Interactions between stacked layers of phenyl-modified silicene

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Abstract. We use density functional theory (DFT) calculations to determine the interaction between phenyl-modified silicene nanosheets. The adhesion energy curves between the nanosheets are compared for different van der Waals density functional (vdW-DF) functionals and the DFT-D2 Grimme method. Our results show that there is a weak attraction between the sheets at close separations, that is stronger when vdWs forces are included. Without including vdWs forces the interaction is negligible and occurs at a much larger separation, highlighting the need to include such forces when modelling these nanosheets. Of the vdWs methods, the optB88 functional gives the strongest interaction energy while the Grimme gives the weakest, with the separation at which the nanosheets adhere more strongly varying between 10.04 and 11.24 Å, as measured by the distance between the silicene layers. As the modified nanosheets are brought closer together at separations as close as ~8 Å, the phenyl groups on the bottom of one nanosheet can fit in between the phenyl groups on the top of the

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adjacent nanosheet allowing some $\pi - \pi$ interaction between the phenyl groups. We showed that the band gap can be modified by compressing the nanosheets together while retaining a small attraction between them. There is also a change from a direct to an indirect band gap. Such a property may be exploited for the application of these nanomaterials in optoelectronic devices.

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1. Introduction

Silicon nanosheets are the most recently discovered form of nanoscale Si [1, 2]. They are a two-dimensional nanomaterial with large lateral dimensions and thickness of only nanometers [3, 4]. A single-layer Si nanosheet is called silicene and can be considered as the analogue of graphene (see [5] and references therein). In contrast to graphene, which is flat, silicene is buckled, but has the same semi-metal properties as graphene. Our group has used a theoretical approach to examine the structure and properties of these unique nanomaterials, from single layer to multi-layered systems [3, 4, 6, 7]. Recently, the group of Nakano and co-workers [1] have grown silicene nanosheets that are functionalized with different groups including amines and phenyl groups, that form Si–N and Si–C bonds, respectively. The phenyl-modified silicene [8] has phenyl groups attached to Si atoms above and below the sheet, with the under-coordinated Si atoms terminated with H atoms. The extent of substitution on the silicon surface is approximately 2:1 -H/-Ph which gives the composition of the organosilicon nanosheet as (Si$_6$H$_4$Ph$_2$). Using density functional theory (DFT) calculations, we showed that this new nanomaterial is semiconducting, with a direct band gap of 1.92 eV [9]. We confirmed that the phenyl groups are covalently bonded to the sheet, however, no details about the way the sheets stack together or the interaction energy between them has been determined. From the experimental synthesis, the nanosheets are obtained in the form of a colourless past wherein the sheets are likely to be stacked at a separation distance of $\sim$1.0 nm [8]. No details are known about the stacking geometry of the sheets, their adhesive force, and also how the separation distance between the sheets could modify the structural or electronic properties.

As it is known that the interaction between the sheets is weak [1], modelling methods that represent dispersion forces need to be employed to examine the stacking of these nanosheets. It has been well-established that DFT does not represent weak forces well, with many generalized gradient approximation (GGA) exchange-correlation functionals being inadequate for the description of dispersion interactions [10]. There has, however, been a recent body of work that has focused on developing methods to incorporate weak forces, such as van der Waals interactions (vdWs), in DFT calculations. One of the methods used is the DFT-D2 method of...
Grimme [11]. Here the vdWs interactions are described via a simple pair-wise force field, which is optimized for several popular DFT functionals. With this method the dispersion forces are calculated as an add-on term to the calculated Kohn–Sham DFT energy.

An alternative to this approach is to use a non-local dispersion term that is included explicitly in the functional. One of the most promising and rigorous methods is the non-local van der Waals density functional (vdW-DF) method which was proposed by Dion et al [12]. This method is a non-local correlation functional that approximately accounts for dispersion interactions. In the Vienna ab initio Simulation Package (VASP) the method is implemented using the algorithm of Roman-Perez and Soler [13] which transforms the double real space integral to reciprocal space and reduces the computational effort. Several proposed versions of the method can be used: the original vdW-DF [12], vdW-DF with exchange functionals optimized for the correlation part [14] and the vdW-DF2 of the Langreth and Lundqvist groups [15].

In this paper we use DFT calculations to determine the adhesion energy between phenyl-modified silicene using different vdW-DF functionals and the DFT-D2 Grimme method. We show that it is necessary to include weak forces when modelling this material using DFT, as the forces holding the layers together are very weak. We also show that the geometry and electronic properties can be altered by changing the separation between the sheets.

2. Method

The phenyl-modified silicene structure employed in this study has been grown using an organic synthesis method [8] and has been characterized previously [9]. For our DFT calculations, the supercell is 6.63 Å (x-direction) × 11.575 Å (y-direction) in size and consists of a single layer Si sheet (silicene) that has four phenyl groups distributed evenly over the surface, two above and two below the sheet (see figure 1 which shows the optimized structure we obtained previously [9] using DFT with the Perdew, Burke and Ernzerhof (PBE) functional). The under-coordinated Si atoms are passivated with H atoms. Application of periodic boundary conditions in the x- and y-directions creates the extended surfaces of the nanosheet along the (111) surface plane (see figure 1). In order to model different separations between the silicene sheets, we changed the size of the vacuum spacer in the z-direction. Very large (or infinite) separation was represented by a vacuum spacer of 15 Å (where no interaction is expected). The interlayer spacing is measured by the distance between the silicene layers (see figure 1). Around the minimum, separations of 0.1 Å were calculated. All atoms where allowed to relax at each interfacial separation until the total energy was converged to $< 10^{-4}$ eV and the Hellmann–Feynman force was $< 0.01$ eV Å$^{-1}$.

We have used a similar procedure previously for metal and oxide surfaces [16–21].

DFT calculations were performed using VASP [22–24] with the projector augmented wave method [25] and GGA. A plane wave basis set with an energy cut off of 400 eV was employed; we determined that the total energy values were converged to $< 2$ meV atom$^{-1}$ using this value. The exchange and correlation functional of PBE [26] was employed. We also use the DFT-D2 method of Grimme [11] and the different vdW-DF and vdW-DF2 functionals [27] as supported in VASP. These are the original vdW-DF method (referred to as revPBE), the optimized vdW-DF methods (optPBE, optB88 and optB86b) and the vdW-DF2 method (rPW86).

A k-point mesh of $8 \times 8 \times 1$, including the $\Gamma$ point, was used for the phenyl-modified silicene sheet at the large separation, while an $8 \times 8 \times 8$ mesh was used for all closer separations.
Figure 1. Structure of phenyl-modified silicene, optimised using DFT (PBE) [9], showing (a) top and (b) side views; (c) schematic picture of the stacking of the sheets, showing the interlayer separation, $d$.

The adhesive energy, $E_{ad}(d)$, is obtained as

$$E_{ad}(d) = \frac{(E(d) - E(\infty))}{A},$$

where $E(d)$ is the total energy of the system calculated at interfacial separation $d$, $E(\infty)$ is the total energy at infinite separation and $A$ is the unit cell surface area in the $x, y$ plane. While we recognize our model does not allow the sheets to slide past each other, a larger model is computationally prohibitive.

3. Results and discussion

The calculated adhesion energy curves for the phenyl-modified silicene nanosheet using the PBE functional, the Grimme potential, as well as the different DFT-vdWs functionals are shown in figure 2. The calculated adhesion energy at the minimum in the curve for each separation distance is summarized in table 1.

Using the PBE functional, it is clear that there is negligible interaction between the nanosheets at all separations. While there is an increased attraction as the sheets are brought closer together it is only 0.5 meV Å$^{-2}$ at a separation of 13.64 Å. Using the DFT-D2 Grimme or vdW-DF2 methods, the adhesion energy is significantly stronger, however, we note that the adhesion is still overall weak. Using the Grimme method, the adhesion energy at the minimum separation (10.04 Å) is calculated to be 8.6 meV Å$^{-2}$. Using the vdW-DF methods, the original vdW-DF method and the vdW-DF2 method give similar adhesion energies ($\sim$9.4 meV Å$^{-2}$), while the three optimised DFT-D2 methods give stronger adhesion energies ($\sim$13.5 meV Å$^{-2}$) than the other methods. Of these methods, the optB88 gives the strongest adhesion energy at a separation of 10.14 Å, which is closer than the minimum separation when dispersion forces are not considered. This separation is in excellent agreement with the experimental x-ray diffraction (XRD) data [8] which indicates the aggregated sheets are separated by a distance of $\sim$10 Å.
Figure 2. Calculated adhesion energy curves for phenyl modified silicene at different separations, $d$, using the functionals indicated.

Table 1. Calculated adhesion energy ($E_{ad}$) values and interfacial separation ($d$) at the minimum, using VASP with the PBE functional, DFT-D2 Grimme method and the different vdW-DF and vdW-DF2 methods: revPBE, optPBE, optB86b, optB88 and rPW86.

| Functional | $E_{ad}$ (meV Å$^{-2}$) | $d$ (Å) |
|------------|--------------------------|---------|
| PBE        | 0.5                      | 13.64   |
| Grimme     | 8.6                      | 10.04   |
| rPW86      | 9.3                      | 10.64   |
| revPBE     | 9.5                      | 11.24   |
| optPBE     | 13.1                     | 10.64   |
| optB86b    | 13.5                     | 10.14   |
| optB88     | 14.1                     | 10.14   |

The calculated binding energy is also in agreement with the interlayer binding energies of other weakly bonded layered compounds that fall in the interval of 13–21 meV Å$^{-2}$ [28].

For the different vdW-DF functionals, except for the revPBE functional, the minimum in the curves only varies by 0.5 Å. The reason for this difference is that this functional has
Figure 3. Optimized geometry of the phenyl-modified silicene using the optB88 functional at the separations, $d$, indicated. Some of the phenyl groups have been recoloured (C = pink; H = blue) to allow the groups on the top of the sheet to be distinguished from those on the bottom at closer separations. Charge density isosurfaces at a value $203.2e\, \text{Å}^{-3}$ are shown for (b) and (c).

been shown previously to be more repulsive at the minimum separation than the other vdW-DF functionals, due to the revPBE energy itself [29].

Our results show that by taking into account vdWs forces, the adhesion energy and minimum separation are stronger and shorter, respectively, than when these weak forces are not included in the DFT calculation. The agreement between our DFT-vdWs calculations and experiment confirms the need to include weak forces when modelling the adhesion between these nanosheets.

In the rest of this section we compare the structural and electronic properties of the stacked nanosheets using the Grimme and optB88 methods in order to determine whether aggregation of the sheets affects the structural or electronic properties. As the different vdWs-DF methods showed little change to the calculated minimum adhesion energy distance, we chose the functional that gave the strongest adhesion energy as we might expect any changes to the properties to be greatest using this functional.
Figure 4. Band structure of phenyl modified silicene using the optB88 functional at separations of (a) 27.64 Å (infinite), (b) 10.14 Å (minimum) and (c) 8.64 Å (close). The band gap ($E_g$) is indicated by the red arrow.

The optimized structure of the stacked nanosheets at three different separations (using the optB88 functional) is shown in figure 3. For the coordinates of these structures, as well as the structure at large separation optimised using the PBE functional, see supplementary material (available from stacks.iop.org/NJP/15/125018/mmedia). At each of these separations we calculated the angle between the phenyl rings and the nanosheet by measuring the angle between the vector encompassing the C atom of the phenyl ring that is bonded to the nanosheet and the C three atoms away, and the vector representing the direction along the $x$-, $y$- or $z$-axis.

At a large separation (27.64 Å), the phenyl rings are oriented perpendicular to the plane of the nanosheet, and relative to the $z$-direction the rings (as measured by the plane of the ring) are only 3.5° off-normal. The silicene layer becomes more buckled in the regions where the phenyl groups are attached, than the regions where the silicene is terminated by H atoms. This structure is essentially the same as that obtained using the PBE functional (without any vdWs corrections) [9] indicating that at this separation the inclusion of vdWs terms has little effect on the geometry as there is no attraction between the nanosheets.

At the minimum interfacial separation of 10.14 Å, the phenyl groups have become tilted on the nanosheet so that the plane of the phenyl groups is tilted by 12.8° off normal, as is also seen in the charge density isosurface plot shown in figure 3(b). This results in a distortion of the silicene layer.
Figure 5. Total DOS of the phenyl-modified silicene using the optB88 functional at separations of 27.64 Å (infinite), 10.14 Å (minimum) and 8.64 Å (close). The region around the band gap is magnified (inset).

At a closer separation of 8.64 Å, the phenyl groups realign themselves so that they are still tilted on the surface, but the terminal C atom is oriented perpendicular to the silicene along the z-direction, which now shows even buckling, irrespective of whether there is an H atom or phenyl group bonded to each Si atom. This orientation reduces steric overlap between the rings and the H atoms bound to the other side of the silicene sheet, as can be seen more clearly in the charge density isosurface (figure 3(c)). For this orientation, the closest distance between C atoms on adjacent rings is still ∼3 Å, however, there is a greater region of overlap between adjacent rings. Hence, this structure becomes more ordered as the layers are compressed together, to allow the phenyl groups above the sheet to fit in between the phenyl groups bonded to the bottom of the adjacent nanosheet. The interaction becomes repulsive at separations below ∼8.6 Å due to steric overlap of the phenyl groups with each other and the hydrogen atoms bonded to the silicene layer. We compared the geometry of the modified nanosheet using the Grimme potential and found that there is little or no change compared to the optB88 structures.

We determined the distribution of charge in the modified nanosheet at different separations by calculating the Bader partial charges on all the atoms, using the optB88 functional. There is little difference in the distribution of charge from large separation to the minimum separation, with 0.02e being transferred from the phenyl groups to the silicene sheet (including terminating H atoms). As the sheets are brought closer together electrons are pushed back into the phenyl groups (0.07e at a separation of 8.64 Å) which we attribute to some π–π interaction between the phenyl groups.

From the calculated band structure (figure 4) and density of states (DOS) (figure 5) of the modified nanosheet at large (infinite) separations, the system shows a direct band gap of 1.99 eV using the optB88 functional. This is larger by 0.07 eV compared to the DFT-PBE calculation [9]. Hence, there is not a major difference in the calculated electronic properties when vdWs forces...
Figure 6. Atom resolved DOS of the phenyl-modified silicene using the optB88 functional at separations of (a) 27.64 Å (infinite), (b) 10.14 Å (minimum) and (c) 8.64 Å (close).

are considered. At the minimum interfacial separation, the sheet retains a direct, but slightly smaller band gap of 1.98 eV. When the sheets are compressed together, however, the band gap increases slightly to 2.01 eV and becomes indirect. We note that the direct gap at this separation is 2.04 eV. It is very interesting that compressing the nanosheets together could alter their optical properties.

From the total DOS in figure 5, we can see that the changes at the top of the valence band or bottom of the conduction band are very small as the nanosheets are brought closer together. The contribution from the states at the top of the valence band becomes somewhat less as the sheets are compressed together, while those at the bottom of the conduction band increase at the smaller separation. These changes lead to the small increase in the calculated band gap at closer separations.

At the large separation, from the orbital and atom resolved DOS (figures 6 and 7), the major contribution to the states at the top of the valence band is from the Si 3p_x and 3p_y states. As the sheets are brought closer together, the contribution from the C 2p_x and 2p_y states increases relatively compared to those from Si due to the greater interaction between the \( \pi \)-bonding regions of the phenyl rings. At the bottom of the conduction band the main contribution at large separations is from the Si s and 3p_z states, followed by the Si 3p_x and 3p_y, as well as C 2p_x and 2p_y states. At closer separations, the contribution from the Si 3 s, 3p_z as well as 3p_x and 3p_y states all increase, as well as the C 2p_x and C s states. The contribution of the H atoms bonded to the C atoms also increases at this separation.
Figure 7. Atom resolved DOS of the phenyl-modified silicene using the optB88 functional at separations of (a) 27.64 Å (infinite), (b) 10.14 Å (minimum) and (c) 8.64 Å (close), showing only the region around the band gap.

4. Conclusion

We have shown that it is necessary to include dispersion forces when using DFT to model the interaction between organo-modified silicene nanosheets. While the geometry and electronic
properties are not significantly affected for the phenyl modified silicene that we studied, the adhesion energy is underestimated when weak forces are not considered in the DFT calculations. Importantly, we show that there is a marked improvement using vdw-DF in the predicted equilibrium separation distance (∼10 Å) determined from experimental measurements.

The adhesion energy curve for the Grimme results agree very well with the vdW-DF and vdW-DF2 methods, however, using the PBE functional (where dispersion forces are not considered), the adhesion energy is minimal and the distance between the sheets at which the strongest adhesion occurs is larger than when vdWs forces are included in the DFT calculation.

For the DFT-D2 functionals, the optB88 functional gives the strongest adhesion energy value, showing a minimum (i.e. strongest attraction) when the sheets are separated by 10.14 Å, in excellent agreement with experiment. At large (or infinite) separations, the modified silicene shows a direct band gap of 1.99 eV. At the separation where the energy reaches a minimum, the sheet retains a direct band gap of 1.98 eV, however, when the sheets are compressed together, the band gap increases to 2.01 eV and becomes indirect. Hence, we have shown that optical properties of this material could be altered by compressing the sheets together.

While it is important to include vdWs forces when modelling this nanomaterial, the phenyl groups stop the layers from interacting strongly with each other and so they act almost like independent layers. We suggest the unique properties of this nanomaterial could be very useful for building stacked structures for optoelectronic applications. It would be interesting to see if other surface modifications provide larger changes to the electronic properties that could also be exploited for optical device applications.

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References

[1] Okamoto H, Sugiyama Y and Nakano H 2011 Synthesis and modification of silicon nanosheets and other silicon nanomaterials Chem.—Eur. J. 17 9864–87
[2] Nakano H, Mitsuoka T, Harada M, Horibuchi K, Nozaki H, Takahashi N, Nonaka T, Seno Y and Nakamura H 2006 Soft synthesis of single-crystal silicon monolayer sheets Angew. Chem. Int. Edn 45 6303–6
[3] Spencer M J S, Morishita T and Snook I K 2012 Reconstruction and electronic properties of silicon nanosheets as a function of thickness Nanoscale 4 2906–13
[4] Morishita T, Spencer M J S, Russo S P, Snook I K and Mikami M 2011 Surface reconstruction of ultrathin silicon nanosheets Chem. Phys. Lett. 506 221–5
[5] Kara A, Enriquez H, Seitsonen A P, Lew Yan Voon L C, Vizzini S, Aufray B and Oughaddou H 2012 A review on silicene—new candidate for electronics Surf. Sci. Rep. 67 1–18
Morishita T, Russo S P, Snook I K, Spencer M J S, Nishio K and Mikami M 2010 First-principles study of structural and electronic properties of ultrathin silicon nanosheets Phys. Rev. B 82 045419

Morishita T, Nishio K and Mikami M 2008 Formation of single- and double-layer silicon in slit pores Phys. Rev. B 77 081401

Sugiyama Y, Okamoto H, Mitsuoka T, Morikawa T, Nakanishi K, Ohta T and Nakano H 2010 Synthesis and optical properties of monolayer organosilicon nanosheets J. Am. Chem. Soc. 132 5946–7

Spencer M J S, Morishita M, Mikami M, Snook I K, Sugiyama Y and Nakano H 2011 The electronic and structural properties of novel organomodified Si nanosheets Phys. Chem. Chem. Phys. 13 15418–22

Snoek I K, Per M C, Seyed-Razavi A and Russo S P 2009 Some comments on the DFT + D method Chem. Phys. Lett. 480 327–9

Grimme S 2006 Semiempirical GGA-type density functional constructed with a long-range dispersion correction J. Comput. Chem. 27 1787–99

Dion M, Rydberg H, Schröder E, Langreth D C and Lundqvist B I 2004 Van der Waals density functional for general geometries Phys. Rev. Lett. 92 246401

Román-Pérez G and Soler J M 2009 Efficient implementation of a van der Waals density functional: application to double–wall carbon nanotubes Phys. Rev. Lett. 103 096102

Jiří K, David R B and Angelos M 2010 Chemical accuracy for the van der Waals density functional J. Phys.: Condens. Matter 22 022201

Lee K, Murray É D, Kong L, Lundqvist B I and Langreth D C 2010 Higher-accuracy van der Waals density functional Phys. Rev. B 82 081101

Yarovšky I, Spencer M J S and Snoek I K 2011 Computational Methods for Large Systems: Electronic Structure Approaches for Biotechnology and Nanotechnology ed J R Reimers (Hoboken, NJ: Wiley) pp 515–59

Spencer M J S, Yarovšky I, Wlodarski W and Kalantar-zadeh K 2011 Interaction of hydrogen with zinc oxide nanorods: why the spacing is important Nanotechnology 22 135704

Spencer M J S, Snoek I K and Yarovšky I 2005 Effect of sulfur coverage on Fe(110) adhesion: a DFT study J. Phys. Chem. B 109 10204–12

Spencer M J S, Snoek I K and Yarovšky I 2004 Effect of sulfur impurity on Fe(110) adhesion: a DFT study J. Phys. Chem. B 108 10965–72

Spencer M J S, Hung A, Snoek I and Yarovšky I 2003 Iron surfaces: pathways to interfaces Surf. Rev. Lett. 10 169

Spencer M J S, Hung A, Snoek I K and Yarovšky I 2002 Further studies of iron adhesion: (1 1 1) surfaces Surf. Sci. 515 L464–8

Kresse G and Hafner J 1993 Ab initio molecular dynamics for liquid metals Phys. Rev. B 47 558

Kresse G and Furthmüller J 1996 Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set Comput. Mater. Sci. 6 15–50

Kresse G and Furthmüller J 1996 Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set Phys. Rev. B 54 11169–86

Blochl P E 1994 Projector augmented-wave method Phys. Rev. B 50 17953–79

Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865–8

Klimeš J, Bowler D R and Michaelides A 2011 Van der Waals density functionals applied to solids Phys. Rev. B 83 195131

Björkman T, Gulans A, Krasheninnikov A V and Nieminen R M 2012 Van der Waals bonding in layered compounds from advanced density-functional first-principles calculations Phys. Rev. Lett. 108 235502

Puzder A, Dion M and Langreth D C 2006 Binding energies in benzene dimers: nonlocal density functional calculations J. Chem. Phys. 124 164105–8