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Stacked Functionalized silicene: a powerful system to adjust the electronic structure of silicene

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Abstract

Herein, we employed first principle density functional periodic calculations to characterize the silicon counterpart of graphene: silicene. We found that silicene is far more reactive than graphene, very stable and strong Si-X bonds, X = H, CH_3, OH and F can be formed. The Si-F bond is the strongest one, with a binding energy of 114.9 kcal/mol. When radicals are agglomerated, the binding energy per functional grows up to 17 kcal/mol. The functionalization with OH radicals produces the largest alterations of the structure of silicene, due to the presence of intralayer hydrogen bonds. The covalent addition of H, CH_3, OH and F onto silicene enables the adjustment of its electronic structure. In effect, functionalized silicene can be a semiconductor or even exhibit metallic properties when the type and concentration of radicals are varied. The most interesting results were obtained when two layers of functionalized silicene were stacked, given that the band gaps experienced a significant reduction with respect to those computed for symmetrically and asymmetrically (Janus) functionalized monolayer silicene. In the case of fluorine, the largest changes in the electronic structure of bilayer silicene were appreciated when at least one side of silicene was completely fluorinated. In general, the fluorinated side induces metallic properties in a large number of functionalized silicenes. In some cases which presented band gaps as large as 3.2 eV when isolated, the deposition over fluorinated silicene was able to close that gap and induce a metallic character. In addition to this, in four cases small gaps in the range of 0.1-0.6 eV were obtained for bilayer silicenes. Therefore, functionalization of silicene is a powerful method to produce stable two-dimensional silicon based nanomaterials with tunable optical band gaps.

1. Introduction

The exfoliation of graphene by the Scotch-tape method[1] opened a new era in all areas of science. In particular, the synthesis of new two dimensional (2D) materials was triggered by the latter achievement. Among the various sheets discovered, we can highlight: a) the transition-metal dichalcogenides, MoS_2, WS_2, TiS_2, TaS_2 and ZrS_2,[2] b) boron nitride,[3] c) graphyne,[4] d) silicene,[5-8] e) phosporene,[9] germanene[10] and also f) two dimensional polymers.[11-12] Silicene is a two dimensional form of Si which has been observed on Ag(111),[7] and Ir(111) substrates.[8] Like graphene, silicene is composed by hexagonal rings, even though they are not planar, since a pseudo Jahn-Teller effect induces symmetric buckling.[13] It has been shown that this buckling can be significantly reduced if silicene is confined inside bilayer graphene.[14] The bands structure of silicene resembles that of graphene and also possess massless Dirac Fermions. Yet, in contrast with graphene, the larger spin-orbit of silicon induces a gap equal to 1.47 meV, at the K point as showed by Sivec et al.[15] In order to develop silicene-based electronics, it is essential to open a tunable band gap. Several methods have been proposed to reach that end. A popular approach to open a gap is to use an adequate substrate. For example, when silicene is over MoS_2, a 70 meV gap appears, which can be modulated under an external field.[16] Using the same substrate, monolayer MoS_2, Li and Zhao showed that silicene is adsorbed in two configurations: high-buckled or low-buckled. The former displays metallic properties whereas the less buckled one is a small gap semiconductor (20-50meV).[17] In the same vein, Liu et al.[18] reported that the Dirac cone is preserved when silicene is over h-BN and hydrogenated Si-terminated SiC(0001) but it becomes metallic if it is placed onto hydrogenated Si-terminated SiC(0001). The band gaps opened in silicene by h-BN and hydrogenated Si-terminated SiC(0001) were 4 and 3 meV, respectively, at the PBE level. Silicene was also deposited on functionalized silicene. When it is over silicane (hydrogenated silicene), a 115 meV gap is opened, but if it interacts with fluorinated silicene, metallic character appears.[19] Gao et al.[20] showed that hydrogenated silicene is an insulator with a band gap of 3.1 eV. A different method to alter the electronic structure of silicene was recently proposed by Kaloni et al.[21] It consists in the adsorption of small organic molecules. In the case of acetone, a gap as large as 0.35 eV was observed. The oxygen atom of acetone becomes bonded to a Si atom, and the SiO bond length is 1.69 Å.

During the last years we have devoted our attention to study the effect of chemical functionalization on the stability and electronic properties of graphene. We showed that for the addition of radicals[22-24] there is a synergic effect which increases the bond energies when they are paired. A similar behavior was observed when organic groups like azomethine ylides[25] and benzynes[26] were agglomerated on the surface of graphene: the bond energies are dramatically increased if certain addition patterns are followed. The functionalization with radicals and organic groups proved to be very effective to open a band gap in graphene. For example, nitrene radicals (NH)[27] open a tunable band gap in the range of 0.3-5.0 eV, while benzynes[26] offered a smaller interval 0.3-2.0 eV. Motivated by our investigations on the chemistry of graphene and by the recent preparation of silicene, we decided to investigate the addition of radicals and their effect on the electronic properties of monolayer and bilayer functionalized silicene. Our results show that silicene exhibits a rich chemistry and because of the larger size of silicon, steric effects that inhibit the addition at full coverage of methylene onto graphene, are absent for silicene. Finally, it is shown that: a) the addition of radicals offers the possibility of tuning the band gap of monolayer silicene, b) the use of two layers of functionalized silicene permits a wider range of adjustment of the electronic properties, from metal to insulator, due to interlayer interactions. We expect that this work can motivate new investigations about the chemistry of silicene.

2. Methods

We performed periodic density functional theory calculations employing the M06-L,[28-29] HSEH1PBE[30-31] and VDW-DF[32] functionals. The VDW-DF calculations were performed with SIESTA[33-34]. We selected the double-zeta basis set with polarization functions and fixed the orbital confining cut-off to 0.01 Ry. The split norm used was 0.15. The DFT implementation in SIESTA can be prone to significant basis set superposition error (BSSE), even with relatively low degree of radial confinement.[22] To avoid this problem we used the counterpoise correction suggested by Boys and Bernardi.[35] We employed relaxed structures to estimate the BSSE corrected binding energies and we took monomer deformation energies into account. The interaction between ionic cores and valence electrons was described by the Troullier−Martins norm conserving pseudopotentials.[36] We checked the convergence of the Mesh cut−off; using a value of 200 Ry we obtained converged binding energies (within 0.02 eV). Geometry optimizations were performed using the conjugate gradient algorithm until all residual forces were smaller than 0.01 eV/Å. To simulate infinite monolayer silicene sheets we used a 3×3 unit cell which is composed by 18 Si atoms. For bilayer silicene we also used a 3×3 unit cell, but the number of atoms is 36. We optimized the unit cells along the *a* and *b* axes and but *c* was large enough to prevent interaction between adjacent sheets (25Å). The unit cells were sampled using a 30×30×1 Monkhorst-Pack sampling, around 500 k-points. The M06-L and HSEH1PBE calculations were performed with Gaussian 2009.[37] The basis set selected was Pople´s 6-31G*.[38] Geometry optimizations were performed the standard thresholds of Gaussian 2009. The unit cells employed were the same as those described above and also 1000 k-points were employed.

3. Results and Discussion

3.1 Functionalized monolayer silicene: four radicals were added at full coverage to silicene: H, CH_3, F and OH. In addition we considered the asymmetrical "Janus" functionalization of silicene.[39] The latter procedure gives six more functionalized silicenes. The optimized unit cells are shown in Figure 1, while the structural, energetic and electronic properties are listed in Table 1. When one type of functional group is used to fully functionalize silicene, hydroxyl induces the largest changes in the cell parameters. As it can be appreciated in Figure 1, the hydroxyl groups form hydrogen bonds between themselves and in order to reduce the OH:::O distance, a strong buckling occurs. As a consequence, the lattice parameters are approximately reduced by 0.5 Å, with respect to pristine silicene. The hydrogen bond distances display a wide range of values, they can be as short as 1.77 Å or as long as 2.35 Å. In contrast with the results obtained for OH, the addition of H, CH_3 and fluorine increases the lattice parameters of

Table 1. Structural parameters (Å), bond energies (kcal/mol per functional group) and optical band gaps (eV) determined for silicene functionalized with several radicals, at full coverage.

	a M06-L	*b* M06-L	Si-X/Si-Y M06-L	Si-Si M06-L	bond energy M06-L	Gap M06-L	Gap VDW-DF	Gap HSE
silicene	11.56	11.56		2.26		0.0	0.0	0.0
silicene+H	11.58	11.58	1.49	2.34	68.7	2.9	2.4	3.2
silicene+CH_3	11.80	11.80	1.91	2.36	65.1	2.2	1.8	2.5
silicene+F	11.69	11.69	1.63	2.35	114.9	1.2	1.1	1.6
silicene+OH	11.09	11.17	1.71[a]	2.34	94.3	1.2	0.7	1.5
silicene+H+CH_3	11.56	11.56	1.49/1.91	2.35	66.9	2.6	2.1	3.0
silicene+H+F	11.62	11.62	1.49/1.63	2.34	92.4	2.3	1.9	2.7
silicene+H+OH	11.37	11.41	1.50/1.70	2.34	81.6	2.2	1.8	2.6
silicene+CH_3+F	11.60	11.60	1.91/1.63	2.35	90.8	1.8	1.6	2.1
silicene+CH_3+OH	11.40	11.44	1.91/1.70	2.3	79.9	1.8	1.4	2.1
silicene+F+OH	11.14	11.04	1.64/1.73	2.34	104.8	1.3	1.0	1.6

a- Average value, because of the presence of hydrogen bonds the Si-OH span from 1.666 to 1.747 Å.

silicene by 0.02, 0.24 and 0.13 Å, respectively. Although the cell parameters are modified by functionalization, it is important to stress that the Si-Si bonds suffer minimal changes, less than 0.1 Å on average. The methyl radical promotes the largest elongation of the sheet because it has the largest size. The H atoms of neighboring methyl groups are separated by 2.3 Å, measured from the closest H atoms.

However, the repulsion between strongly electronegative fluorine atoms is not evidenced given that they are separated by 3.9 Å.

The strongest bond with silicene is formed by fluorine. At the M06-L/6-31G* level, the average binding energy (BE) per fluorine atom is as large as 114.9 kcal/mol. The OH radical is also strongly attached to silicene, but in this case the BE per OH group is 20.6 kcal/mol lower than that computed for fluorine. Finally, hydrogen and the methyl radical present BE of 68.7 and 65.1 kcal/mol, respectively.

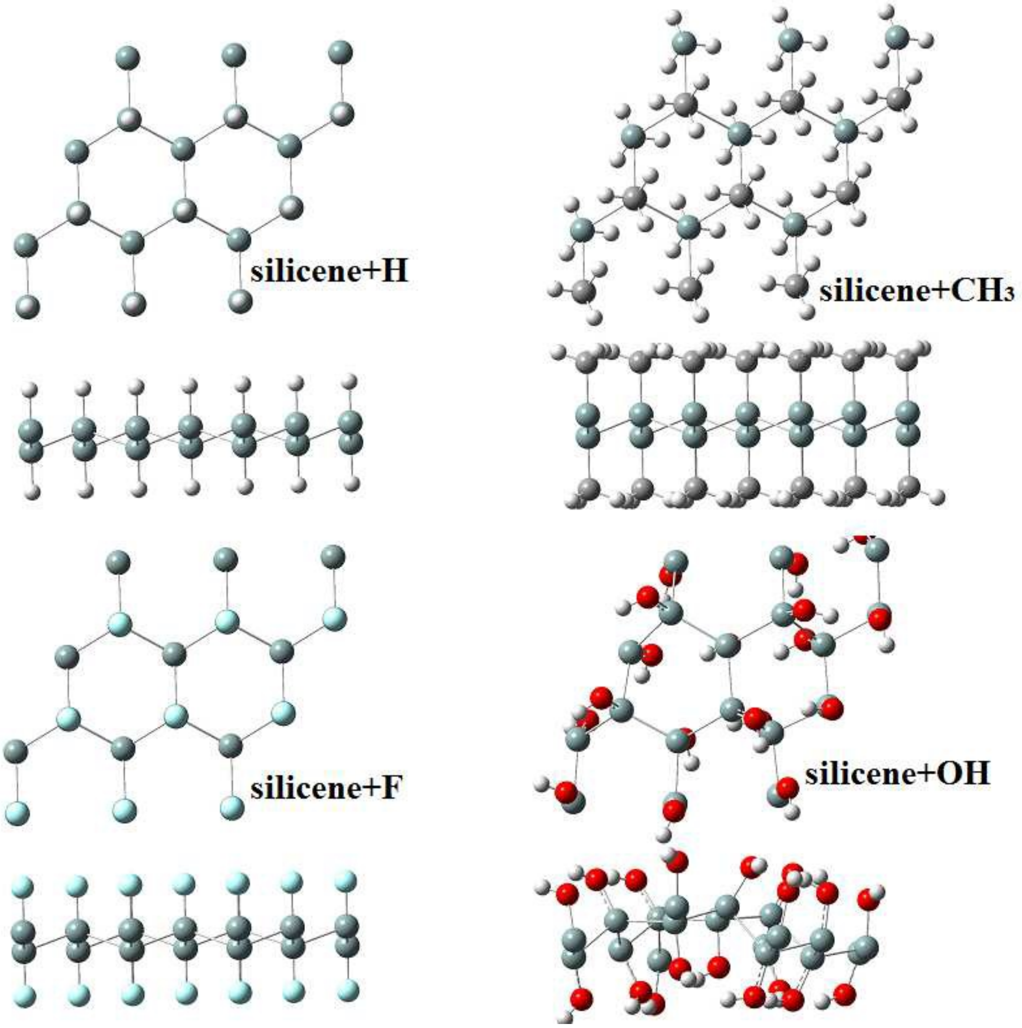

Figure 1. Optimized 3×3 unit cell of silicene functionalized with H, CH_3, F and OH at full coverage, at the M06-L/6-31G* level. (top and side views are presented for each structure)

These values are much smaller than those determined for F and OH, but still useful to form stable bonds with silicene. The higher reactivity of silicene as compared to graphene becomes evident if we recall the BE determined for the addition of H to graphene, namely, 16.7 kcal/mol or that of fluorine, which is 30.2 kcal/mol. The latter values are 4.1 and 3.8 times smaller than those computed for silicene. In order to gauge the effect of agglomerating radicals, we computed the BE for the addition of one radical and two radicals on opposite side of the sheet and onto a Si-Si unit. The values are presented in Table 2.

Table 2. Binding energies (kcal/mol per functional group) determined for the addition of different radicals to silicene, at the M06-L/-631G* level of theory.

	1 group	2 groups	full coverage
H	51.5	59.1	68.7
CH_3	50.6	57.8	65.1
F	102.7	108.5	114.9
OH	76.6	83.7	94.3

In general, the BE determined for the addition of one radical are 12-18 kcal/mol smaller than those obtained at full coverage. The largest variation occurs for the OH radical whose BE increases 17.7 kcal/mol per functional group when passing from one group to full coverage. It is important to mention that part of this increment cannot be attributed to the agglomeration of radicals but to the intralayer hydrogen bonds formed by the OH groups once they are attached to silicene. In line with the strong electronegativity of fluorine, this radical presents the lowest enhancement of the BE at full coverage, 12.2 kcal/mol. Finally, we also computed the BE for the addition of two radicals onto a Si-Si bond. The BE are increased by 6-8 kcal/mol with respect to the addition of one radical, and the values are in the middle between those BE computed at full coverage and the corresponding to one radical. The sole exception again is OH, since the BE determined for two OH is 10.6 kcal/mol lower than that computed at full coverage. The reason behind the apparent low BE determined for the addition of two OH is that they cannot form the hydrogen bonds that were found at full coverage. For this reason, the BE at full coverage is larger than the value that one can predict using the BE determined for one or two OH.

The covalent functionalization of silicene at full coverage opens a band gap of 1.2, 1,2, 2.5 and 3.2 eV for F, OH, CH_3 and H, respectively, at the M06-L/6-31G* level. The use of the more accurate HSEH1PBE functionals increases the band gap by 0.3-0.4 eV. At this level, the largest gap obtained was 3.2 eV for hydrogen. These values are in good agreement with those reported previously by Gao et al.[20] This value is approximately a half of the one computed at the same level for graphane.[27] To gain further insight, the band structures obtained at the VDW-DF/DZP level are presented in Figure 2. At the latter level the band gaps opened are 2.4, 1.8, 1.1 and 0.7 eV for H, CH_3, F and OH, respectively, at the VDW-DF/DZP level. They are all direct and occur at the gamma point. At lower coverage the functionalization induces different consequences on the electronic structure of silicene. We found that when 2 fluorine atoms or 2 OH groups are attached to a SiSi bond, a weak metallic behavior appears as indicated by HSEH1PBE/6-31G* calculations. In contrast, for H and CH_3, band gaps are opened; they values are 0.1 and 0.2 eV, respectively, at the HSEH1PBE/6-31G* level. Therefore, using one type of radical at variable concentrations, it is possible to induce different consequences on the electronic structure of silicene, it can be turned metallic, a wide gap semiconductor or a small gap can be opened.

The Janus functionalization is obtained when the sides of the sheet react with different radicals, a recent example is the addition of different aryl diazonium salts onto both sides of graphene, as recently exemplified by Bisset et al.[39] The six structures assayed are presented in Figure 3 and the lattice parameters, relevant bond distances, BE and band gaps are gathered in Table 1. As observed for symmetrically functionalized silicene, the addition of OH groups on one side contracts the lattice parameters of silicene, being the case of silicene functionalized with F and OH the most important one.

The HO:::HO bond distance between OH groups located in meta position on the same hexagonal ring is 2.18 Å. This is an important difference with respect to graphene, because the larger bond length between

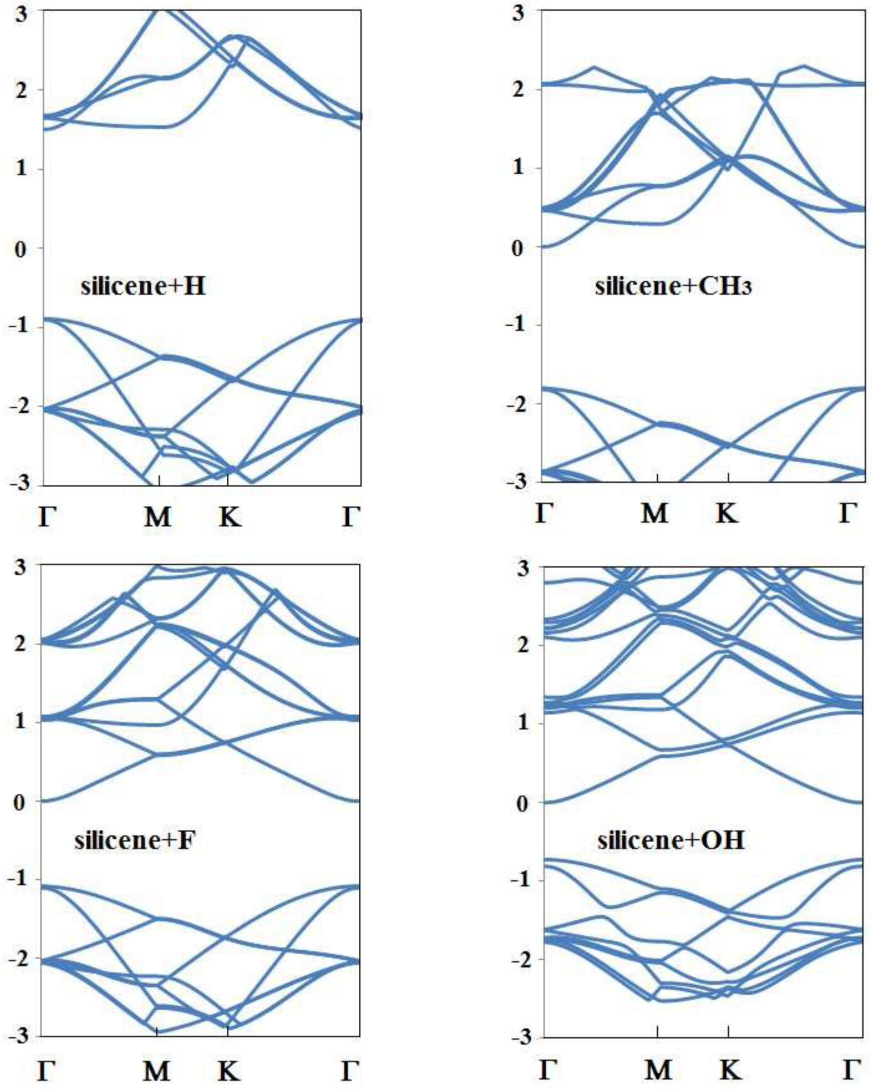

Figure 2. Band structure determined for 3×3 silicene functionalized at full coverage with H, CH_3, F and OH, at the VDW-DF/DZP level.

the Si atoms, allows a better formation of hydrogen bond in a hexagonal ring. In all cases the BE per functional group are over 66 kcal/mol, which is a strong indication of the stability of the functional groups attached to silicene. The ordering of the BE follows the one found in symmetrically functionalized silicene, the largest BE is computed for the F/OH pair and the weakest one corresponds to the H/CH_3 pair. The band structures of the Janus functionalized silicene computed at the VDW-DF/DZP level are presented in Figure 4. The band gaps are similar to those calculated for symmetrically functionalized silicene, as the F/OH pair presented the smallest gap and H/CH_3 the largest one. Thus, in terms of gap opening functionalization al full coverage enables the tuning of the band gap from 1.5 to 3.2 eV. Although gaps are similar for the six functionalized silicenes, there are important differences in the position of the conduction band minimum (CBM) and valence band maximum (VBM). For example,

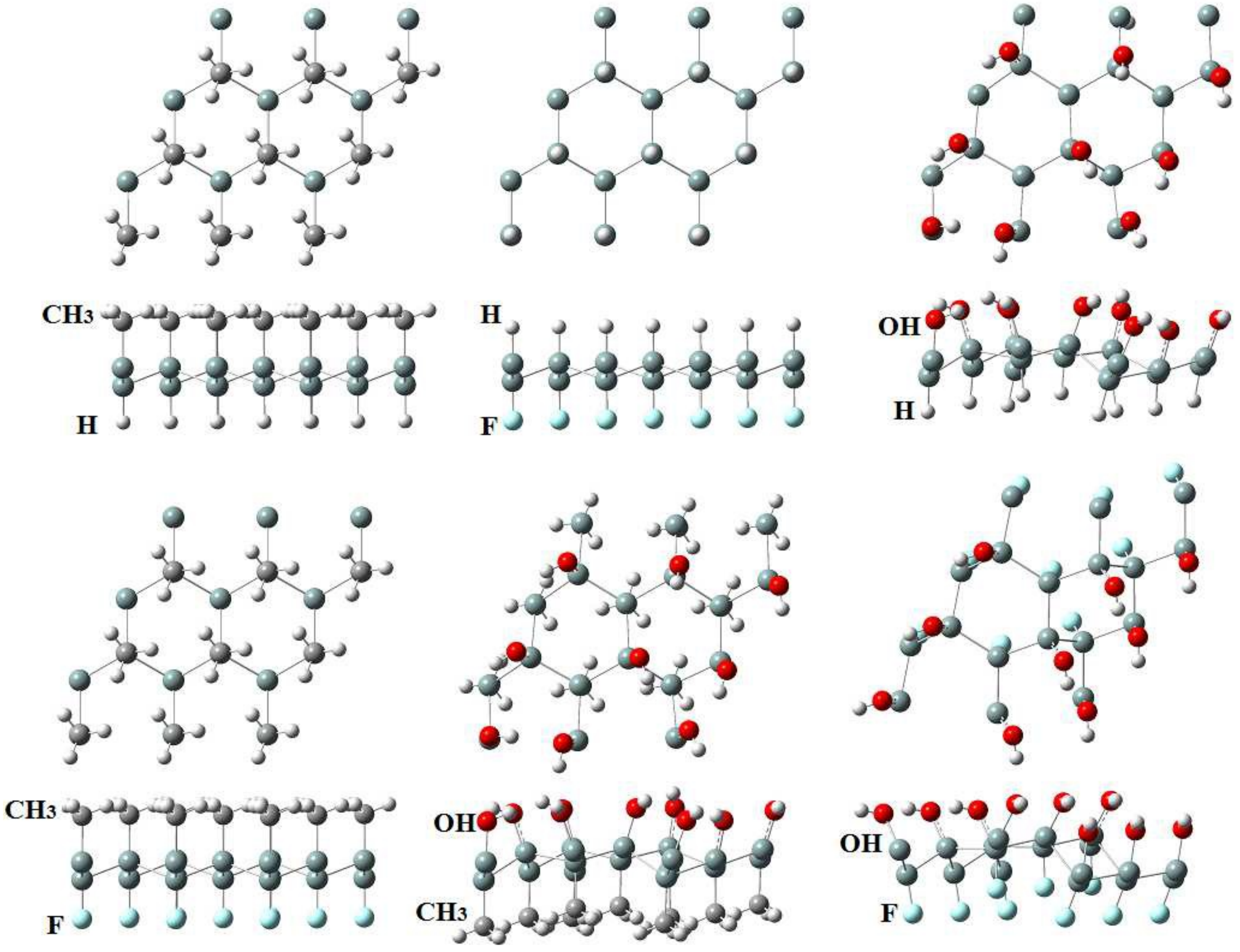

Figure 3. Optimized 3×3 unit cell of asymmetrically “Janus” functionalized silicene with H, CH_3, F and OH at full coverage, at the M06-L/6-31G* level. We dubbed X-Si-Y a silicene monolayer functionalized with radical X on one side and radical Y on the other. (top and side views are presented for each structure)

at the gamma point, the VBM of silicene+H+CH_3 is located much close to the Fermi level than in any of the symmetrically functionalized silicenes. Also, in general the CBM are placed slightly above the Fermi level for Janus functionalized silicene, in contrast with the symmetry case in which for CH_3, OH and F the CB are much closer to the Fermi level. Therefore, we reasoned that if two layers of functionalized silicene are coupled, it may be possible to obtain an improved control of the band gap opened if the functional groups are selected in such a way that the interact via non bonded interactions. For this reason, in the following section we studied the two layered material.

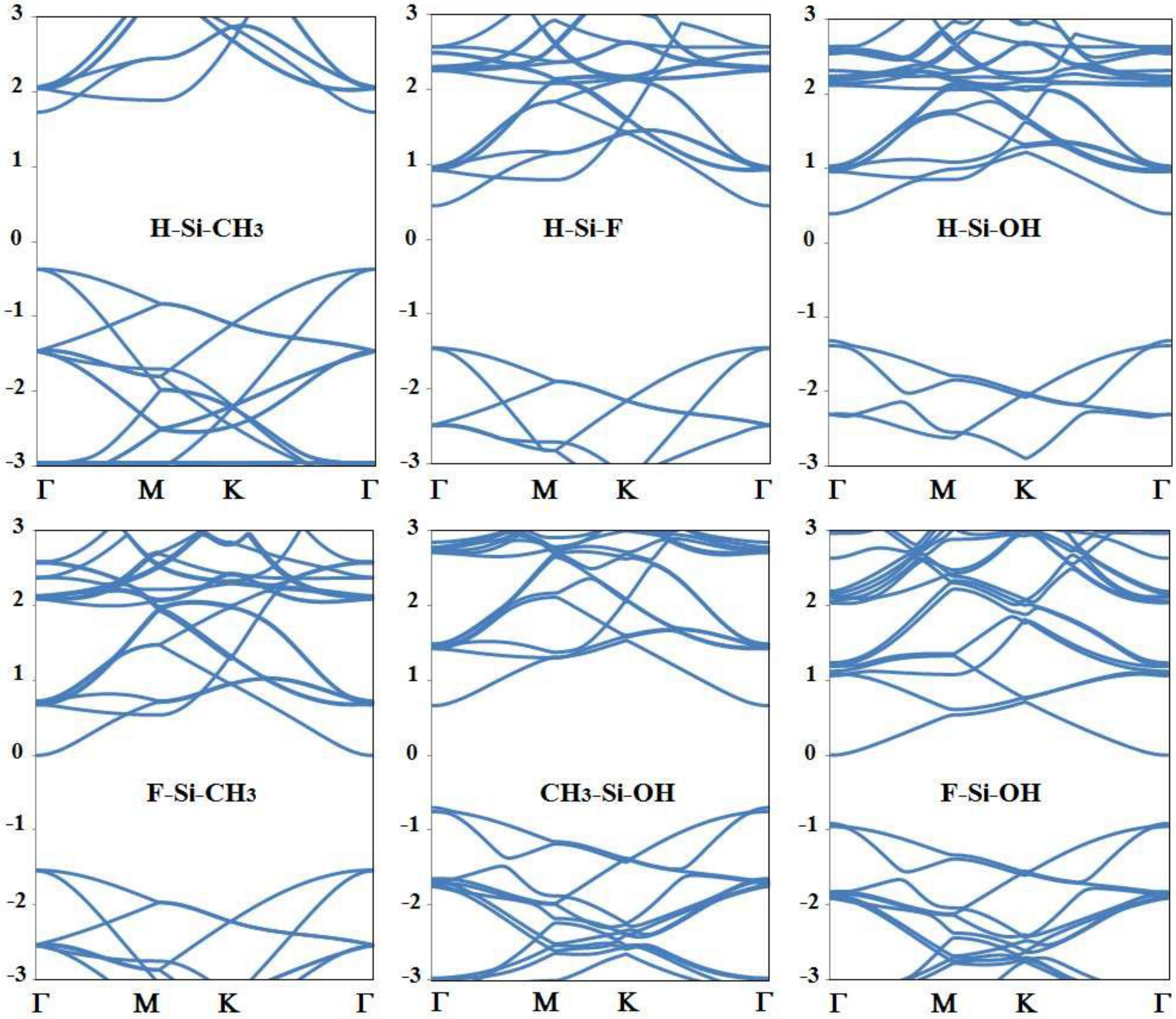

Figure 4. Band structure determined for 3×3 asymmetrically "Janus" functionalized silicene with H, CH_3, F and OH at full coverage, at the VDW-DF/DZP level. We dubbed X-Si-Y a silicene monolayer functionalized with radical X on one side and radical Y on the other.

3.2 Functionalized bilayer silicene: There are at least 137 bilayer functionalized silicenes that can be constructed using the 10 symmetrically and asymmetrically functionalized monolayer silicenes studied in the previous section. Among them, we studied 20, in which the functional groups can be coupled more strongly via inter-sheet hydrogen bonds or H:::H contacts. Although more bilayer silicenes can be studied, using the 20 models selected it is possible to obtain an improved adjustment of the band gap and the use of more models will confirm the results. The most important structural parameters, interlayer interaction energies (IIE) and gaps are gathered in Table 3. Selected structures and band gaps are shown in Figures 5, 6 and 7, respectively. We dubbed X-Si-Y a silicene monolayer functionalized with radical X on one side and radical Y on the other, while X-Si-Y/W-Si-Z indicates a bilayer silicene with two sheets X-Si-Y and W-Si-Z stacked.

As explained by Li et al.[40] there are four stacking patterns when graphane and fluorographene monolayers are stacked. In the same way, four stacked silicenes can be constructed using two functionalized silicenes. In Figure 5 we show the four types of stacked structures. In line with the results obtained by Li et al.,[40] we found that structures AA-II and AB-IV, which allow the formation of bifurcated interactions, are more stable than the AA-I and AB-III. However, in contrast with the results obtained for graphane/fluorographene bilayers, the AA-II structure is more stable than the AB-IV one by 0.0726 and 0.0280 eV/unit cell, for H-Si-H/H-Si-H and H-Si-H/F-Si-H, respectively, at the M06-L/6-31G* level. Thus, we will restrict the study of the rest of the bilayer silicenes to the AA-II conformation. We note that the stacking pattern has a minimal influence on the band gaps, as previously showed by Li et al.[40] In effect, the band gap of the four H-Si-H/F-Si-H structures are similar (between 0.5 and 0.6 eV) and in the case of H-Si-H/H-Si-H the band gap of the AA-II and AB-IV structures differ by 0.05 eV.

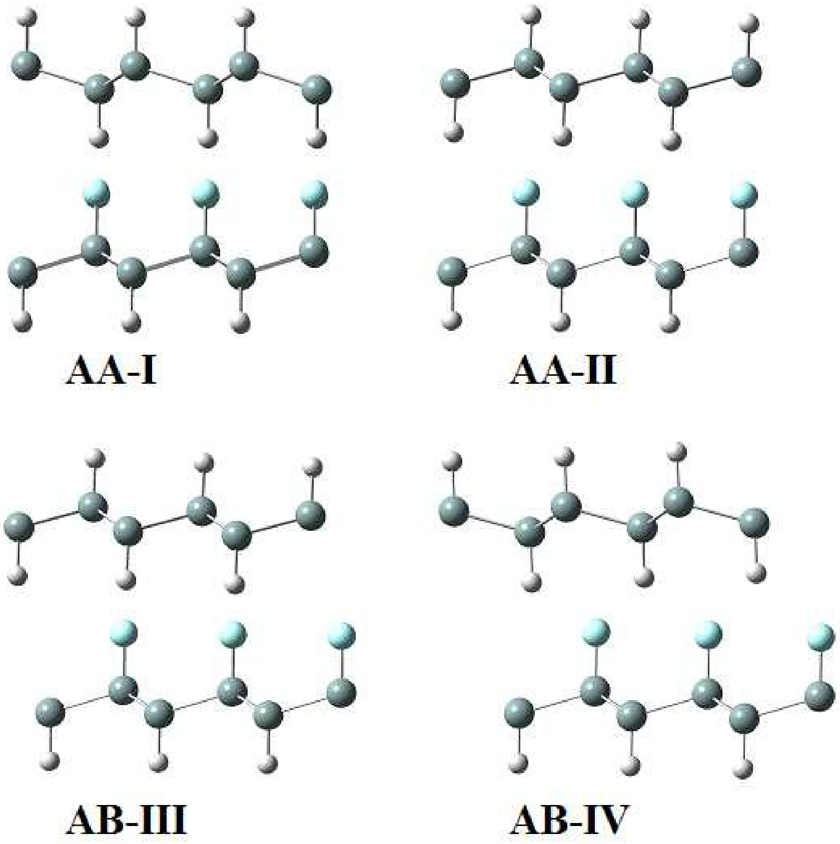

Figure 5. Stacked structures considered for functionalized silicene, AA and BB denotes the stacking orientations of the hexagons, parallel and parallel displaced, respectively.

In the case of two layers of H-Si-H stacked, the H atoms can interact via H:::H bonds. The distance between hydrogen atoms of different sheets is 2.5 Å and the IIE is 0.0356 eV per H atom. This value is quite impressive since it is almost twice the one computed for bilayer graphene. In effect, at the M06-L/6-31G* level of theory the stacking interaction of 5×5 bilayer graphene is 0.02 eV per carbon atom, so the interaction in bilayer silicane is almost twice that of bilayer graphene. As regards the effect of the interlayer interaction on the band gap it is minimal since it is reduced by 0.1 eV. For two layers of CH_3-Si-CH_3 we found that the AA and AB structures are nearly degenerate. Indeed, at the M06-L/6-31G* level the AA is more stable by 0.018 eV, on the contrary VDW-DF/DZP calculations suggested that the AB is more stable by 0.0015 eV. As expected, because of the presence of more hydrogen atoms, the IIE is larger than that computed for silicane. At the M06-L/6-31G* level, the energy required to separate both layers is 0.04 eV per CH_3 group. The H:::H distance between the closest H atoms is 2.5 Å, similar to bilayer silicane. However, the band gap is reduced by 0.1 eV with respect to the monolayer case, so despite the larger interaction, the effect of the band gap is similar as for functionalization with hydrogen. The third example considered in which H:::H interactions are important is H-Si-H/CH_3-Si-H. The IIE is smaller than those computed in the previous two cases. This result was not expected because the presence of more H atoms than in bilayer silicane maybe correlated with a larger IEE, yet it was not the case and the IEE is 0.0023 eV/Si atom smaller. In contrast with the results obtained above we found that the combination of H-Si-H and a CH_3-Si-H layers has a strong effect on the gap as it is reduced to 2.0 eV. This results shows the importance of coupling at least one Janus functionalized silicene in order to modulate the band gap, as in the previous two cases we used symmetrically functionalized sheets. The latter value is 0.6 and 0.9 eV smaller than those computed for CH_3-Si-H and H-Si-H, respectively. The band structures displayed in Figure 7 show that the gap is direct and occurs at the gamma point.

Table 3. Structural parameters (Å), interlayer interaction energies (eV/Si atom) and optical band gaps (eV) determined for bilayer silicene functionalized with several radicals, at full coverage.

Layer1/Layer2	*a* M06-L	*b* M06-L	interlayer interaction M06-L	Gap M06-L	Gap VDW-DF	Gap HSE
H-Si-H/H-Si-H	11.60	11.60	0.0356	2.8	2.4	3.1
CH_3-Si-CH_3/CH_3-Si-CH_3	11.56	11.56	0.0400	2.1	1.8	2.4
H-Si-H/CH_3-Si-H	11.59	11.59	0.0333	2.0	1.6	2.2
H-Si-H/F-Si-H	11.60	11.60	0.0269	0.6	0.2	0.8
F-Si-H/F-Si-H	11.61	11.61	0.0303	0.3		0.5
H-Si-CH_3/F-Si-H	11.61	11.61	0.0281	metal	metal	metal
CH_3-Si-CH_3/F-Si-H	11.61	11.60	0.0287	metal		metal
CH_3-Si-CH_3/F-Si-CH_3	11.59	11.59	0.0296	metal		metal
CH_3-Si-H/F-Si-H	11.61	11.62	0.0254	0.3		0.7
H-Si-OH/F-Si-H-buckled	11.32	11.32	0.0555	1.0		
H-Si-OH/F-Si-H-not-buckled[a]	11.83	11.83		metal		
HO-Si-H/F-Si/H	11.58	11.61	0.0164	0.2	metal	0.5
H-Si-OH/HO-Si-H	11.75	11.57	0.1017	1.9	1.5	2.3
H-Si-CH_3/HO-Si-CH_3	11.54	11.54	0.0266	1.5	1.3	1.5
H-Si-H/HO-Si-H	11.44	11.57	0.0288	2.2	1.6	2.5
F-Si-CH_3/F-Si-F	11.63	11.63	0.0428	metal		metal
CH_3-Si-CH_3/F-Si-F	11.63	11.61	0.0367	metal		metal

F-Si-F/F-Si-F	11.65	11.71	0.0817	1.3	1.0	1.7
H-Si-H/F-Si-F	11.50	11.56	0.0373	0.40		
H-Si-CH_3/F-Si-F	11.63	11.57	0.0354	semimetal		metal

a-structure found only at the VDW/DZP level.

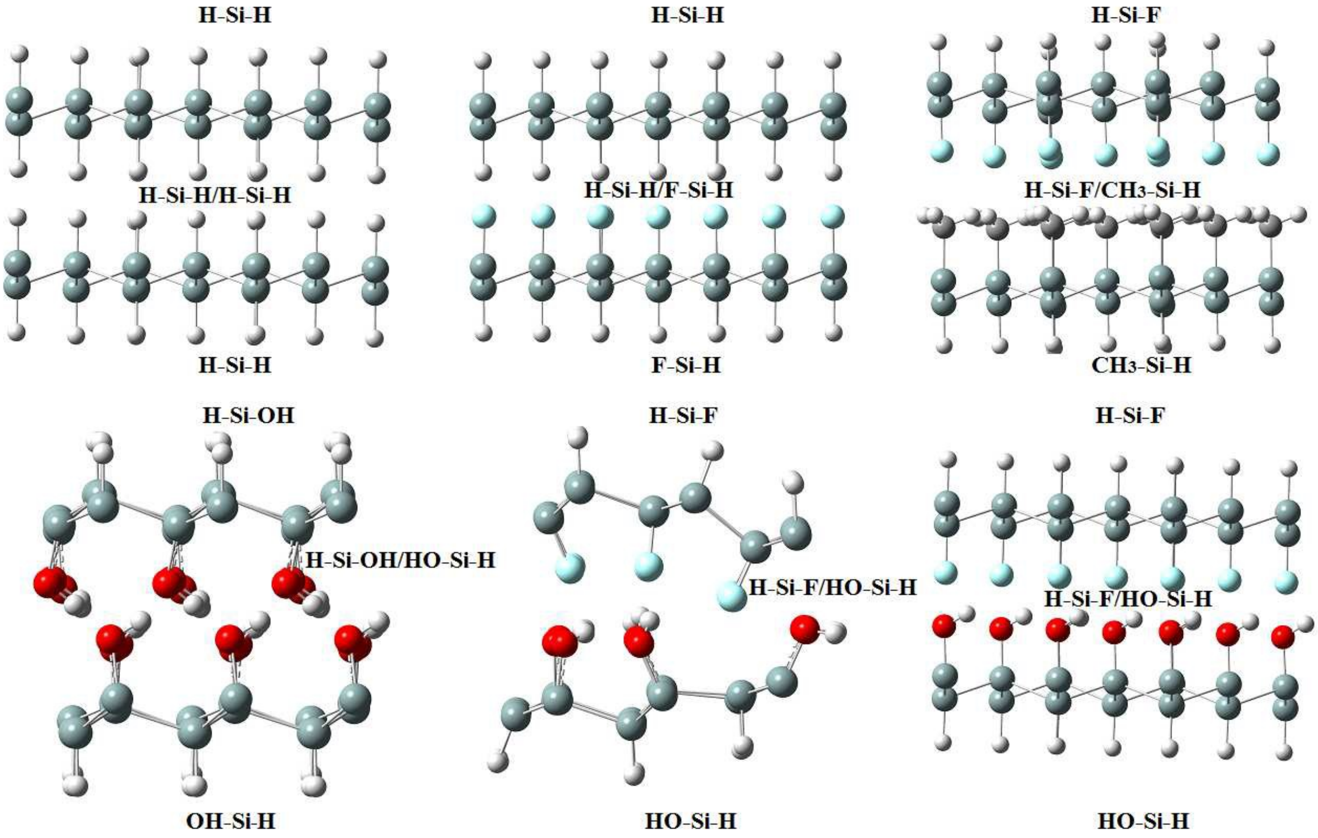

Figure 6. Selected optimized 3×3 unit cell of functionalized bilayer silicene with H, CH_3, F and OH at full coverage, at the M06-L/6-31G* level. We dubbed X-Si-Y a silicene monolayer functionalized with radical X on one side and radical Y on the other. (side views are presented for each structure)

The next cases considered are those which involve at least one layer covered with fluorine atoms, which are 13 bilayer silicenes. For H-Si-H/F-Si-H we found that even though the IIE is only 0.0269 eV/Si atom, the band gap experiences a tremendous diminution since it is 0.6 eV, at the M06-L/6-31G*. This outcome represents a reduction of 1.7 and 2.3 eV with respect to monolayer F-Si-H and H-Si-H. These findings are in line with the results obtained by Li et al.[40] for graphane/fluorographene bilayers. By means of PBE+D calculation Li and coworkers showed that the latter system has an optical band gap of 0.5 eV, about 4.5 and 3 eV smaller than those computed for graphane and fluorographene monolayers. The reason behind the band gap reduction that we observe is similar to that explained by Li et al.[40]: the valence band maximum and conduction band minimum are located in different layers and thus, a small gap is obtained. In the case of silicene the VBM and CBM are located in H-Si-H and F-Si-H, respectively as indicated by the analysis of the partial density of states. In our case, the VBM and CBM can be manipulated a bit more, because more functionals groups were employed and Janus functionalization was considered. For this reason, the gap can be reduced even more if two H-Si-F layers are coupled in the H-Si-F/H-Si-F fashion. Indeed, at the M06-L/6-31G* level it is as small as 0.3 eV and the IIE is increased to 0.0303 eV. Interestingly, when the H atoms are replaced by CH_3 groups we found that and the gap of the monolayers becomes closed and the systems are exhibit metallic properties. Specifically, this transition occurs for H-Si-CH_3/F-Si-H, CH_3-Si-CH_3/F-Si-H and CH_3-Si-CH_3/F-Si-CH_3. It is quite impressive that the change of the H atoms of one layer in H-Si-H/F-Si-H to H-Si-CH_3/F-Si-H closes the 0.6 eV gap present in the former bilayer silicene. Since, the H atoms replaced are those which interact with fluorine, it is a change in the interlayer interaction which rises the metallic character. Yet, the change in IEE is not so significant since that of H-Si-CH_3/F-Si-H

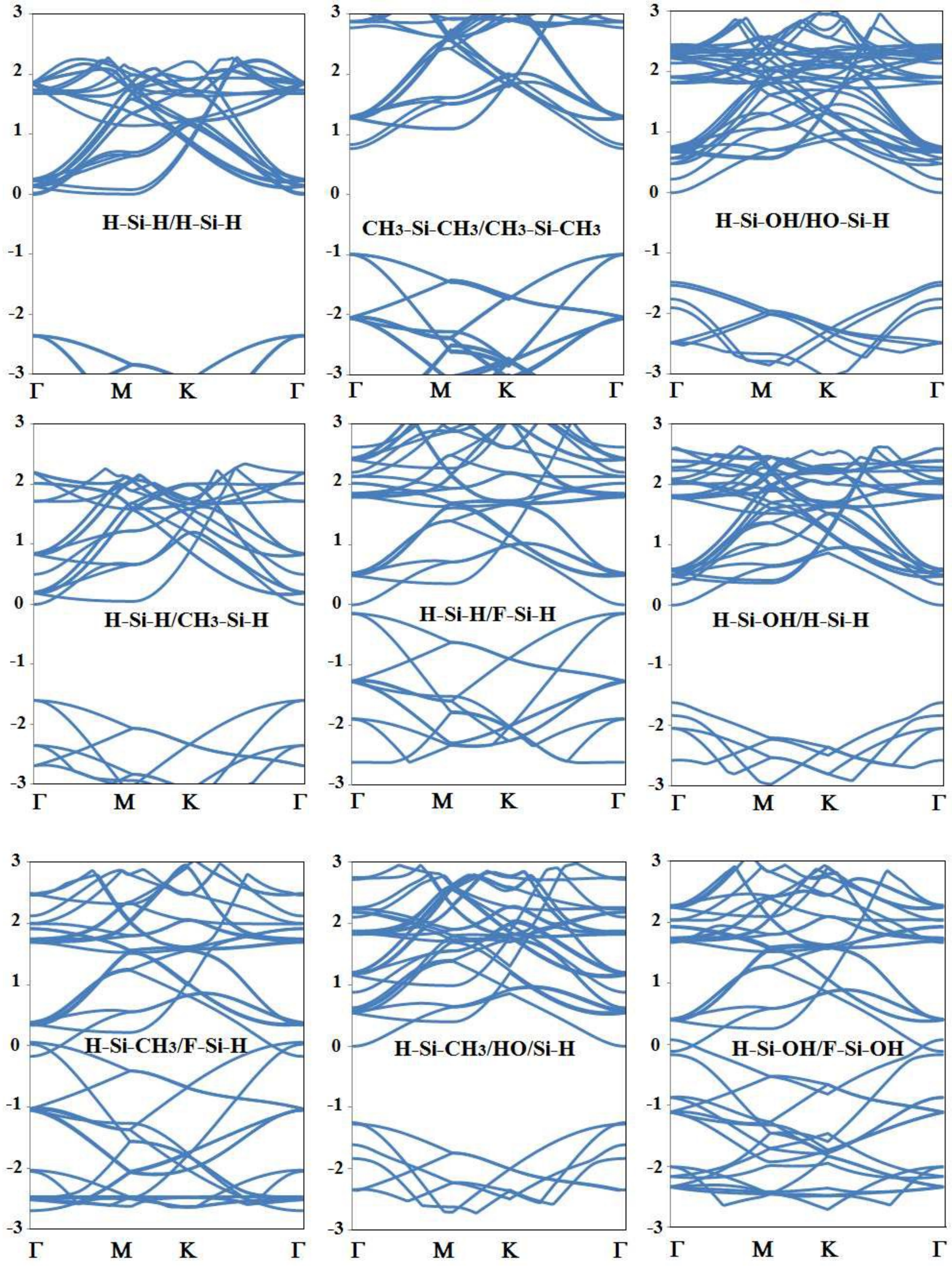

Figure 7. Band structure determined for 3×3 functionalized bilayer silicene with H, CH_3, F and OH at full coverage, at the VDW-DF/DZP level. We dubbed X-Si-Y a silicene monolayer functionalized with radical X on one side and radical Y on the other, while X-Si-Y/W-Si-Z indicates a bilayer silicene with two sheets X-Si-Y and W-Si-Z stacked.

is only 0.0012 eV larger. The F::H distances are close to 2.8-2.9 Å. The band structures shown for both systems in Figure 7, at the VDW-DF/DZP level are very similar, residing the key difference in the position of the CB. In the case of H-Si-CH_3/F-Si-H it crosses the Fermi level while in H-Si-H/F-Si-H it is slightly above. It is rewarding to see that the M06-L/6-31G*, VDW-DF/DZP and HSEH1PBE/6-31G* results agree in the existence of the semiconductor to metal transition, when passing through H-Si-H/F-Si-H to H-Si-CH_3/F-Si-H. Although the H-Si-CH_3/F-Si-H is metallic, when the H-Si-CH_3 is switched and H interacts with fluorine, we found that H-Si-CH_3/F-Si-H is a 0.3 eV gap semiconductor, confirming the importance of the CH_3:::F interaction. The last system brought to interact with F-Si-H was H-Si-OH. We found that H-Si-OH/F-Si-H exists in two forms: a) a 1.0 eV semiconductor which is strongly distorted, the lattice parameters are contracted, intralayer hydrogen bonds are formed between the OH groups, and F:::HO interlayer hydrogen bonds exist. b) a metallic system, in which the intralayer hydrogen bonds are absent, the lattice parameters are increased with respect to bare silicene and interlayer hydrogen bonds dominate the interaction with a F:::HO distance of 2.0Å. At the VDW-DF/DZP level, the latter system is more stable by 0.3 eV, but at the M06-L/6-31G* level only the semiconducting (buckled) structure could be optimized. The reason behind the 1.0 eV gap found for structure a) is not that fluorine is not effective in reducing the gap but that the structure is strongly buckled. In effect, when the structure is not buckled as in b), fluorine induces a metallic character as shown before. Thus, fluorinated silicene is not only able to induce a metallic character in perfect silicene as shown by Li et al.,[19] but also in functionalized silicenes presenting a wide optical band gap.

Taking into consideration the results obtained when one side of monolayer silicene is covered with fluorine we decided to study bilayered systems in which one of the layers is F-Si-F. It is important to mention that several structures are possible for fluorinated silicene and several are energetically degenerated as indicated by Ding et al.[41] In this work we restrict ourselves to the hexagonal-like ones, even though, as we shall explain below the bilayered system presented some peculiarities. For F-Si-

CH_3/F-Si-F, H-Si-CH_3/F-Si-F and CH_3-Si-CH_3/F-Si-F we found that they are metals or semimetals in agreement with the results obtained for F-Si-H. In the case of H-Si-H/F-Si-F a small gap of 0.3 eV is opened, just 0.3 eV smaller than the one computed for H-Si-H/F-Si-H, so fluorine is so powerful to modify the electronic structure that even when it is not direct contact with the other layer, it can induce a reduction of the band gap. These results are in line with the recent findings by Gunasinghe et al.,[42] which indicated that semi-fluorinated graphene has distinctive electronic properties. For the sake of completeness, we subjected to calculations the fully fluorinated system F-Si-F/F-Si-F. We found that the band gap is similar to that computed for one F-Si-F layer, but quite unexpectedly, the interaction between layers is not repulsive but very attractive as the IIE is 0.0817 eV and a band gap equal to 1.5 eV is opened.

The last systems assayed are those which incorporate the OH radical, which can form strong interlayer and intralayer hydrogen bonds and also strongly alter the lattice parameters. Three systems were considered: H-Si-H/HO-Si-H, H-Si-OH/HO-Si-H and H-Si-CH_3/HO-Si-CH_3. They are semiconductors with a gap of 2.2, 1.9 and 1.5 eV, respectively. Notwithstanding the fact that the latter optical band gaps are smaller than those computed for H-Si-H (2.9 eV), HO-Si-H (2.2), H-Si-CH_3 (2.6 eV) and HO-Si-CH_3 (1.8 eV), the reduction is much less significant than for fluorine. Even in the case of H-Si-OH/HO-Si-H, which has the largest IIE, namely, 0.1 eV per Si atom, the gap decreases by just 0.3 eV with respect to H-Si-OH. The large IIE found for the latter structure is a consequence of the existence of 18 HO:::HO interlayer hydrogen bonds, with an average distance of 1.7 Å.

4. Conclusions

The effect of covalent functionalization on the structure and electronic properties of monolayer and bilayer silicene was investigated with the aid of M06-L/6-31G*, VDW-DF/DZP and HSEH1PBE/6-31G* periodic calculations as implemented in Gaussian 2009 and Siesta. The following points are the most important conclusions of the study:

1- Silicene is extremely more reactive than graphene, being the addition of fluorine and hydrogen four times stronger. As a consequence, functional groups like H, CH_3, F and OH can form stable strong Si-X bonds. The Si-F bond is the strongest one with a binding energy of 114.9 kcal/mol. Also, in no case the bond energy of the radicals assayed is lower than 65 kcal/mol.

2- Among the functional groups studied, the hydroxyl radical is the one which induces the largest structural changes in the structure of silicene, due to the presence on intralayer hydrogen bonds which reduce the lattice parameters by 0.5Å.

3- As observed for graphene, the pairing of radicals increases the binding energy per functional group by up to 17 kcal/mol.

4- The functionalization of monolayer silicene with the radicals mentioned in point 1 enables the adjustment the optical band gap of silicene. It can be as large as 3.2 eV for silicane or a small gap semiconductor when a functionalization of 5.6% is achieved with H or CH_3. On the contrary, when F or OH are added at the latter percentage of coverage silicene becomes metallic.

5- When two layers of functionalized silicene are stacked we found that the band gaps are reduced with respect to those computed for the isolated symmetrically and asymmetrically (Janus) functionalized silicene.

6- Fluorine is the radical which can induce the largest changes in the electronic structure of bilayer silicene as it was able to induce metallic properties for systems which presented gaps as large as 3.2 eV, while in other four cases small gaps in the range of 0.1-0.6 eV were obtained.

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