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J. Phys.: Condens. Matter 26 (2014) 285301 (6pp)

First-principles study of siloxene and germoxene: stable conformations, electronic properties, and defects

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Received 29 January 2014, revised 15 May 2014 Accepted for publication 2 June 2014 Published 19 June 2014

Abstract

Interest in two-dimensional (2D) forms of Si and Ge has surged recently, with a focus on silicene and germanene, the Si- and Ge-based analogues of graphene, as well as their derivatives. Siloxene and germoxene are 2D materials made of honeycomb Si and Ge backbone sheets that are decorated with H atoms and OH groups. Here we use first-principles calculations to probe the properties of their various conformations. We show that the most stable siloxene (and germoxene) polymorph is the so-called washboard structure, and not the chair geometry assumed in previous studies. The stability of the washboard configuration relates to the formation of a network of hydrogen bonds between its hydroxyl groups. We also find with hybrid functional calculations that siloxene and germoxene are wide band-gap semiconductors with gap values of 3.20 eV and 2.64 eV, respectively. Finally, we show that H and OH vacancies introduce spin polarization in these 2D materials and have a tendency to pair up in stable di-vacancies.

Keywords: graphene, silicene, wide band-gap semiconductors

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

1. Introduction

Motivated by the unique properties of graphene and its chemical derivatives [1-4], there has been intense interest recently in other emerging two-dimensional (2D) materials [5–7], particularly those based on silicon and germanium [8–14]. Several experimental studies have demonstrated the growth of silicene (the honeycomb form of Si) on metal substrates [8, 9] and theoretical works have probed the properties of silicene and germanene, either as suspended films [11–13], or as overlayers on various surfaces [15–17]. Like graphene [18–22], silicene and germanene derivatives can also be synthesized and potentially employed in various applications. Examples are so-called silicane and germanene, respectively [23–25].

In fact, the route for synthesis of silicane and germanane has been well-known for a long time [26]. Starting from CaSi₂ (or CaGe₂), de-intercalation of the calcium atoms in the

presence of HCl acid leads to the formation 2D-Si (or 2D-Ge) sheets that are decorated with H atoms and, depending on the experimental temperature, OH groups. When both H and OH species are present, the materials are known as siloxene and germoxene. While siloxene is believed to be produced routinely [27–30] during de-intercalation of CaSi₂, there is no clear evidence thus far that germoxene has been formed in pertinent experiments [31–33].

Theoretical studies have probed the properties of siloxene crystals [34–36] and nanotubes [37]. These studies have shown siloxene to be stable against emission of H_2O molecules [35], but unstable with respect to formation of Si–O–Si bonds [34, 35]. All these works have assumed one particular structural form of siloxene, the so-called chair configuration, with H atoms on one side and hydroxyl groups on the other. However, even in the case of silicane (or germanane), with only H adatoms, it is known that different polymorphs exist with varying electronic properties [25]. Clearly, siloxene and germoxene can appear in an even greater number of

polymorph geometries, with complex re-arrangements of the H and OH adsorbates.

In this paper, we report the results of first-principles calculations on the relative stability of several distinct siloxene and germoxene conformations. We find that the most stable siloxene (or germoxene) configuration is not the previous *ad hoc* studied chair polymorph, but the washboard geometry, with H and OH species on opposite sides. The most important factor for stability of the washboard polymorph is the formation of strong hydrogen bonds between hydrogen and oxygen atoms on the hydroxylated side. Both siloxene and germoxene are predicted to be wide band-gap semiconductors. The formation of hydrogen and hydroxyl vacancies on siloxene is endothermic and can induce spin-polarization or defect clustering in this 2D material.

2. Method

The results were obtained with density-functional theory (DFT) calculations using the code VASP [38]. We set the energy cutoff at 450 eV for the plane-wave basis of valence wavefunctions and used projector-augmented waves [39] for the description of interactions between valence electrons and ionic cores. In the following we describe results obtained with a generalized-gradient approximation [40] (GGA) functional to account for exchange and correlation (xc) effects. Use of a local-density approximation [41] (LDA) xc-functional led to the same conclusions. All structures were relaxed until the total energy converged within 10⁻⁴ eV using the Mohnkorst-Pack scheme [42] and a $12 \times 12 \times 1$ k-grid for sampling reciprocal space (the z-axis is assumed to be perpendicular to the 2D-sheet). The high energy cutoff and large number of k-points ensure results converge and enable the comparison of stability between different configurations. A similar approach has been followed in previous DFT studies on various materials [43, 44], including Si- and Ge-based systems [45, 46].

Electronic density of states (DOS) calculations employed the tetrahedron method for *k*-integration [47], the hybrid PBE0 xc-functional, [48, 49] and $9 \times 9 \times 1$ *k*-meshes. Calculations with denser *k*-grids gave practically the same results for the most important cases discussed below. Periodic images of the 2D sheets along the *z*-direction were separated by at least 10 Å. We have performed calculations with and without taking into account spin-orbit coupling (SOC). The inclusion of SOC does not produce any noticeable change in the band structure of the most stable configurations, or with respect to relative stability of structures (within about 1 meV per Si or Ge atom). We have also used the so-called DFT-D2 method [50] that includes van der Waals interactions as post-DFT corrections. Unless stated otherwise, the results reported below are those based on PAW-GGA calculations.

3. Results and discussion

In the following we present the results of the DFT calculations on the stability and electronic properties of the materials of interest. In the first part we report findings on pristine



Figure 1. Siloxene polymorphs with 50% H and 50% OH content: (*a*) chair (side view), (*b*) chair (top view), (*c*) washboard (side view), and (*d*) washboard (top view). The distance between the H and O atoms shown with arrows is 3.2 Å (1.6 Å) in the chair (washboard) polymorph. The shaded area shows the unit cell of the structure (Si: gray (dark yellow), O: dark gray (red), H: white spheres).

and defective siloxene. We then present results on germoxene and we conclude with a comparison with graphenol, i.e., a graphene-based 2D material decorated with H and OH species.

3.1. Siloxene

Figure 1(a) shows the so-called chair configuration for siloxene, the polymorph that has been considered in previous studies [34–36]. The H and OH adsorbates are arranged so that every Si–H entity is surrounded by three Si–OH species. In this arrangement, the primitive unit cell is trigonal with two Si atoms. As shown in the top view of figure 1(b), the O–H bonds point in the same direction as underlying Si–Si bonds, while the distance between the H atom of one OH group and the O atom of a neighboring OH species is 3.2 Å. We have examined several other chair configurations; for example, structures with OH groups on nearest-neighbor Si atoms and on opposite sides (so that also half of the H adatoms lie on one side and the other half on the other side of the silicene sheet). All these other configurations are less stable than that of figure 1(a) by at least 10 meV per Si atom.

The washboard conformation relates to an alternating sequence of up and down zig–zag stripes of backbone atoms, as shown in figures 1(c) and (d). Similar to the case of chair siloxene, several different washboard structures are possible, depending on the relative arrangement of H and OH species. The most stable geometry is the one depicted in the two bottom panels of figure 1. As a matter of fact, this conformation is the most stable among all siloxene structures considered in this work. The Si–Si, Si–O, Si–H, and O–H bond lengths in this structure are 2.36 Å, 1.69 Å, 1.50 Å, and 1.01 Å, respectively. The key factor that enhances the stability of this polymorph is the formation of a network of strong hydrogen bonds. As depicted in the top view of figure 1(d), the distance between a H atom of an OH group and the O atom of a neighboring



Figure 2. Siloxene boat polymorph with 50% H and 50% OH content: (*a*) side view, (*b*) top view. The distance between the H and O atoms shown with arrows is 1.9 Å. The shaded area shows the unit cell of the structure (Si: gray (dark yellow), O: dark gray (red), H: white spheres).

Table 1. *a* and *b* lattice parameters along the *x*- and *y*-directions for the siloxene and germoxene polymorphs of the type shown in figures 1 and 2. ΔE is the energy difference (per Si or Ge atom) with respect to the most stable configuration.

Material	Structure	a (Å)	<i>b</i> (Å)	∆E (meV)
Siloxene	Figure $1(a)$	3.90	6.75	82
Siloxene	Figure $1(c)$	3.92	5.22	0
Siloxene	Figure $2(a)$	3.88	6.37	83
Germoxene	Figure $1(a)$	4.12	7.14	80
Germoxene	Figure $1(c)$	4.13	5.43	0
Germoxene	Figure $2(a)$	4.10	6.67	81

Si–OH complex is only 1.6 Å. The end result is that the energy of the washboard geometry is lower than that of the chair conformation of figure 1(a) by 82 meV per Si atom. The corresponding DFT-D2 energy difference is 131 meV per Si atom.

The third conformation we studied in this work is the socalled boat configuration shown in figure 2. In this geometry, the shortest distance between H and O atoms of proximal OH groups is 1.9 Å, indicating the formation of a hydrogen bond. Nevertheless, this bond is not as strong as the one in the washboard polymorph and the boat structure of figure 2 is less stable than that shown in figure 1(c) by 83 meV (122 meV) per Si atom, based on PAW-GGA (DFT-D2) calculations. Similar to the afore-mentioned cases of the chair and washboard polymorphs, several other boat configurations were examined and found to have higher energy compared to the one shown in the figure.

Table 1 summarizes the equilibrium lattice parameters a and b along the x- and y-directions for the siloxene configurations shown in figures 1 and 2. The lattice parameters were determined by minimizing the energy of the system with respect to a, b and the position of the atoms within the unit cell of each conformation. In addition, the position of the energy minimum E_{min} was confirmed, with two-dimensional plots of the energy as a function of a and b. In these calculations a 5×5 grid was used with (a, b) points in the vicinity of E_{min} . Figure 3(a) shows one such plot for the washboard siloxene polymorph of figure 1(c). Though the response to large compressive stresses is not the subject of the present study, we note that similar 2D materials, namely graphane [21], silicane, and germanane [25] develop interesting patterns of extreme bending and superstructures under high levels of compression.



Figure 3. Dependence of energy for the washboard structure of figure 1(b) on in-plane *a* and *b* lattice parameters along the *x*- and *y*-direction, respectively: (*a*) siloxene, (*b*) germoxene. Each contour line represents an increase of 7.5 meV (5.6 meV) in energy for siloxene (germoxene) with the dark (blue) area at the center surrounding the equilibrium point.

Figure 4 shows the DOS and the band structure for the most stable washboard siloxene configuration of figure 1(*c*). As mentioned above, the DOS results were obtained with calculations based on the PBE0 hybrid xc-functional [48]. The energy gap between the valence and conduction bands is equal to 3.20 eV. In the case of chair siloxene of the type shown in figure 1(*a*) the calculated gap is 2.94 eV. This value is significantly larger than the previous [35] LDA value of 1.7 eV. The discrepancy can be attributed mainly to the well-known underestimation of energy-band gaps in LDA approaches. As shown in figure 4, the band gap of washboard siloxene is direct with the valence band maximum and conduction band minimum, both located at the origin Γ of reciprocal space. The most stable conformation of siloxene is a direct wide band-gap semiconductor.

The same trend of relative stability between washboard, chair, and boat configurations applies when the hydroxyl content increases to 100%, with one OH group per Si atom. As in the case of 50% OH content, the most stable structure is the one that resembles the geometry of figure 1(c), but with OH groups on both sides of the silicene backbone. With respect to this configuration, chair and boat geometries with 100% OH content are less stable by 229 meV and 172 meV per Si atom, respectively. By calculating all relevant total energies, we find that there is a very small energy gain of 3 meV per Si atom when the structure shown in figure 1(c) separates into a chair silicane phase with 100% H content and a washboard polymorph with 100% OH content.

3.2. Hydrogen and hydroxyl vacancies on siloxene

Defects and impurities play a crucial role for the performance of materials in electronic devices [51, 52]. Here we have investigated with DFT calculations the stability and electronic properties of native defects of siloxene in the form of hydrogen or hydroxyl vacancies. In the standard process of siloxene formation, through de-intercalation of CaSi₂, hydrogen atoms and hydroxyl groups are deposited on the silicene backbone from an HCl solution [27–30]. When complete coverage by H and OH species is not achieved, the siloxene sheet will bear



Figure 4. (*a*) Electronic density of states (DOS) and (*b*) band structure for the washboard siloxene polymorph of the type shown in figure 1(c). Zero energy is set at the valence band maximum.

H and OH vacancies. To study these native defects we used large supercells, with a dimension of about 15.6 Å in the two in-plane directions. The defect-free supercells contained 48 Si atoms, 24 H atoms, and 24 OH groups. Only the Γ point was employed in reciprocal space.

Figure 5(a) shows a hydroxyl single vacancy on washboard siloxene. The arrow points to the three-fold coordinated silicon atom with the OH vacancy. The neighboring H atom, that used to form a hydrogen bond with the missing OH group, has now turned to form such a bond with the next OH species. The defect is spin-polarized, with a magnetic moment of $1\mu_{\rm B}$. Likewise, a hydrogen mono-vacancy, depicted in figure 5(b), has a spin polarization of $1 \mu_{\rm B}$. The origin of spin-polarization relates to the fact that a single (H or OH) vacancy creates a state around the middle of the energy band gap. When spinpolarization is allowed, this state splits to one occupied level above the valence band and one empty state below the conduction band of siloxene. Formation of isolated H vacancies is an endothermic process when the missing H atoms are supposed to come off as H2 molecules. The associated energy penalty is 5.6 eV per H vacancy.

When vacancies approach each other they start to interact and form stable defect pairs. Figure 6 shows two such pairs, on the left a defect with H and OH vacancies on neighboring sites, and on the right an OH–OH double vacancy. If, instead of removing the OH group in the defect of figure 6, we take away a second H atom (the one encircled in the figure) we obtain the lowest energy H–H di-vacancy. All these defects are stable against dissociation from remote single vacancies. To calculate the binding energy of an H–OH di-vacancy we: add the absolute values of the energies of a defect-free supercell, and of a supercell with the double vacancy; then, we subtract the sum of the absolute energy values of a supercell with a single H mono-vacancy and of a supercell with a single OH



Figure 5. Spin density in the vicinity of: (*a*) a hydroxyl single vacancy, or (*b*) a hydrogen mono-vacancy on siloxene. The arrows point to the silicon atom missing an H- or OH-bond. The spin density is localized around this atom (Si: gray (dark yellow), O: dark gray (red), H: white spheres).



Figure 6. Vicinal vacancy pairs on siloxene: (*a*) hydrogen and hydroxyl vacancies, (*b*) two hydroxyl vacancies (Si: gray (dark yellow), O: dark gray (red), H: white spheres).

mono-vacancy. The difference is positive (1.18 eV), which means that the H–OH vacancy is indeed stable. Binding energies of the H–H and OH–OH double vacancies are calculated in the same way to be 0.52 eV and 0.64 eV, respectively. In contrast to the single-vacancy cases discussed above, the di-vacancies are not spin-polarized. It should be noted that the formation of an H–OH di-vacancy through the concurrent emission of an H₂O molecule from pristine siloxene, is an endothermic process with an energy cost of 2.35 eV. This result confirms the finding of the previous LDA study [35] that siloxene is stable against H₂O emission.

3.3. Germoxene

Similar to the siloxene study, we examined the relative stability of the three main germoxene polymorphs; namely, the chair, washboard, and boat geometries depicted in figures 1 and 2. As for siloxene, the most stable germoxene conformation is the washboard configuration. Its energy per Ge atom lies 80 meV and 81 meV lower than that of the chair and boat germoxene polymorphs, respectively. The corresponding DFT-D2 values are 146 meV and 127 meV. The Ge–Ge, Ge–O, Ge–H, and O–H bond lengths in the washboard structure are 2.49 Å, 1.84 Å, 1.56 Å, and 1.01 Å, respectively. The underlying decisive factor of stability is once again the formation of hydrogen bonds between a H atom of an OH group and the O atom of a neighboring OH species. Their distance is only 1.63 Å. This distance increases to 1.9 Å in boat-germoxene, and to 3.4 Å for the chair configuration.

Figure 3(b) shows the variation of the energy of washboard-germoxene as a function of its in-plane *a* and *b* lattice



Figure 7. (*a*) Electronic density of states (DOS) and (*b*) band structure for the washboard germoxene polymorph of the type shown in figure 1(c). Zero of energy is set at the valence band maximum.

parameters. The electronic density of states, and the band structure for the equilibrium washboard structure, are plotted in figure 7(a). These data, calculated with the hybrid PBE0 functional, show that germoxene has an indirect energy gap of 2.64 eV between the valence and conduction bands. The corresponding value for chair germoxene, with 50% OH content, is only 1.71 eV. The gap of germoxene is smaller than that of siloxene, but both materials can be regarded as wide band-gap semiconductors in their most stable washboard conformations. We should finally note that, as in the siloxene case, a germoxene sheet with 100% OH content crystallizes in the washboard geometry with significant energy differences (respectively, 221 meV and 162 meV per Ge atom) compared to the chair and boat conformations. Phase separation of a germoxene layer with 50% OH and 50% H content into areas of chair germanane and washboard germoxene with 100% OH concentration is energetically favorable by 12 meV per Ge atom.

3.4. Graphenol

In analogy to siloxene and germoxene, graphenol [53-55] is the graphene derivative with OH adsorbates. Though this material has not been realized in experimental studies thus far, it is relevant for the development of models of graphene oxide [54]. Since graphane bears certain similarities with silicane and germanane [21, 25], it is reasonable to examine whether graphenol is stabilized in a washboard configuration that resembles the siloxene and germoxene structures of the type in figure 1(*c*). We have found that this is not true. In the case of graphenol, a washboard polymorph, with 50% H and 50% OH content, packs together neighboring OH groups in such high density that the H and O atoms from proximal OH species are separated by only 1.13 Å. As a result of this dense packing,

the washboard configuration is significantly less stable than the chair geometry, by 1.1 eV per C atom.

4. Conclusions

In summary, using DFT calculations, we have identified the most stable polymorphs of siloxene and germoxene, two emerging 2D-materials that could be employed in various applications as wide band-gap semiconductors. The most stable configuration, the so-called washboard conformation, differs from previous *ad hoc* predictions of a chair geometry. By contrast, a chair structure is strongly preferred in the case of graphenol. We have also shown that single hydrogen and hydroxyl vacancies on siloxene are spin-polarized and that vacancies tend to form stable defect pairs.

Acknowledgments

The authors acknowledge useful discussions with D Kaltsas. The calculations used resources of the EGEE, HellasGrid and LinkSCEEM infrastructures.

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