i>d</i> (X–H)	<i>d</i> (X–F)	<i>d</i> (Y–H)	<i>d</i> (Y–F)	Δz	<i>E</i> _B	<i>E</i> _F	<i>E</i> _g
α -C ₂	2.468	1.425					0	−7.848		0.0
C ₂ H ₂	2.539	1.536	1.110				0.459	−5.161	−0.111	3.47
C ₂ F ₂	2.609	1.583		1.382			0.488	−5.403	−0.802	3.10
α -Si ₂	3.897	2.250					0	−3.894		0.0
β -Si ₂	3.867	2.279					0.459	−3.914		0.0
Si ₂ H ₂	3.968	2.392	1.502				0.687	−3.379	−0.297	2.11
Si ₂ F ₂	3.968	2.395		1.634			0.697	−4.656	−2.019	0.70
α -Ge ₂	4.127	2.383					0	−3.114		0.0
β -Ge ₂	4.061	2.444					0.690	−3.243		0.0
Ge ₂ H ₂	4.091	2.473	1.563				0.730	−2.882	0.107	0.95
Ge ₂ F ₂	4.182	2.492		1.790			0.617	−3.892	−1.349	0.19
α -Sn ₂	4.798	2.770					0	−2.581		0.0
β -Sn ₂	4.639	2.841					0.947	−2.728		0.0
Sn ₂ H ₂	4.719	2.846	1.738				0.824	−2.517	−0.030	0.45
Sn ₂ F ₂	5.028	2.951		1.970			0.531	−3.625	−1.581	0.0
α -SiC	3.100	1.790					0	−5.905		2.54
β -SiC	3.098	1.788					0.001	−5.906		2.54
SiCH ₂	3.124	1.892	1.108		1.497		0.573	−4.366	−0.288	4.04
SiCF ₂	3.168	1.914		1.445		1.609	0.563	−5.096	−1.463	1.94

^a The table presents the lattice parameter (*a*); interatomic distances (*d*); buckling distances (Δz); and binding (*E*_B), formation (*E*_F), and electronic band-gap (*E*_g) energies. Interatomic distances, binding and formation energies, and electronic band-gap energies are given, respectively, in Å, eV/atom, and eV.

charge states. The formation energy (*E*_F) of a certain hydrogenated (or fluorinated) sheet was computed as the difference between the binding energy of the graphene-like structure and the binding energies of the respective (stable) graphene-like structure and those energies of the diatomic molecules H₂ (or F₂). In group IV materials, we found that the stable graphene-like structure was the buckled configuration (lower in energy), except for carbon.

The total energies of the isolated atoms and diatomic molecules were obtained considering a large simulation cell and the same methodological approximations of all the other calculations described in the previous paragraphs.

To check the validity of all approximations used in this investigation, we compared the properties of graphene with available data from experiments and other theoretical investigations. The computed that the binding energy of graphene was −7.848 eV/atom, being 0.136 eV/atom lower than the respective energy of the diamond cubic structure. Those two values are in excellent agreement with other investigations.^{27,28} In terms of the structural properties of graphene, the carbon–carbon interatomic distance was 1.425 Å, which is in excellent agreement with the respective experimental values (1.42 Å),¹ but a little larger than the one (1.414 Å) of a recent theoretical investigation.¹⁵ It should be pointed out that, whereas our investigation used a generalized gradient approximation, the other investigation used the local density approximation, which is known to underestimate interatomic distances.¹⁵

RESULTS

Figure 1 presents a schematic representation of graphene-like structures in flat (labeled α) and buckled (labeled β) configurations

and their hydrogenated and fluorinated graphene-like forms. Table 1 presents the structural properties of group IV graphene-like sheets and their respective binding energies. According to the table, graphene-like structures of Si, Ge, and Sn in flat (α) configurations are metastable, with the respective buckled ones (β) being energetically more favorable, consistent with other investigations for Si.^{15,16}

Figure 2 presents the theoretical interatomic distances and binding energies of all group IV graphene-like and graphane-like structures as a function of the respective properties in the (diamond cubic or zinc-blende) crystalline solid phases, in which all group IV atoms are in the sp³ hybridization.²⁹ According to Figure 2a, interatomic distances between group IV atoms in flat graphene-like structures are, on average, 5% shorter than those distances in the respective solid phases. These results show that the group IV atoms, in an sp² environment, behave essentially the same way as carbon atoms do. For the buckled configurations, those distances are always larger than the respective ones in the flat configurations. Buckling distances (Δz) are consistent with recent theoretical results for buckled sheets of silicon and germanium.¹⁶

Figure 2b shows that the binding energies of most group IV graphene-like structures in either flat or buckled configurations, except for carbon, are higher than the respective energies in the solid stable phases. This indicates that graphene-like structures, with atoms in the sp² hybridization, are not very stable when compared to the respective solid phases, in which atoms are in the sp³ hybridization. These results are consistent with the generally large energy difference between those two hybridizations in most covalent materials, being small only for carbon. Additionally, the binding energy of the buckled configurations is larger than the one of the flat configurations, except for carbon. In

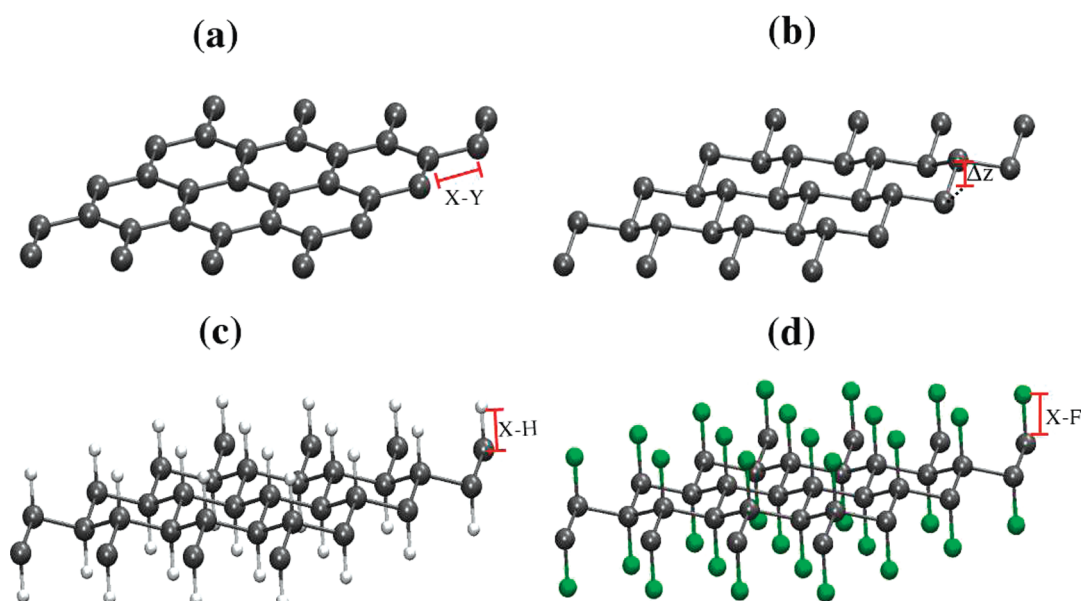


Figure 1. Schematic representation of group IV two-dimensional materials: (a) flat graphene-like (α), (b) buckled graphene-like (β), (c) hydrogenated graphene-like, and (d) fluorinated graphene-like structures. The figure also indicates the interatomic distance labels, consistent with the ones in Table 1. Black, gray, and green spheres represent group IV, hydrogen, and fluorine atoms, respectively.

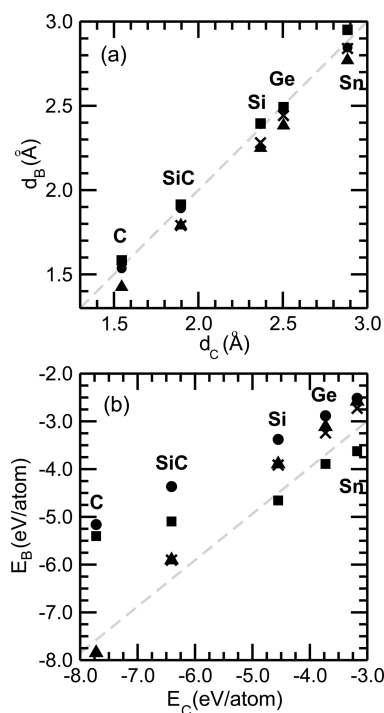


Figure 2. Properties of group IV (C, SiC, Si, Ge, and Sn) graphene-like (in flat and buckled sheets) and graphene-like structures (with full coverage of H or F atoms). The figure shows the (a) interatomic distances (d_B) and (b) binding energies (E_B) of those structures as a function of the respective distances (d_C) and binding energies (E_C) in the diamond cubic (or zinc-blende) crystalline structures. The \blacktriangle , \times , \bullet , and \blacksquare symbols represent, respectively, the flat graphene-like (α), buckled graphene-like (β), hydrogenated graphene-like, and fluorinated graphene-like structures. The dashed lines are only a guide to the eye, representing the properties $d_B = d_C$ in (a) and $E_B = E_C$ in (b).

the case of carbon, the calculations indicated that the buckled configuration is unstable, relaxing toward the flat one. An interesting

case is SiC, in which the binding energy difference between flat and buckled configurations is only 1 meV/atom and the buckling is also very small. All those graphene-like structures, in either flat or buckled configurations, presented a null electronic gap, except for SiC, which presented a large gap of 2.54 eV. This value is in excellent agreement with a recent theoretical investigation using similar approximations.^{12,13}

Figure 3 presents the electronic band structure of all graphene-like structures in flat and buckled configurations. All group IV graphene-like structures (of C, Si, Ge, and Sn) in a flat configuration (Figure 3a) present a similar electronic band structure, with a band crossing in the Dirac (K) points at the Fermi level. For all of those materials, there is linear dispersion around those Dirac points, a property that results from the honeycomb structure. In buckled configurations (Figure 3b), the linear dispersion around those Dirac points is maintained.

The electronic band structures of the flat graphene-like configurations differ among themselves only by the fact that, in structures of C and Si, the system is semimetallic, being metallic in Ge and Sn ones. Such a difference in the band structure could be understood by the following explanation. For graphene-like flat structures of C and Si, there is a specific energy band that stays over the Fermi level in all the Brillouin zone. However, for graphene-like flat structures of Ge and Sn, the same band crosses the Fermi level in the $\Gamma \rightarrow M$ symmetry direction, and the system is metallic. The electronic band structures of the flat and buckled configurations differ by the fact that the later ones do not present the band crossing described in this paragraph.

Because the electronic band structure of group IV graphene-like materials, in flat configurations, are equivalent to the one of carbon, we computed the carrier velocities around their respective Dirac points. From the results of Figure 3, the computed carrier velocities in those points are $0.91, 0.58, 0.59$, and 0.52×10^6 m/s for flat graphene-like of C, Si, Ge, and Sn, respectively. The computed carrier velocities in those points are $0.46, 0.69$, and 0.95×10^6 m/s for buckled graphene-like of Si, Ge, and Sn, respectively. Those results

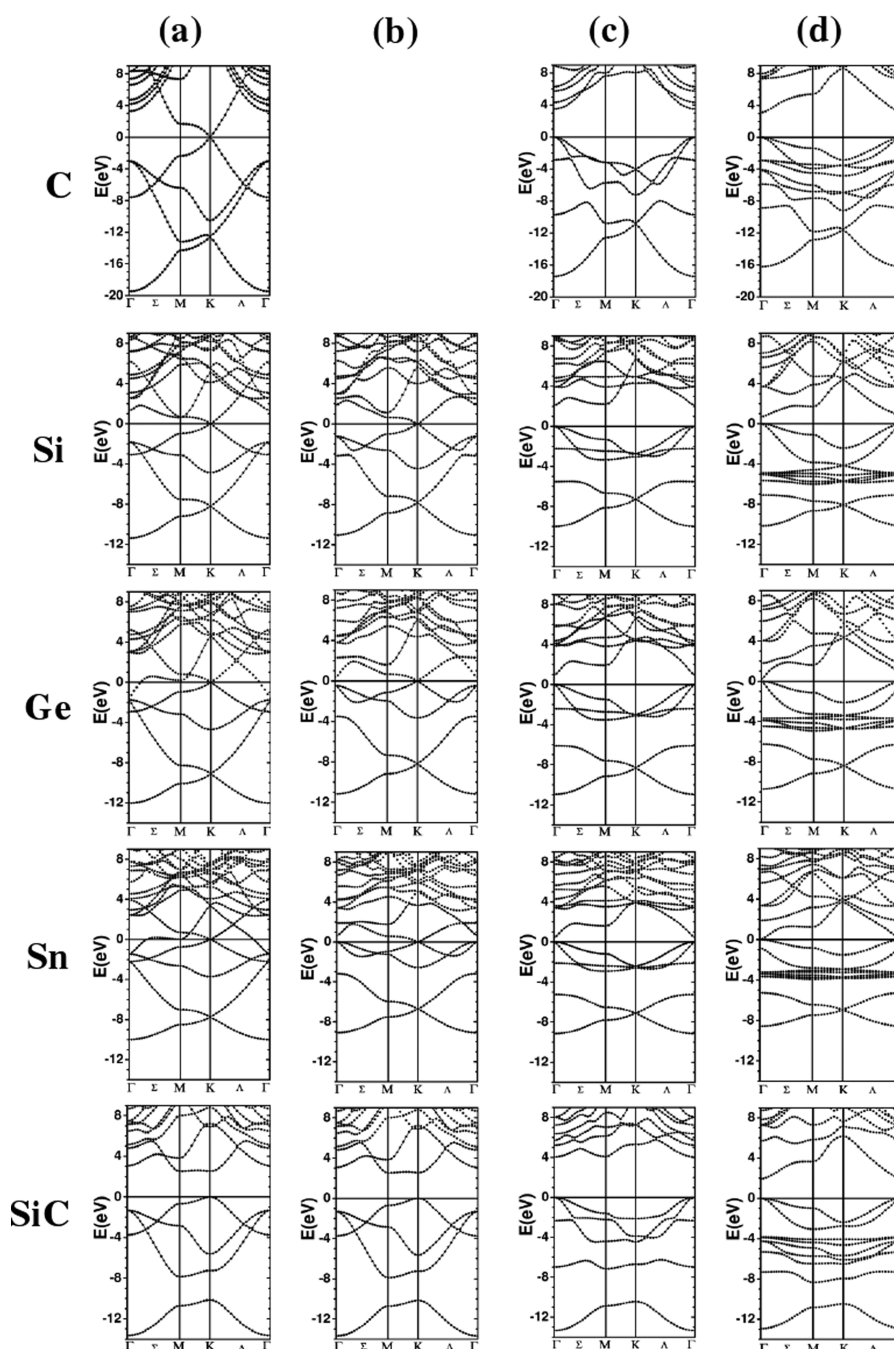


Figure 3. Electronic band structure of group IV in (a) flat graphene-like (α), (b) buckled graphene-like (β), (c) hydrogenated graphene-like, and (d) fluorinated graphene-like structures.

indicate that carrier velocities around the Dirac points could be very large in the buckled configurations. Our result for graphene is in good agreement with the experimental value of 1.1×10^6 m/s (refs 2 and 30) and with the theoretical one of 0.63×10^6 m/s (ref 15).

Table 1 presents the structural parameters for hydrogenated and fluorinated graphane-like structures and their respective binding and formation energies. Here, we considered only systems associated with the chairlike configurations and neglected the boatlike isomeric ones. This is justified by recent theoretical investigations for graphane^{10,31} and fluorinated graphane,³² indicating that the chairlike configuration is energetically more favorable than the boatlike one. As described in Figure 1c (or Figure 1d),

the chairlike configuration has hydrogen (or fluorine) atoms alternating over and below the plane containing the group IV atoms. Incorporation of either hydrogen or fluorine atoms leads to very stable structures, with binding energies (per atom) for graphane-like structures larger than the ones for graphene-like, as shown in Figure 2b. Additionally, the graphane-like structures have large formation energies in most cases, consistent with other theoretical investigations for hydrogen incorporation in graphene¹⁰ and in boron nitride graphene-like structures.¹⁸

Figure 2b shows the trends in the binding energies (per atom) for hydrogenated and fluorinated graphane-like structures. The fluorinated structures are energetically more stable than the

hydrogenated ones and become considerably favorable for Si, Ge, and Sn materials. These results are consistent with available experimental results for graphane and fluorinated graphane structures.^{11,31} Therefore, it is expected that those fluorinated graphane-like forms should be easily synthesized in the laboratory.

In terms of the structural properties of hydrogenated and fluorinated forms, Table 1 presents the interatomic and buckling distances. The interatomic distances between the group IV atoms and hydrogen (or fluorine) atoms are in excellent agreement with the respective distances in typical organic molecules. For example, in graphane (C_2H_2), the C–C, C–H, and buckling (Δz) distances are 1.536, 1.110, and 0.459 Å and agree very well with recent theoretical results¹⁵ of 1.520, 1.084, and 0.45 Å, respectively. For the fluorinated graphane-like structure (C_2F_2), the C–C and C–F distances are 1.583 and 1.382 Å, which agree well with recent theoretical results³¹ of 1.579 and 1.371 Å, respectively. According to Figure 2a, along the series, interatomic distances between group IV atoms, in either hydrogenated or fluorinated forms, are all very close to the interatomic distances in their respective crystalline forms.

The results indicate that group IV atoms, in hydrogenated and fluorinated graphane-like structures, are 4-fold coordinated and have a near tetrahedral configuration, and their interatomic distances and binding are close to the ones in a crystalline environment. The structures deviated from a tetrahedral configuration, evidenced by the buckling distance (Δz), due to some ionic character in the binding between the group IV atoms and the hydrogen (or fluorine) neighboring atoms. The results suggest that hydrogenation or fluorination may generate two-dimensional structures that could be easily incorporated in the surface of the respective three-dimensional crystalline counterparts. Therefore, although integration of graphene-like structures in three-dimensional devices is still difficult, due to large lattice mismatch, it may be easier for hydrogenated and fluorinated graphane-like structures.

According to Figure 3c,d, hydrogenation and fluorination open the electronic gap of the graphene-like structures. In all cases, the electronic gap is larger in the hydrogenated configurations than in the fluorinated ones. An interesting case is the fluorinated graphane-like tin (Sn_2F_2), in which, although tin atoms have a 4-fold coordination, the material has a null gap. This result indicates that carrier velocities should be very large in this system, even with tin atoms with all valence electrons paired with neighboring atoms.

SUMMARY

In summary, we have investigated the trends of the structural and electronic properties of graphene-like structures made of group IV atoms, in terms of their energetics and electronic band structure. The results indicated that, whereas the graphene-like structures (of Si, Ge, Sn, and SiC) appear to have low stability, the respective hydrogenated and fluorinated graphane-like ones are very stable and should be easily synthesized in the laboratory.

The hydrogenated and fluorinated graphane-like structures presented the group IV atoms in a 4-fold configuration and in a near tetrahedral configuration. Interatomic distances in those configurations were close to the respective ones in the solid phase counterparts, a property that could facilitate integration of those two-dimensional structures within three-dimensional nanodevices.

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