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Molecular functionalization of silicene/Ag(111) by covalent bonds: a DFT study

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Received Xth XXXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXXXX 200X

DOI: 10.1039/b000000x

Among the 2D crystals, silicene, which forms sp^2 - sp^3 bonds, is expected to present a higher reactivity than graphene, characterized by sp^2 bonds only. However, silicene functionalization, in particular with organic molecules, remains an open question. By means of density functional theory, we study the adsorption of benzene, a model organic molecule, on the (3×3) silicene on (4×4) Ag(111) surface. Our calculations show that the dispersion interactions must be taken into account in order to describe this system properly. The adsorption energy is calculated by means of the semi-empirical dispersion-corrected density functional theory (DFT-D2) and the optB86b-vdW density functional. The charge density and electrons localization function maps indicate that the molecule is chemisorbed on the silicene surface by means of two Si–C covalent bonds. In agreement with charge density difference calculations, two C–C double bonds are formed in the benzene molecule, which adopts a butterfly configuration. The silicene lattice is slightly deformed upon benzene adsorption, but the Si–Si distance remains the same as in bare silicene/Ag(111). Bader analysis shows a charge transfer from top Si atoms to both molecule and Ag substrate. Finally, we show that the covalent functionalization of silicene is possible.

1 Introduction

In the last few years silicene has been the subject of numerous works^{1,2}. Indeed this material is expected to exhibit remarkable electronic properties such as a high mobility or a low effective mass for the electrons^{3–5}. Amongst others, silicene is easily compatible with a mainly Si-based electronic technology^{6,7}. An exciting research pathway is to confer new properties to this material by adding atoms or molecules. Indeed, the functionalization of silicene is a major issue, in particular for band-gap engineering, but also, for example, for the design of molecule sensors^{5,8–12}. Moreover, the Si atoms in silicene are mainly sp^2 - sp^3 hybridized. This suggests that its reactivity is higher than for graphene, which exhibits sp^2 bonds only¹³. In this respect, the functionalization of freestanding silicene with various small organic molecules^{5,14} has been theoretically studied. Kaloni et al. have shown that the studied molecules, in particular benzene, methane, or toluene, are more stable than on graphene⁵. Spencer et al. carried on calculations for silicene modified with phenyl groups^{15,16}. They show that it is possible to modify the electronic properties of this system by exchanging the functionalizing molecules.

However, only supported silicene has been experimentally realized so far, namely on Ag^{17–23}, Ir²⁴, or ZrB₂²⁵. On Ag(111), various silicene phases have been observed. The (3×3) silicene on (4×4) Ag(111) is the most studied phase. It is the most stable phase²¹, and large monodomain areas can be grown¹⁷, without domain boundaries as in the

$(\sqrt{7} \times \sqrt{7})R19.1^\circ$ silicene on $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ Ag,²¹ which would present a different reactivity to that of the silicene surface²⁶. For (3×3) silicene/ (4×4) Ag(111), one in three Si atoms lies at a higher position than the others; thus pure sp^3 and sp^2 - sp^3 bonds are formed¹⁷. It appears that the silicene/Ag interface plays a major role, with the presence of localized charges between the bottom Si plane and the Ag surface²⁷. Moreover, electrical charge is transferred from the top Si atoms to the Ag substrate as well as to the other Si atoms. As a result, the top Si atoms are slightly discharged, which may lower the reactivity of the silicene towards molecules. Now the adsorption of small inorganic molecules by silicene on Ag(111) has been investigated. The calculations of Tsetseris et al. show that a silicene layer on Ag(111) can be partially or fully hydrogenated, leading to a silicene monolayer²⁸. As far as oxidation is concerned, experimental measurements and DFT calculations indicate that the (3×3) silicene on (4×4) Ag(111) surface is highly reactive towards molecular oxygen²⁹. In contrast, another study claims that silicene is not altered even by high doses of molecular oxygen, and is only slowly oxidized by atomic oxygen²³. Consequently the functionalization of Ag-supported silicene is not an obvious issue, and needs to be studied in detail.

In this work, thanks to density functional theory (DFT), we study the functionalization of (3×3) silicene on (4×4) Ag(111) with benzene. Benzene is as small organic molecule which has been widely used as model molecule^{30–35}. We show that the covalent functionalization of silicene is possible. Two

covalent Si–C bonds are formed, and the benzene molecule adopts a butterfly configuration.

2 Calculation details

We used the projector augmented plane-wave (PAW) method^{36,37} in the frame of the Vienna ab-initio simulation package (VASP)^{38–41}. In a first step the electron-electron exchange-correlation interactions were described by the generalized gradient approximation (GGA) using the functional of Perdew, Burke, and Ernzerhof (PBE)^{42,43}, and by the local density (LDA) approximation⁴⁴. In a second step, in order to take into account the van der Waals interactions, the calculations were carried out by means of the semi-empirical dispersion-corrected density functional theory (DFT-D2) and the optB86b-vdW density functional. The optB86b-vdW is a van der Waals density functional which takes into account the long range interactions^{45,46}, while in the DFT-D2 method the semi-empirical energetic correction of Grimme is added to the total energetic calculations^{47–49}. The Brillouin zone is sampled by means of $(3 \times 3 \times 1)$ k -points, as done in previous works^{17,27,50}. A plane-wave energy cutoff of 400 eV has been taken. When the components of the forces are less than 0.01 eV/Å, the structure is considered as relaxed. Once the atomic structure is obtained, the density of states (DOS) of the system is calculated using $(7 \times 7 \times 1)$ k -points. The slab is built (from bottom to top), with 10 Ag layers of 16 atoms, the (3×3) silicene mesh containing 18 Si atoms, and the C_6H_6 molecule. Thus there are 190 atoms in the supercell, with a vacuum spacing of 15 Å. The atoms belonging to the bottom Ag layer only are kept fixed during the relaxation process. The different charge transfers are studied in the Bader scheme by means of a partial charge approach^{51,52}. The total number of 1862 electrons is reproduced with an error lower than $7 \times 10^{-4} e^-$. In order to draw the isodensity pictures, the visual molecular dynamics software developed by the Theoretical and Computational Biophysics Group in the Beckman Institute for Advanced Science and Technology at the University of Illinois at Urbana-Champaign has been used⁵³. The electron localization function map is displayed thanks to the VESTA software⁵⁴.

3 Results and discussion

3.1 Energetic study

Figure 1a presents a top view of the benzene molecule positioned on top of the silicene lattice. There is one C_6H_6

molecule per (3×3) silicene mesh. Before benzene adsorption, the silicene (3×3) surface presents a honeycomb lattice where 6 Si atoms (hereafter denoted top Si atoms) lie at a higher position than the 12 others (bottom atoms)^{17,50,55–60}. These top Si atoms are the most accessible for the benzene molecule. As we are looking for a possible chemisorption of the benzene molecule, the latter is positioned so that two top Si atoms are located below two opposite C atoms (denoted C_1 and C_4 in figure 1), and that no other top Si atoms are close to the molecule. Note that on Si(100), the benzene C_1 and C_4 atoms are those which form bonds with Si atoms from a dimer^{30–32,34}.

In order to test the stability of this configuration, we calculated the adsorption energy of the molecule on the silicene surface as following:

$$E_{ads} = E_{benzene/silicene/Ag} - E_{benzene} - E_{silicene/Ag}$$

$E_{benzene/silicene/Ag}$ is the total system energy, while $E_{benzene}$ and $E_{silicene/Ag}$ are the energy of the free benzene molecule and the (3×3) silicene layer on top of the Ag slab, respectively. The obtained adsorption energies is +0.07 eV using GGA, and and -1.10 eV with LDA. These apparently contradictory values show that the functionalization of the silicene surface is still an open question. In this respect we would like to emphasize that GGA tends to underestimate the interactions, and thus to delocalize the charges, while with LDA the interactions are overestimated. As a result, the bond lengths are shorter with LDA than with GGA, and the charges are more localized⁶¹. For example, another 2D crystal studied by Li *et al.*, namely germanene, could not be stabilized on a BN substrate when using GGA, while with LDA the adsorption energy was -0.058 eV, attesting a possible stabilization of the germanene layer⁶².

Now here we are dealing with an organic molecule deposited on a surface. This means that van der Waals interactions are present, which must be taken into account in the calculations, as has been systematically performed for molecular systems in recent years^{5,30,63}. In this purpose, two different methods have been taken. The DFT-D2 method, which is widely used and has the advantage of being fast, describes the non-local dispersion interactions by adding a semi-empirical attractive term as proposed by Grimme^{47–49}. In contrast, in the optB86b-vdW functional, the van der Waals interactions are included within the functional^{45,46}. The adsorption energy obtained with the DFT-D2 and the optB86b-vdW methods are -0.62 eV and -0.79 eV, respectively. Clearly, when the van der Waals interactions are taken into account, the benzene molecule can be stabilized on the silicene layer. The adsorption energy lies between that obtained on freestanding silicene (-0.30 eV)⁵, and on the Si(100) surface (-1.55 eV)³⁰.

Now let us study the atomic structure of the benzene ad-

* Theoretical and Computational Biophysics Group - Beckman Institute for Advanced Science and Technology - University of Illinois, Visual Molecular Dynamics software, <http://www.ks.uiuc.edu/Research/vmdl/>

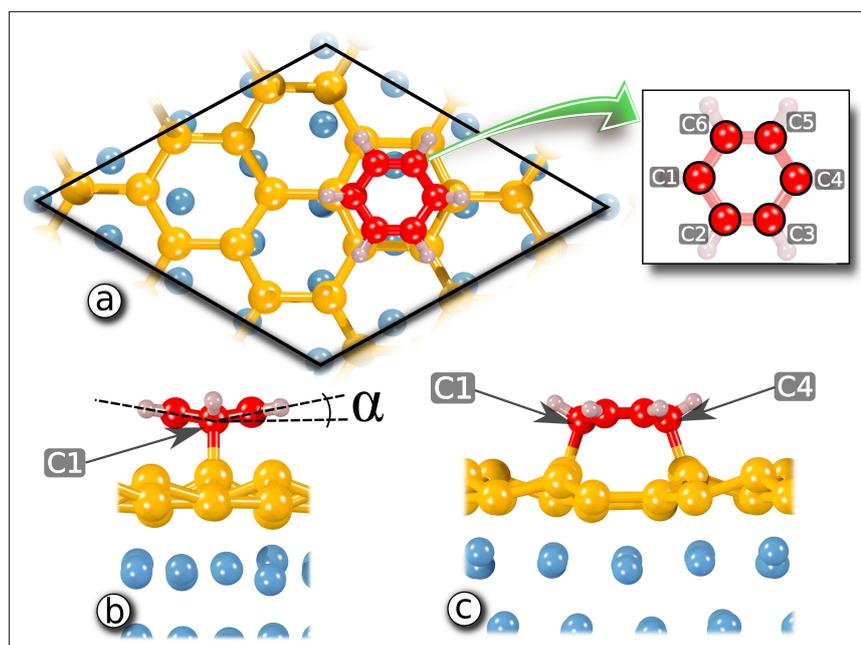


Fig. 1 Ball-and-stick model of the relaxed atomic structure of the benzene molecule adsorbed on the (3×3) silicene/ (4×4) Ag(111) phase. C, H, Si and Ag atoms are represented by red, light pink, yellow and blue balls, respectively. (a) unit cell top view, the inset provides the carbon atoms labels. For clarity, only the first Ag plane is presented. (b) side-view showing the butterfly configuration of the benzene molecule. (c) side-view presenting the positions of the C_1 and C_4 atoms with respect to the nearest top Si atoms

sorbed on the silicene surface. We found that GGA, LDA, DFT-D2 and optB86b-vdW calculations lead to similar atomic positions, and that both the DFT-D2 and the optB86b-vdW methods give analogous electronic density maps. Consequently our presented results will be inferred from the DFT-D2 method only.

3.2 Structural study

Figure 1b and c display side views of the benzene molecule on top of the silicene sheet resulting from the relaxation of the system. One can see that the $C_6 H_6$ molecule is bent ($\alpha \sim 10^\circ$), and that two atoms (C_1 and C_4) are located at a lower position than the others C. Clearly the benzene molecule adopts the butterfly configuration which has been already found on the Si(100)^{30–32,34} or SiC(001)– (3×2) ³⁵ surfaces. We find that the $C_2 - C_3$ and $C_5 - C_6$ bond lengths are 1.35 \AA , while the other C–C distances are 1.49 \AA . The C_1 and C_4 have bond angles of $\sim 109^\circ$, whereas for the other carbon atoms their value is about 120° , which can be related to sp^3 and sp^2 hybridized C atoms, respectively. Finally, the distance between the C_1 and C_4 atoms and the nearest Si atoms is 2.02 \AA , while the other C–Si distances are about 3.27 \AA .

We can wonder how the silicene lattice is modified by benzene adsorption. The calculations show that the top Si atoms

located below the C_1 and C_4 are at a higher position (0.10 \AA) than for the bare silicene/Ag system. In fact it appears that the whole silicene mesh is disturbed by the organic molecule. Indeed, two other top Si atoms, and the four bottom Si atoms located below the benzene molecule, lie lower than in silicene/Ag (0.12 \AA , and 0.17 \AA , respectively). Thus the vertical position of several Si atoms is influenced by $C_6 H_6$ adsorption. In this respect, the bond angles for the top Si atoms, which are $\sim 109^\circ$ for silicene/Ag¹⁷, have a value of $\sim 105^\circ$ (Si atoms located below C_1 and C_4) and $\sim 112^\circ$ (other top Si atoms), in the presence of $C_6 H_6$. As regards to the bottom Si atoms, their bond angle stays at $\sim 117^\circ$. Now, are the Si–Si bond lengths altered with respect to the silicene/Ag(111) system? We find that the Si–Si distances lie between 2.34 \AA and 2.37 \AA for bare silicene/Ag, and between 2.34 \AA and 2.41 \AA after benzene deposition. In other words, they vary only very slightly, in spite of the vertical position and bond angles modifications described above. The whole lattice rearranges itself upon benzene adsorption, which may be related to the low stiffness of silicene⁶⁴.

3.3 Electronic structure

In order to characterize the electronic structure of the system, we present in Fig. 2 a map of the charge density. The ben-

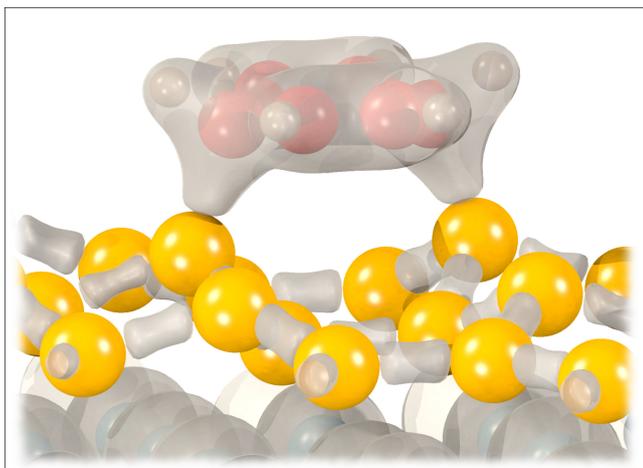


Fig. 2 Side-view of the charge density map (in translucent grey) at $0.50 e^-$ per \AA^3 . C, H, Si, and Ag atoms are represented by red, light pink, yellow and blue balls, respectively

zene C–C and C–H covalent bonds, as well as the silicene Si–Si ones, are clearly visible. However there is also an obvious charge accumulation between the lowest C atoms (C_1 and C_4), and the nearest top Si atoms, indicating clear interactions between these atoms. In order to further characterize the system electronic density, we display in Fig. 3a a side-view of the electron localization function (ELF) taken in a plane perpendicular to the surface, passing through the atoms depicted in Fig. 3b. The ELF can indeed give useful elements concerning topological aspects of chemical bonding⁶⁵. In particular, ELF values close to one indicate the presence of strongly localized valence electrons. For example, the large red zones at the top of Fig.3a correspond to the C–H bonds. The interesting features here are located between the C atoms (C_1 and C_4) and the nearest Si atoms. They mean that the C and Si atoms share electrons, and thus form two covalent bonds. Therefore we can conclude that the benzene molecule is chemisorbed on the silicene surface, in agreement with the C–Si distances of 2.02\AA , close to those obtained for the covalent adsorption of benzene on Si(100) (1.98\AA)^{31,32} or Si(111) (1.99\AA – 2.02\AA)⁶⁶.

Now the formation of covalent bonds may imply a drastic charge reorganization in the system. Thus, we calculated Bader charges variations for the different atomic elements. We find that the top Si atoms lose a total of 2.86 electrons, while the benzene molecule, the Ag crystal, and the down Si atoms gain 1.95, 0.79, and 0.12 electrons, respectively. This means that a charge transfer takes place from the top Si atoms to the molecule, the Ag substrate, and the down Si atoms. The transfer from the Si atoms to the molecule can be related to the formation of covalent bonds, and to the fact that the carbon electro-negativity (2.55) is higher than for silicon

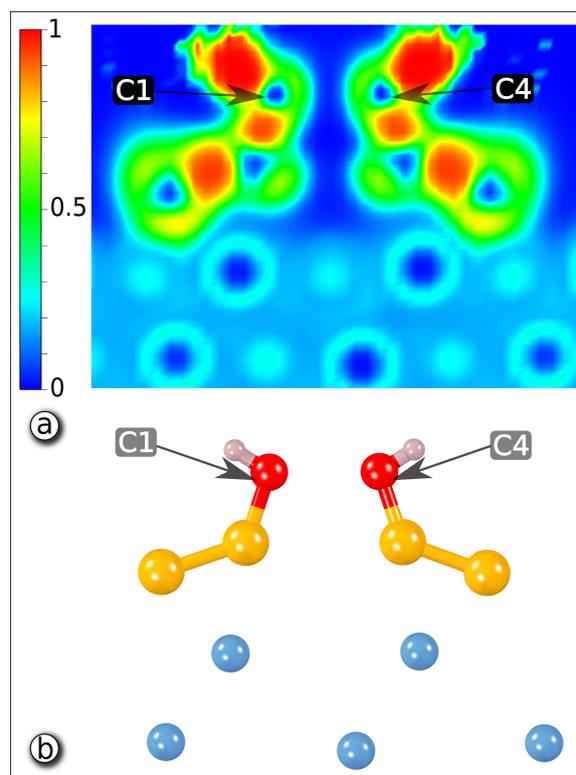


Fig. 3 (a) Side-view of the electron localisation function map taken perpendicularly to the surface through the atoms presented in (b). C, H, Si and Ag atoms are represented by red, light pink, yellow and blue balls, respectively.

(1.90)⁶⁷. We would like to emphasize that for the bare silicene on Ag(111), the total Ag charge is $-0.77 |e|$ (where $|e| = 1.6 \times 10^{-19} C$), which is similar to the charge obtained for the $C_6 H_6$ /silicene/Ag(111) system ($-0.79 |e|$). Moreover, for silicene/Ag, each of the twelve bottom Si atoms has a charge of $-0.03 |e|$, close to the mean bottom Si atom charge of $-0.01 |e|$ in the presence of a benzene molecule. In other words, the formation of the Si–C covalent bonds affects only slightly the charge transfer between the silicene layer and the Ag substrate.

At this point let us describe the spatial redistribution of the electrons for the whole benzene molecule and the Si atoms upon molecule adsorption. We present in Fig. 4 charge density difference maps (side-view and top view) obtained as following. In a first step the charge density has been calculated for the benzene/silicene/Ag ensemble. In a second step we obtained the charge density of the bare silicene/Ag system on one side, and of the benzene molecule on the other side, taken at the same atomic positions than in the grouped system. Finally the charge difference between benzene/silicene/Ag and the silicene/Ag and benzene systems has been extracted. This

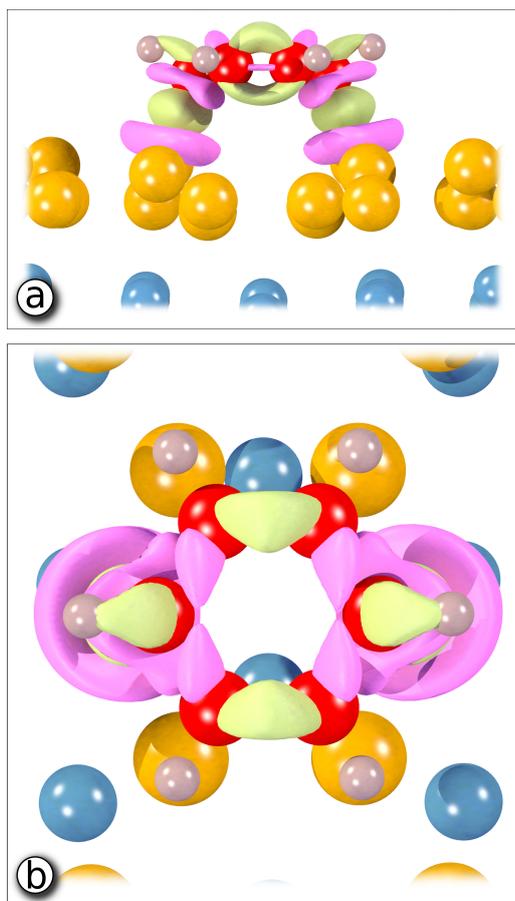


Fig. 4 Electron density difference (at $0.03e^-$ per \AA^3) maps induced by benzene deposition on the silicene/Ag(111) surface. Light green and pink plots correspond to an augmentation and a diminution of the local electron density, respectively. C, H, Si and Ag atoms are represented by red, light pink, yellow and blue balls, respectively. (a) side-view. (b) top view, for clarity, only the first Ag plane is presented.

allows visualizing the charge reorganization in terms of charge gain or loss when the benzene and the silicene/Ag systems are brought together. The light green and pink areas in Figure 4 indicate an electron gain isodensity of $0.03 e^-$ per \AA^3 , and an electron loss of $-0.03 e^-$ per \AA^3 , respectively. For the C_1 and C_4 atoms, an electron gain can be seen between the carbon and the nearest Si atom (Fig 4a), compensated by a loss around the top of the Si (large pink rings in Fig.4b), and at the C atom (small pink rings). This charge redistribution is related to the formation of the two Si–C covalent bonds, which means that the Si and the C atoms share electrons upon benzene chemisorption. However the whole benzene electronic structure is modified. In particular there is an electron gain above and below the line connecting the C_2 and C_3 atoms, and

also the C_5 and C_6 atoms. This electronic reorganization indicates the formation of one π bond between the C_2 and C_3 , and one between C_5 and C_6 . Consequently the C_6H_6 molecule exhibits two double bonds, in agreement with the calculated C_2-C_3 and C_5-C_6 short distances (1.35\AA). In contrast, the electronic density diminishes both above and below the C_1-C_2 , C_1-C_6 , C_4-C_5 , and C_3-C_4 lines, pointing to the formation of true simple bonds, as attested by the lengthening of the C–C distance (1.49\AA ,) with respect to that in the benzene molecule in gas phase (1.40\AA). Similar C–C extensions and shortenings (1.50\AA for the simple bonds and 1.35\AA for the double bonds) have been observed upon chemisorption of benzene on Si(100)^{31,32}. As a result, from the six delocalized electrons of the benzene molecule in gas phase, two Si–C covalent bonds and two C–C double bonds are formed, which means that a cycloaddition occurs upon C_6H_6 adsorption on the silicene surface.

In order to understand how the silicene electronic states are impacted by molecule adsorption, we present in Fig. 5 density of states curves for the atomic structure described previously. In Fig. 5a, the DOS of the whole silicene layer is displayed before and after benzene adsorption. It can be seen that the curves are very close to each other, indicating that the molecule hardly modifies the global electronic structure of the silicene layer. A careful study of the DOS of each atom shows that only the DOS of the two top Si atoms forming a covalent bond with the molecule are strongly affected by benzene adsorption. This corresponds to 2 in 18 Si atoms for the total silicene layer, thus explaining why the total silicene layer DOS is not significantly modified. Fig. 5b and 5d show the DOS of the Si bonded to C_1 and C_4 atoms, along with their projected density of states (PDOS), in the absence and presence of benzene, respectively. The main effect of benzene adsorption is the attenuation of the p_z states between -1 and $+2$ eV. According to Fig. 5c, the spatial distribution of the electronic charge related to the occupied part of these p_z states (between -1 eV and E_F) corresponds to the dangling bond of the top Si atoms. After formation of the covalent bond, the charge is rather located near the C atom (Fig. 5e) and not at the Si atom anymore, in agreement with the diminution of the Si p_z PDOS around the Fermi level. We note that the charge distribution above the other top Si atoms is not modified.

4 Conclusion

By means of DFT calculations taking into account the van der Waals interactions, we have shown that the organic benzene molecule can be chemisorbed through a cycloaddition reaction on a silicene layer deposited on Ag(111). Two covalent Si–C bonds are formed and the benzene molecule adopts a butterfly configuration as already observed on the Si(100) surface^{30–32}. However the benzene stability on 2D silicene seems lower

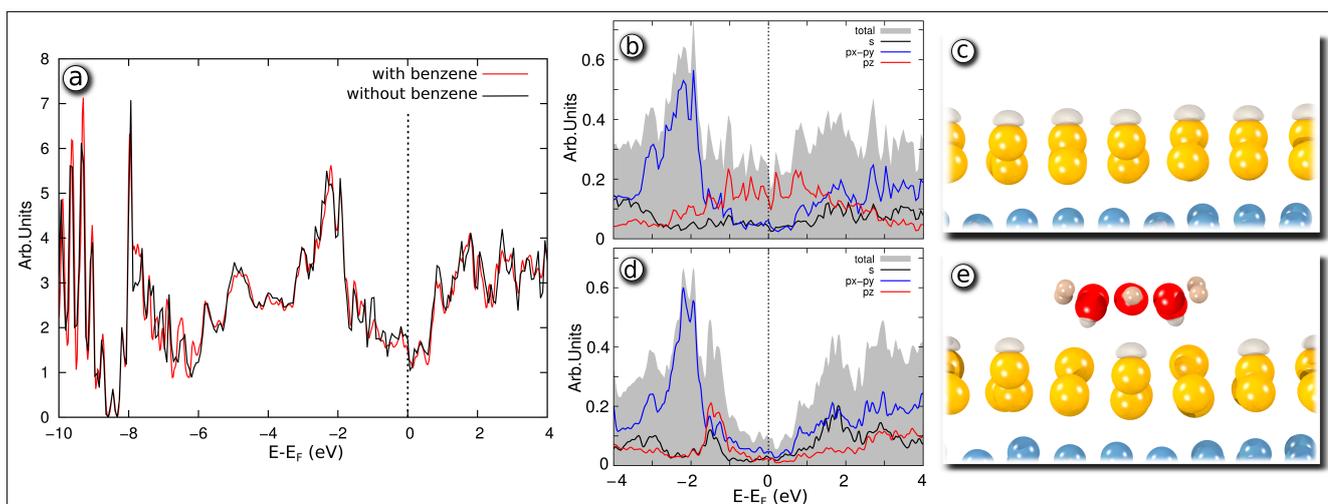


Fig. 5 DOS of the whole silicene layer without and with the C_6H_6 molecule (a); DOS and PDOS of the top Si atoms bonded to the C_1 and C_4 atoms without (b) and with (d) benzene; charge density map at $0,07 e^-$ per \AA^3 taken between -1 eV and E_F corresponding to the p_z states without (c) and with (e) benzene. C, H, Si, and Ag atoms are represented by red, light pink, yellow and blue balls, respectively.

than on usual Si surfaces. We find that, on silicene/Ag(111), the adsorption energy is -0.62 eV with the DFT-D2 method, and -0.79 eV with the optB86b-vdW method, while it reaches -0.94 to -1.05 eV on Si(111)³³ and -1.55 eV on Si(100)³⁰. Now, for the Si(111) surface, the dangling bond is occupied by an electron. In contrast, in silicene/Ag(111), there is a charge transfer from the top Si atoms to the Ag substrate, with the result that these Si atoms carry in a positive charge²⁷. One could expect a charge reorganization implying a possible modification of this charge transfer upon benzene adsorption; however our calculations show that the latter is only weakly influenced by the presence of the C_6H_6 molecule. Our results suggest that the silicene reactivity is limited with respect to a Si(100) or Si(111) surface, which in turn makes its functionalization more difficult, but not impossible. Clearly experiments should be carried out at various surface temperatures to investigate the possibility to functionalize silicene with organic molecules, via covalent bonds.

5 Acknowledgments

This work was performed using HPC resources from GENCI-IDRIS and the supercomputer facilities of the Mésocentre of Strasbourg.

References

- N. Takagi, L. C.-L., K. Kawahara, E. Minamitani, N. Tsukahara, M. Kawai and R. Arafune, *Progress in Surf. Sci.*, 2015, **90**, 1.
- A. Dimoulas, *Microelectronic Engineering*, 2015, **131**, 68.
- S. Cahangirov, M. Topsakal, E. Aktürk, H. Sahin and S. Ciraci, *Phys. Rev. Lett.*, 2009, **102**, 236804.
- N. Roome and J. Carey, *Appl. Mater. Interfaces*, 2014, **6**, 7743.
- T. Kaloni, G. Schreckenbach and M. Freund, *J. Phys. Chem. C*, 2014, **118**, 23361.
- L. Tao, E. Cinquanta, D. Chiappe, C. Grazianetti, M. Fanciulli, M. Dubey, A. Molle and D. Akinwande, *Nature Nanotechnology*, 2015, doi:10.1038/nnano.2014.325.
- G. Le Lay, *Nature Nanotechnology*, 2015, doi:10.1038/nnano.2015.10.
- M. Houssa, E. Scalise, K. Sankaran, G. Pourtois, V. V. Afanasev and A. Stesmans, *Appl. Phys. Lett.*, 2011, **98**, 223107.
- N. Gao, W. Zheng and Q. Jiang, *Phys. Chem. Chem. Phys.*, 2012, **14**, 257.
- Z. Ni, H. Zhong, X. Jiang, R. Quhe, G. Luo, Y. Wang, M. Ye, J. Yang, J. Shi and J. Lu, *Nanoscale*, 2014, **6**, 7609.
- A. Jose, D. and Datta, *J. Phys. Chem. C*, 2012, **116**, 24639.
- W. Hu, N. Xia, X. Wu, A. Liab and J. Yang, *Phys. Chem. Chem. Phys.*, 2014, **16**, 6957.
- H. Sahin and F. M. Peeters, *Phys. Rev. B*, 2013, **87**, 085423.
- P. Rubio-Pereda and N. Takeuchi, *J. Chem. Phys.*, 2013, **138**, 194702.
- M. Spencer, T. Morishita, M. M., I. Snook, Y. Sugiyamawd and H. Nakano, *Phys. Chem. Chem. Phys.*, 2011, **13**, 15418.
- M. Spencer, M. Bassett, T. Morishita, I. Snook and H. Nakano, *New Journal of Physics*, 2013, **15**, 125018.
- P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet and G. Le Lay, *Phys. Rev. Lett.*, 2012, **108**, 155501.
- P. Vogt, P. Capiod, M. Berthe, A. Resta, P. De Padova, T. Bruhn, G. Le Lay and B. Grandidier, *Appl. Phys. Lett.*, 2014, **104**, 021602.
- A. Kara, H. Enriquez, A. P. Seitsonen, L. L. Y. Voon, S. Vizzini, B. Aufray and H. Oughaddou, *Surf. Sci. Reports*, 2012, **67**, 1–18.
- D. Chiappe, C. Grazianetti, G. Tallarida, M. Fanciulli and A. Molle, *Adv. Mater.*, 2012, **24**, 5088–5093.
- A. Resta, T. Leoni, C. Barth, A. Ranguis, C. Becker, T. Bruhn, P. Vogt and G. Le Lay, *Scientific reports*, 2013, **3**, 2399.
- R. Arafune, C.-L. Lin, K. Kawahara, N. Tsukahara, E. Minamitani, Y. Kim, N. Takagi and M. Kawai, *Surf. Sci.*, 2013, **608**, 297 – 300.

- 23 H. Oughaddou, H. Enriquez, M. Tchalala, H. Yildirim, A. Mayne, A. Bendounan, G. Dujardin, M. Ali and A. Kara, *Progress in Surf. Sci.*, 2015, **90**, 46.
- 24 L. Meng, Y. Wang, L. Zhang, S. Du, R. Wu, L. Li, Y. Zhang, G. Li, H. Zhou, W. A. Hofer and H.-J. Gao, *Nano Letters*, 2013, **13**, 685–690.
- 25 A. Fleurence, R. Friedlein, T. Ozaki, H. Kawai, Y. Wang and Y. Yamada-Takamura, *Phys. Rev. Lett.*, 2012, **108**, 245501.
- 26 F. Dulot, M.-C. Hanf and P. Wetzel, *Surf.Sci.*, 2008, **602**, 1447.
- 27 R. Stephan, M.-C. Hanf and P. Sonnet, *J. Phys.: Condens. Matter.*, 2015, **27**, 015002.
- 28 L. Tsetseris and D. Kaltsas, *Phys.Chem.Chem.Phys.*, 2014, **16**, 5183.
- 29 X. Xu, J. Zhuang, Y. Du, H. Feng, N. Zhang, C. Liu, T. Lei, J. Wang, M. Spencer, T. Morishita, X. Wang and S. Dou, *Scient. Rep.*, 2014, **4**, 7543.
- 30 P. Czekala, C. Panosetti, H. Lin and W. Hofer, *Surf.Sci.*, 2014, **621**, 152.
- 31 W. Hofer, A. Fisher, G. Lopinski and R. Wolkow, *Phys.Rev.B*, 2001, **63**, 085314.
- 32 W. Hofer, A. Fisher, G. Lopinski and R. Wolkow, *Surf.Sci.*, 2001, **482-485**, 1181.
- 33 I. Petsalakis, J. Polanyi and G. Theodorakopoulos, *Surf. Sci.*, 2003, **544**, 162.
- 34 M. Mamatkulov, L. Stauffer, C. Minot and P. Sonnet, *Phys. Rev. B*, 2006, **73**, 035321.
- 35 J. Wiefelink, P. Krueger and J. Pollmann, *Phys. Rev. B*, 2008, **78**, 165315.
- 36 P. E. Blochl, *Phys. Rev. B*, 1994, **50**, 17953.
- 37 G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758.
- 38 G. Kresse and J. Hafner, *Phys. Rev. B*, 1993, **47**, 558.
- 39 G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251.
- 40 G. Kresse and J. Furthmüller, *Comput. Mat. Sci.*, 1996, **6**, 15.
- 41 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.
- 42 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 43 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.
- 44 W. Kohn and L. Sham, *Phys. Rev.*, 1965, **140**, A1133.
- 45 J. Klimes, D. R. Bowler and A. Michaelides, *Phys. Rev. B*, 2011, **83**, 195131.
- 46 F. Hanke, M. Dyer, J. Bjrk and M. Persson, *J. Phys.: Condens. Matter*, 2012, **42**, 424217.
- 47 S. Grimme, *Journal of Computational Chemistry*, 2004, **25**, 1463–1473.
- 48 S. Grimme, *Journal of Computational Chemistry*, 2006, **27**, 1787–1799.
- 49 S. Grimme, J. Antony, T. Schwabe and C. Mck-Lichtenfeld, *Org. Biomol. Chem.*, 2007, **5**, 741.
- 50 S. Cahangirov, M. Audiffred, P. Tang, A. Iacomino, W. Duan, G. Merino and A. Rubio, *Phys. Rev. B*, 2013, **88**, 035432.
- 51 R. F. W. Bader, *Chem. Rev.*, 1991, **91**, 893–928.
- 52 G. Henkelman, A. Arnaldsson and H. Jnsson, *Comput. Mater. Sci.*, 2006, **36**, 354 – 360.
- 53 W. Humphrey, A. Dalke and K. Schulten, *J. of Mol. Graph.*, 1996, **14**, 33 – 38.
- 54 K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272–1276.
- 55 C.-L. Lin, R. Arafune, K. Kawahara, N. Tsukahara, E. Minamitani, Y. Kim, N. Takagi and M. Kawai, *Applied Physics Express*, 2012, **5**, 045802.
- 56 Z.-X. Guo, S. Furuya, J.-i. Iwata and A. Oshiyama, *J. Phys. Soc. Jpn.*, 2013, **82**, 063714.
- 57 Z.-X. Guo, S. Furuya, J.-i. Iwata and A. Oshiyama, *Phys. Rev. B*, 2013, **87**, 235435.
- 58 J. Gao and J. Zhao, *Sci. Rep.*, 2012, **2**, 861.
- 59 J. Avila, P. De Padova, S. Cho, I. Colambo, S. Lorcy, C. Quaresima, P. Vogt, A. Resta, G. Le Lay and M. Asensio, *J. Phys: Condens. Matter*, 2013, **25**, 262001.
- 60 P. Gori, O. Pulci, F. Ronci, S. Colonna and F. Bechstedt, *J. of Appl. Phys.*, 2013, **114**, 113710.
- 61 P. Haas, F. Tran and P. Blaha, *Phys. Rev. B*, 2009, **79**, 085104.
- 62 L. Li, and M. Zhao, *Phys.Chem. Chem. Phys.*, 2013, **15**, 16853.
- 63 K. Boukari, E. Duverger and P. Sonnet, *J. Chem. Phys.*, 2013, **138**, 084704.
- 64 Q.-X. Pei, Z.-D. Sha, Y.-Y. Zhang and Y.-W. Zhang, *J. Appl. Phys.*, 2014, **115**, 023519.
- 65 A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.*, 1990, **92**, 5397–5403.
- 66 Z. Wang, Y. Cao and G. Xu, *Chem. Phys. Lett.*, 2001, **338**, 7.
- 67 A. Allred, *J. Inorg. Nuc. Chem.*, 1961, **17**, 215.