Volume 1 | Number 1 | Jan 2013 | Pages 1–100

PCCP

Physical Chemistry Chemical Physics
www.rsc.org/pccp

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

ARTICLE TYPE

Impurity effect in ultra-thin hydrogenated silicene and germanene. A first principles study

Caroline J. Rupp,[a] **Sudip Chakraborty,**[b] **Rajeev Ahuja,**[bc] **and Rogério J. Baierle**[‡a]

Spin polarized density functional theory within the GGA-PBE and HSE06 approach for the exchange correlation term has been used to investigate the stability and electronic properties of nitrogen and boron impurities in single layers of silicane and germanane. We have observed that these impurities have lower formation energies in silicane and germanane when compared to their counterparts in graphane. We also have noticed that the adsorption of H atoms in the vicinity of defects stabilizes the system. In addition, we have obtained that the electronic properties of silicane and germanane can be tuned when N and B are incorporated in the Si and Ge network. N–doped and B–doped give rise to n-type and p-type semiconductor properties. However, the adsorption of H atoms quenches the doping effects.

1 Introduction

Carbon, silicon and germanium are isoelectronic atoms (belongs to the same column of the periodic table). However, in bulk form carbon is more likely in the hexagonal phase (graphite) with the sp^2 hybridization while silicon and germanium are more stable in the cubic (zinc blend) phase with sp^3 hybridization. Recently carbon has been synthesized in an isolated single hexagonal (honeycomb) two-dimensional (2D) form. The 2D form of carbon structure is known as graphene and presents unique electrical and mechanical properties never observed in conventional three-dimensional materials.[1,2] The small (almost negligible) band gap and the fact that graphene is inert to many important chemical compounds reduce its applicability. Chemical doping can open the band gap and increase the graphene sensibility to the chemical environment. In fact, N- and B-doped graphene are likely to tailor the electronic properties of graphene enhanced its potential application.[3–5]

The fully hydrogenated graphene (graphane) is also stable and keeps the hexagonal structure, however the hybridization changes to sp^3 and graphane exhibits an appreciable band gap of approximately 3.5 eV.[6] B- and N-doped graphane was studied by Y. Wang *et al.*[7] They observed that B-doped (N-doped) pushed the Fermi level to the VBM (CBM) that leads to the p-type (n-type) electronic properties of graphane.

The counterparts of graphene are silicene and germanene. These structures are obtained on a substract[8–10] and they properties are dependent on the substrate.[11] The calculated phonon spectra shows that there are no soft modes, which indicates that they are stables.[12–14] These systems have similar properties than graphene like quantum spin hall effect (QSHE). However, the QSHE effect in Si and Ge are larger than in C. Recently, it has been shown that strain-induced in a mixed nanostructure (GeCH$_3$) present larger QSHE, which turns these structures with potential aplication in room temperature.[15] The Si and Ge 2D nanomaterials have a corrugated structure and an intermediate hybridization between sp^2 and sp^3, which favors their functionalization by chemical adsorption.[16]

The adsorption of N and B atoms in silicene has been studied by Sivek *et al.*[17] They observed that the B atom adsorbs on a valley site while N atom is more likely to absorb on a bridge. Both adsorbed impurities lead the silicene with a new electronic configuration around the Fermi energy. When a B atom is absorbed (boron substitutes a silicon, B$_{Si}$) the system preserves the Dirac cone but the Fermi energy shift to lower energies that leads silicene with p–type properties. On the other hand, absorption of an N atom (nitrogen substitutes a silicon, N$_{Si}$) destroys the Dirac cone leading the silicene with a local metallic character.

The hydrogenation of silicene and germanene transforms these almost 2D structures with mixed hybridization between sp^2 and sp^3 into the sp^3 hybridization, forming the silicane and germanane, respectively. Silicane and germanane have been studied in different possible configurations: the top configuration, where all the H are adsorbed on the same side, the chairlike configuration, where H are alternating the both

[a] Departamento de Física, Universidade Federal de Santa Maria, 97105-900, Santa Maria, RS, Brazil.
[b] Condensed Matter Theory Group, Department of Physics and Astronomy, Box 516, Uppsala University, S-75120 Uppsala, Sweden.
[c] Applied Materials Physics, Department of Materials and Engineering, Royal Institute of Technology (KTH), S-100 44 Stockholm, Sweden.
‡Author Correspondance: E-mail: rbaierle@smail.ufsm.br (Rogério J. Baierle)

sides, and boatlike configuration where are alternating in pairs the two sides. Details about the configuration can be find in references.[18,19] These calculations have shown that the chair-like is the most stable configuration. These new 2D systems retain the hexagonal structure and are semiconductors. For silicane, the direct or indirect gap character depends on the atomic configuration while germanane has a direct band gap in the Γ point, which does not depend on the atomic configuration.[19]

The success in functionalizing silicene and germanene[17,20–22] paves the way for N- and B-doped hydrogenated structures in order to produce the desirable n-type and p-type semiconducting materials. First principles calculations are essentially free of parameters and are reliable to predict new electronic and optical properties of defective materials, being a powerful tool to be used in design and engineered materials tailored for specific application.

In this work we use first principles calculations to investigate the stability and the new electronic properties when a N or B substitution impurity is present in silicane and germanane in the most stable configuration (the chair configuration). Our results show that these impurities present lower formation energies in silicane and germanane than in graphane.[7] In addition, we have observed that the doped nanostructures show different electronic properties as compared to the pristine form. We have observed that B-doped silicane and germanane could shows p-type electronic properties while N-doped shows n-type semiconductor properties. We also have noticed that for silicane the band gap character changes from indirect (pristine system) to direct. The rest of this manuscript is organized as follows: in the next section we present the computational methodology, in section III we show the results and discussion regarding the hydrogenated systems where there is a lack or excess of H atoms and when N and B impurities are present. Finally we have conclude the work with a brief outlook as far the application perspective concerned.

2 Methodology

The present calculations are based on the spin polarized density functional theory (SP-DFT) formalism. The generalized gradient approximation for the exchange-correlation functional of the Perdew-Burke-Ernzerhof (PBE)[23] form has been employed to obtain the structural optimization and the total energy of the systems. It is known that due to the self–interaction problem present in the GGA-PBE functional, calculations using this functional not predict the correct band gap of semiconductor systems. In order to avoid this problem by including the screened Coulomb potential, We have employed the hybrid functional formalism named HSE06[24–27] to explore the electronic band structure for pristine and doped systems. This functional have already been employed in

pristine systems and the calculated band gap is in quite accordance with the experimental results.[28,29] The calculations have been performed using the VASP-code,[30,31] which performs fully self-consistent calculations by solving the standard Kohn–Sham (KS) equations using both GGA-PBE and HSE06 type exchange-correlational functional.[26] The KS orbitals have been expanded in a plane wave basis set with a cutoff energy of 500 eV and the core electrons as well as the interaction between valence and core are described by projector augmented wave (PAW) method.[32,33]

The supercell consists of threefold basic unit cells to obtain the geometric optimizations, energetic stabilities along with the electronic properties of the defective systems. In order to avoid interactions between neighboring layers a vacuum region of 15 Å has been added normal to the single layer. The BZ has been sampled with a $5\times5\times1$ mesh of $\vec{k}$–point within the Monkhorst-Pack scheme.[34] All the structures are optimized until the calculated Hellman-Feynman forces acting on each atomic specie are smaller than 1.0×10^{-5} eV/Å.

The formation energies (E^{form}) of doped system (N or B in a Si or Ge site) per supercell have been obtained using total energy (E_t) calculations, according to the following equation:

$$E^{\text{form}}[X_Y] = E_t[X_Y] - E_t[pristine] - \mu_X + \mu_Y. \quad (1)$$

Here μ_X is the atomic chemical potential (X = B or N) of the foreign atom while μ_Y is the chemical potential of the removed atom (Si or Ge). We also considered that H atoms can be removed (added) when an impurity is present, hence the chemical potential of the H atom (μ_H) must be added (subtracted) in equation 1. The chemical potential for B and N depends on the primary material used in doped silicane and germanane. In this work we have considered that the doping process occurs when the impurities are in rich growth conditions, then the chemical potential for the B atom is the total energy of a B atom in the α–boron bulk and the chemical potential of the N atom is the half part of the total energy of the N_2 molecule. The chemical potential of H atom is the half part of total energy of the H_2 molecule, μ_{Si} and μ_{Ge} are the energy per atom of Si and Ge in the zinc blend structure.

3 Results and Discussions

Firstly we have studied the pristine systems in the chair conformation. We have obtained that both silicane and germanane form corrugated structures with a buckling distance of 0.72 and 0.73 Å, respectively. These buckling distances are higher by 0.27 and 0.14 Å than the non-hydrogenated systems. The calculated binding energies are -3.39 and -2.87 for eV/atom for silicane and germanane, respectively. The binding (E_b) energy is defined as the difference between the total energy of the stable structure and the total energies of the respective iso-

lated atoms in their neutral charge states. By calculating the formation energy we have observed that the hydrogenation of silicene and germanene is an exothermic process. The calculated formation energies are -0.30 and -0.14 eV per adsorbed H. It is worth pointing out that our results are in accordance with previous similar calculations. [14,35–38]

Silicane in the chair conformation is semiconductor with an indirect band gap of 2.94 eV. The VBM localizes in the Γ point while the CBM localizes in the M point. The difference between direct (in the Γ point) and indirect band gap is 0.16 eV. Germanane has a smaller and direct band gap (the VBM and CBM localize in the Γ point). We have obtained a band gap of 1.61 eV. Again, these results are in accordance with previous calculations. [28,35,37–40] In Fig.s 1 (a) and (d) we have show the calculated electronic band structure for silicane and germanane using HSE06 functional.

The hydrogenation can leads the systems with a lack or excess of H atoms. When there is a lack of H, some Si (Ge) atoms will be threefold coordinated (a dangling bond will be present). Otherwise, whether there is a excess of H some Si (Ge) atoms will be fivefold coordinated. When there is a fivefold coordinated atom the distance between this atom and its neigboring atoms increase (decreasing the bond strength), and the fivefold coordinated atom moves in direction to the adsorbed H in the other side of the plane, decreasing the buckling distance. The calculated formation energies indicate that the systems with excess of H are less stable when compared to similar system where the lack of H occurs. For silicane (germanane) we obtained formation energies of 1.37 (1.07) and 2.07 (2.25) eV, when the systems present lack or excess of H, respectively.

The calculated electronic band structures within the HSE06 functional show that dangling bonds give rise to two spin polarized non dispersive electronic states. For silicane the electronic level with spin up is occupied and resonant with the VBM while the electronic level with spin down is empty and localized in the band gap, around 0.7 eV below the CBM, see Fig. 1 (b). For germanane due to the differences in the electronic band structure as compared to the silicane (germanane has a smaller and direct band gap) the empty (spin down) state is resonant with the CBM, as can be seen in Fig. 1 (e).

For a Si (Ge) atom fivefold coordinated two spin polarized eletronic levels have been also observed. However, these eletronic levels show a small dispersion in the band structure (see Figs. 1 (c) and (f)). Here we observe how important is the used of a non local approximation to calculate exchange term in DFT. The use of HSE06 not only gives a more reliable value of the band gap for semiconductor systems, but also using HSE06 we obtained a greater energy separation between the occupied (spin up) and the empty (spin down) electronic states as compared to the GGA calculations. In fact, for germanane the GGA functional indicated that when there

is a fivefold coordinated Ge atom the system presents a half metallic characteristic.
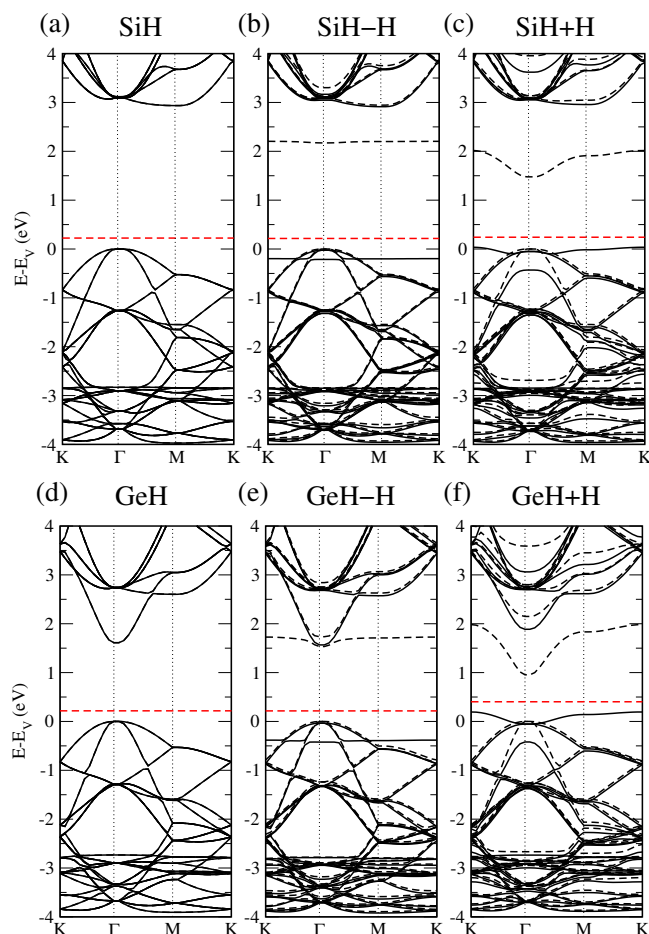

Fig. 1 (Color online) Electronic band structures for silicane [(a)–(c)] and germanane [(d)–(f)]. Parts (a) and (d) refer to the pristine system while the other panels represent the systems with lack [(b) and (e)] or excess [(c) and (f)] of hydrogen. The Fermi energy is represented by a trace (red) line. Continuous and point lines represent the spin up and spin down sub–bands, respectively.

When a nitrogen atom substitutes a Si:H (Ge:H) unit in silicane (germanane), the number of electrons does not change. In this case, three of the five electrons from the N atom form three stable bonds with Si (Ge) atoms, the other two electrons give rise to a localized state resonant with the valence band. The N–Si and N–Ge bond distances are 1.87 and 2.01 Å for N-doped silicane and germanane, respectively. The calculated formation energies are 0.72 and 1.45 eV, respectively. The smaller formation energy for N–doped silicane is in accordance with the greater stability for Si_3N_4 bulk system as compared to the Ge_3N_4. [41] The band gap value of the N-doped systems decreases when compared to the pristine systems, as can be noticed when we compare Fig.s 2 (a) and 2 (d) with

Fig.s 1 (a) and 1 (d) for silicane and germanane, respectively.

We can also observe that for N–doped silicane, the band gap changes from indirect (pristine system) to direct in the Γ point. The smaller covalent radius of the impurity (N) as compared to the host (Si) atom compresses the N–Si bond lengths with respect to the original Si–Si distances. The Si neighbors to the impurity relax inward by 0.06 Å . An increasing in the Si–Si bond lengths decreases the Si–Si bond strengths and the empty states shift to lower energies, reducing the band gap. This shift is greater in the Γ point as compared to other points (mainly for the M point) leading the CBM to be localized in the Γ point. The analysis of the charge density in the Γ point for the CBM, Fig. 3 (a), shows that it is mostly localized in the N atom and in the three Si (Ge) nearest neighbors. As can be observed in Figure 3 the electronic charge distribution is delocalized, in accordance with the great (around 1.45 eV) dispersion of the lowest unoccupied crystalline orbital (LUCO). Similar results are observed for the LUCO in N–doped germanane. We can also notice that the electronic state is mostly an anti-bonding state, there is no charge density between the N impurity and the three neighbors Si (Ge) atoms. The changes in the band gap due to a stretching in the Si–Si bonds have also been observed for silicane under strain.[42]

When a H atom is adsorbed on the N impurity the Si–N and Ge–N increase to 2.03 and 2.14 Å, respectively. The electronic band structures show that now the systems are metallic, see Fig.s 2 (b) and (e). To understand these metallic characteristics we have to analyze the total and projected electronic density of states (DOS and pDOS) for the occupied states. We observe that N_{Si-H} (N_{Ge-H}) gives rise to a localized peak in the DOS resonant with the valence band, approximately 1.0 eV from the VBM. This state is doubly occupied and localized in the N atom. Two electrons from the N atom form this state and the other three electrons complete the bonds with the nearest Si (Ge) atoms, as already discussed before. When the adsorbed H atom bonds to the impurity a strong N–H bond forms with a bonding (doubly occupied and resonant in the valence band) and an anti–bonding state (empty and resonant with the conduction band). To form these states the N–Si (N–Ge) bond strength decreases and the CBM shifts to lower energies (see Fig.s 2 (b) and (e) for silicane and germanane, respectively). To form the N–H bond one of the two electrons from the localized state bonds to the H atom and the other electron will occupy the CBM, leads to the system's metallic characteristics.

The calculated formation energy shows that the adsorption of H atom is energetically unfavorable for silicane but favorable for germanane. The formation energy of the system increases by 0.09 eV and decreases by 0.37 eV for silicane and germanane, respectively. These results indicate that in H atmosphere N_{Si} is stable while N_{Ge} is unstable, in accordance with the greater stability for the Si:N structures as compared
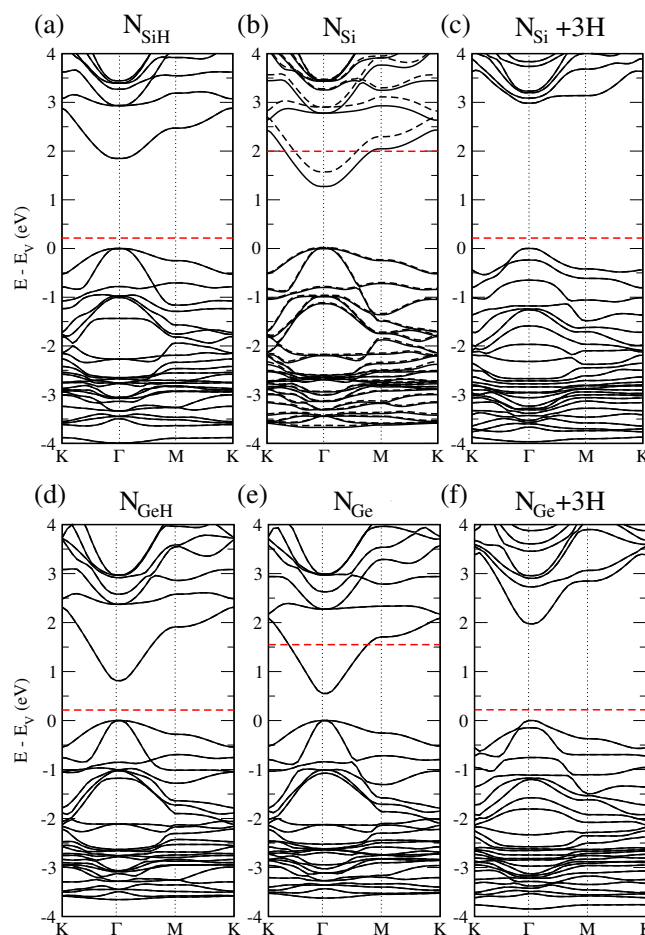

Fig. 2 (Color online) Electronic band structures for N-doped silicane [(a)-(c)] and N-doped germanane [(d)-(f)], respectively.

to similar Ge:N structures.

The same energetic trend is observed when a second H atom is adsorbed on the N atom. The formation energy increases by 0.75 eV for silicane and decreases by 0.42 eV for germanane and there are some threefold coordinated atoms. For N–doped silicane, two of the N–Si bonds are broken (the N–Si distances are 2.80 Å). The N atom bonds with a Si (bond lenght of 1.76 Å) and two H (bond distances of 1.01 Å). For germanane the scenario is quite different. We observed that only one N–Ge brokes (the N–Ge distance is 3.14 Å) and the N atom is fourfold coordinated, bond with two Ge (bond distances of 2.10 Å) and two H atoms (bond distances of 1.04 Å). For both materials the electronic band structure presents semiconductor properties with defective electronic states inside the band gap. An analysis of the charge density localization for these defective states as well as the pDOS shows that these defective levels comes from the threefold coordinated Si (Ge) atoms.

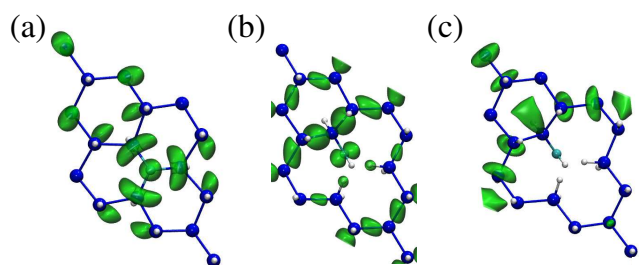We checked whether the adsorption of H atoms by the Si

Fig. 3 (Color online) Isosurfaces of the electronic charge density for electronic states for N–doped silicane. Pannel (a) represent the CBM for N_{Si} while pannel (b) and(c) are the VBM and CBM when H atoms are adsorbed in two Si atoms near the N impurity. Great (blue) and small (white) balls represent Si and H atoms, respectively. The N atom is represented by the cyan ball and the charge density isosurface (in green) used is 0.02 e/Å^3.

(Ge) atoms with a dangling bond could stabilize the defect. In fact, our first principles calculations have show that the adsorption of more two H atoms (one in each Si or Ge atom nearest to the N atom) is energetically favorable and the defective systems with adsorbed H atoms stabilize. The formation energies for these defects are -0.86 eV and -0.22 eV for silicane and germanane, respectively. The negative values indicate that this defect is thermodynamically stable, an exothermic process. However, as we have already shown in the methodology section the formation energies depends on the chemical potential used for the impurity. By using the N chemical potential for Si (Ge) from the Si_3N_4 (Ge_3N_4) bulk structure in a Si (Ge) rich growth condition we have to add the heat of formation of these structures to derives the chemical potential for the N impurity. In fact, by using the chemical for the N atom from Si_3N_4 (Ge_3N_4) the calculated formation energy for the N impurity with two H adsorbed to saturate the dangling bonds is 1.01 (-0.31) eV for silicane (germanane). In this case, we observe that this defect is not an exothermic process for silicane but it still is for germanane. The changes in the formation energies are again in accordance with the fact that the calculated heat formation for Si_3N_4 is negative (a thermodynamic stable system) while for Ge_3N_4 the calculated heat of formation is positive (a thermodynamic unstable system). The electronic band structures show that both materials are semiconductor with a direct band gap, see Fig.s 2 (c) and (f). In Figure 2 we can also notice that the symmetry of the VBM decreases (the degenerescence breaks). For silicane, the band gap is 2.98 eV and direct in the Γ point while for germanane the band gap is smaller, 1.97 eV. The greater values for the band gap when H atoms are adsorbed are in agreement with the increase in the Si–Si and Ge–Ge bond strength near the defect. In Fig. 3 (b) and (c) we show the electronic charge density of the VBM and CBM in Γ point for silicane. We can observe that these states

are delocalized but with different symmetry. The VBM is a bonding state (the charge density is mainly localized in the vicinity of the impurity) while the CBM is an anti–bonding state and the contribution from the N impurity is neglegible. We can also notice that the two bi-hydrogenated Si atoms, which are in a tetrahedral symmetry, does not contribute for the VBM and CBM. The VBM and CBM split from the pristine systems due to a lower symmetry.

When a B atom substitutes a Si:H (Ge:H) unit in silicane (germanane), the three electrons from the B atom form three stable bonds with the nearest neighbors Si (Ge) atoms. The B–Si (B–Ge) bond distances and the calculated formation energies are 2.08 (2.16) Å and 1.88 (2.05) eV, respectively. The doped system presents an empty state in the band gap, as can be seen in Fig.s 4 (a) and (c). The analysis of the electronic charge densities (Γ point) for these states (also indicate in Figure 4) shows that for germanane the charge density is localized in the impurity while for silicane there are contributions from the impurity and the three nearest Si atoms.
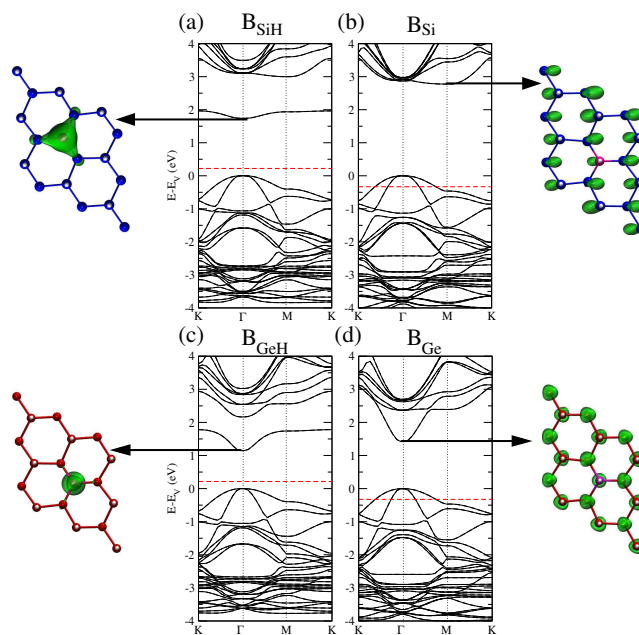

Fig. 4 (Color online) Electronic band structures for B-doped silicane [(a) and (b)] and germanane [(c) and (d)], respectively. In this Figure we also show the isosurface of the electronic charge density for the CBM. The isosurface (in green) used is 0.02 e/Å^3.

Adsorbing an H atom a strong H–B bond forms. The B atom relax outward by 0.1 Å, increasing the B–Si and B–Ge to 2.09 and 2.17 Å, respectively. The calculated formation energies indicate that the H adsorption stabilizes the system for both the materials. We have obtained formation energies of 1.17 and 1.09 eV for silicane and germanane, respectively. The analysis of pDOS shows that the new level in the band

structure, at approximately 2.2 eV below the VBM (see Fig.s 4 (b) and (d)) comes from the H–B bond. To form this doubly occupied bond an electron (hole) is removed (created) from (in) the VBM. Due to the high doping concentration the Fermi energy enters in the valence band, giving a metallic characteristics to the system, see Fig.s 4 (b) and (d). In a more realistic situation (low concentration of impurities) the metallicity must disappear and the system with a B impurity must be a p–type semiconductor. We can also observe that the main features of the CBM is preserved. In Figure 4 we also show the isosurface of the electronic charge density for the CBM when a B atom substitutes a Si or Ge atom. As can be noticed the CBM is delocalized and very similar to the pristine system.

The adsorption of a second H atom by the B impurity lowers the formation energies, the calculated formation energies are 0.68 and 0.79 eV for silicane and germanane, respectively. However, we have obtained two almost degenerated configurations for these defects, which are shown in Figure 5. The energy difference between the two configurations are 0.11 and 0.09 eV for germanane and silicane, respectively. In the metastable configuration (parts (b) and (d)) the two adsorbed H bond with the B atom, which is fivefold coordinated. The B–Si (B–Ge) bond lenght increases by 0.13 (0.18) Å, decreasing the bond strenght between the B atom and the nearest Si (Ge) neighbors. In the most stable configuration (parts (a) and (c)) the B impurity and one Si (Ge) increase their relative distance significantly while the distance to other Si (Ge) neighbor almost unchanges; at same time the adsorbed H moves onto a bond center (BC) position, thus avoiding the formation of dangling bonds.

It is worth pointing out that the presence of a H atom in the BC ("bridge configuration") and the bond stretching was already observed for the excited state in Si nanoparticles.[43] The bond stretching in the surface of Si nanoparticles[44] and in Si nanosheet[45] gives rise to localize states ("trapped excitons") in the extremum of valence and conduction bands and are used to explain the photoluminescent properties in these nanomaterials. Details were shown in previous works.[43,44]

In Figure 6 we can notice that in both configurations the CBM moves to lower energies and independently of the configuration the systems are semiconductor with a direct band gap in the Γ point. The band gaps for silicane (germanane) are 2.44 (1.43) and 2.36 (1.22) eV, for the bridge and the metastable configuration, respectively. In Figure 6 we also show the electronic charge density for the CBM (Γ point) for the two geometric configurations. As can be observed, in the bridge configurations the CBM mainly comes from the two atoms of the bridge while in the metastable configuration the CBM mostly comes from the two atoms Si (Ge) atoms bonded with the fivefold coordinated B atom.

It is worth pointing out that our first principles calculations for the N and B impurity indicate that these impurities
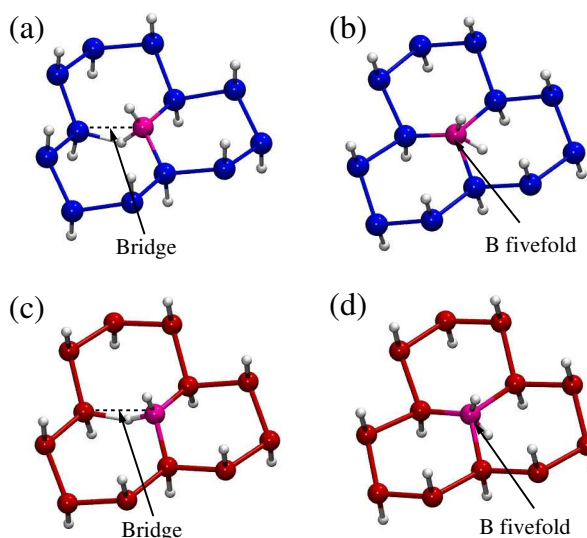

Fig. 5 (Color online) Sketching of the two possible configurations when two H atoms are adsorbed on the B_{Si} [panels (a) and (b)] and B_{Ge} [panels (c) and (d)], respectively.

have lower formation energies in silicane and germanane as compared to graphane.[7] Similar to graphane the N-doped (B-doped) shifts the Fermi energy into the CBM (VBM) giving n-type (p-type) properties to these two 2D systems. We have also noticed that these impurities have similar formation energies in hydrogenated and non hydrogenated Si and Ge 2D systems. We have obtained formation (binding) energies of 0.34 (-5.35) eV and 0.56 (-3.99) eV for B_{Si} and N_{Si}, respectively. These binding energies are in accordance with the calculated values by Sivek *et al.*[17] where the local density approximation (LDA) was used. For germanene the formation (binding) energies are 1.28 (-4.56) and 1.41 (-3.30) eV for B_{Ge} and N_{Ge}, respectively. The higher (lower) formation (binding) energies indicate that the impurity is more likely in silicane then germanane.

The electronic and optical properties of B absorbed in silicane (B_{Si}) have already been studied by Pi *et al.*[46] within the GGA approximation. They observed that the Fermi energy enters in the valence band and the band gap changes from indirect to direct. Our GGA calculations show that the energy difference between direct (in the Γ point) and indirect band gap for a boron concentration of 5.6 % is negligible, in agreement with their calculations. However, when the electronic band structure is obtained using the HSE06 functional we obtained an indirect band gap; see Fig. 4 (b). The energy difference between direct and indirect band gap is 0.09 eV and the charge density analysis for the CBM (in the M point) shows that CBM is delocalized and very similar to the pristine system (see Fig. 4 (b)). However, for N–doped the impurity
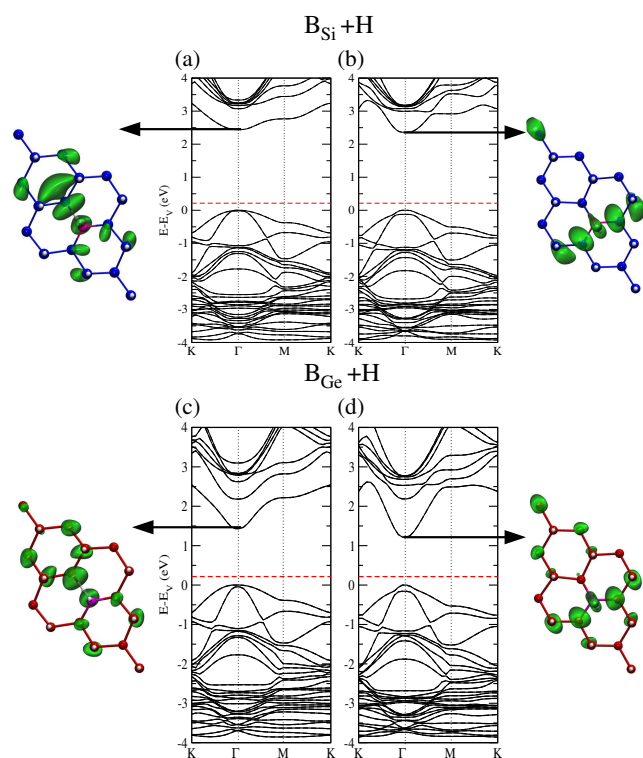
B$_{Si}$ +H
(a) (b)

B$_{Ge}$ +H
(c) (d)

Fig. 6 (Color online) Electronic band structures for the adsorption of two H atoms on B–doped silicane [(a) and (b)] and germanane [(c) and (d)], respectively. Panels (a) and (c) represent the band structures for the most stable configuration while panels (b) and (d) are the band structures for the metastable configuration. In this figure we also show the isosurfaces of the electronic charge density for the CBM. The isosurface (in green) used is 0.02 e/Å^3.

changes the CBM characteristics (the CBM is mainly localized in the impurity and in the three neighbors atoms) and a direct band gap is observed. For functionalized silicene and germanane with other chemical species adsorbed (for example fluorinated silicene and germanane) the same trend in the electronic properties are expected. However, we have to considered that the band gap depends on the chemical atomic specie adsorbed. For example for fluorinated system the band gap are smaller than the hydrogenated systems while the binding energies are greater,[35,38] then certainly the formation energies must increase and the localization of the defective electronic levels (inside the band gap or resonant with the valence and conduction bands) depends on the band gap value.

4 Conclusions

Our first principles calculations have been showed that the chemical doping of silicane and germanane by N and B impurity is a powerful feature to functionalize these nanostructures.

We have found that these impurities have lower formation energies in Si and Ge 2D systems as compared to their counterparts in graphane. When H atoms are adsorbed on the N impurity this defect stabilizes. The N impurity stretches the Si-Si (Ge-Ge) bond decreasing the band gap value and for silicane the band gap changes from indirect to direct (in the Γ point). B$_{SiH}$ and B$_{GeH}$ give rise to a localized electronic state in the band gap. The adsorption of one H atom by the impurity (B or N) leads silicane and germanane with *p* (B impurity) and *n* (N impurity) semiconductor properties. However, the adsorption of a second H atom stabilizes the system and both materials present direct band gap in the Γ point.

References

1 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos and A. A. Firsov, *Nature*, 2005, **438**, 197.

2 A. K. Geim and K. S. Novoselov, *Nature Mat.*, 2007, **6**, 183.

3 L. S. Panchakarla, K. S. Subrahmanyam, S. K. Saha, A. Govindaraj, H. R. Krishnamurthy, U. V. Waghmare and C. N. R. Rao, *Adv. Mater.*, 2009, **21**, 4726.

4 H. Wang, T. Maiyalagan and X. Wang, *ACS Catalysis*, 2012, **2**, 781.

5 J. Dai, J. Yuan and P. Giannozzi, *App. Phys. Lett.*, 2009, **95**, 232105.

6 J. O. Sofo, A. S. Chaudhari and G. D. Barber, *Phys. Rev. B.*, 2007, **75**, 153401.

7 Y. Wang, Y. Ding, S. Shi and W. Tang, *Appl. Phys. Lett.*, 2011, **98**, 163104.

8 P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet and G. L. Lay, *Phys. Rev. Lett.*, 2012, **108**, 155501.

9 B. Lalmi, H. Oughaddou, H. Enriquez, A. Kara, S. Vizzini, B. Ealet and B. Aufray, *Appl. Phys. Lett.*, 2010, **97**, 223109.

10 M. E. Dávila, L. Xian, S. Cahangirov, A. Rubio and G. Le Lay, *New J. of Phys.*, 2014, **16**, 095002.

11 W. Wei, Y. Dai, B. Huang, M.-H. Whangbo and Timo Jacob, *J. Phys. Chem. Lett.*, 2015, **6**, 1065.

12 Y. Ding and Y. Wang, *Appl. Phys. Lett.*, 2012, **100**, 083102.

13 V. Zlyomi, J. R. Wallbank and V. I. Falko, *2D Mater.*, 2014, **1**, 011005.

14 Q. Peng and S. De, *Nanoscale*, 2014, **6**, 12071.

15 Y. Ma, Y. Dai, W. Wei, B. Huang and M.-H. Whangbo, *Sci. Rep.*, 2014, **4**, 7297.

16 P. Rubio-Pereda and N. Takeuchi, *J. Chem. Phys.*, 2013, **138**, 194702.

17 J. Sivek, H. Sahin, B. Partoens and F. M. Peeters, *Phys. Rev. B*, 2013, **87**, 085444.

18 L. C. L. Y. Voon, E. Sandberg, R. S. Aga and A. A. Farajian, *Appl. Phys. Lett.*, 2010, **97**, 163114.

19 M. Houssa, E. Scalise, K. Sankaran, G. Pourtois, V. V. Afanas'ev and A. Stesmans, *Appl. Phys. Lett.*, 2011, **98**, 223107.

20 S.-s. Li, C.-w. Zhang, W.-x. Ji, F. Li, P.-j. Wang, S.-j. Hu, S.-s. Yan and Y.-s. Liu, *Phys. Chem. Chem. Phys.*, 2014, **16**, 15968.

21 H. Sahin and F. M. Peeters, *Phys. Rev. B*, 2013, **87**, 085423.

22 T. Hussain, S. Chakraborty and R. Ahuja, *Chemphyschem*, 2013, **14**, 3463.

23 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev.Lett.*, 1996, **77**, 3865.

24 J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2003, **118**, 8207.

25 J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2006, **124**, 219906.

26 J. Paier, M. Marsman, K. Hummer, G. Kresse, I. Gerber and J. G. Ángyán, *J. Chem. Phys.*, 2006, **124**, 154709.

27 K. Hummer, J. Harl and G. Kresse, *Phys. Rev B*, 2009, **80**, 115205.

28 E. Bianco, S. Butler, S. Jiang, O. D. Restrepo, W. Windl and J. E. Goldberger, *ACS Nano*, 2013, **7**, 4414.

29 Z. Liu, Z. Lou, Z. Li, G. Wang, Z. Wang, Y. Liu, B. Huang, S. Xia, X. Qin, X. Zhanga and Y. Daib, *Chem. Commun.*, 2014, **50**, 11046.

30 G. Kresse and J. Furthmüller, *Comput. Mat. Sci.*, 1996, **6**, 15.

31 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.

32 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953.

33 G. Kresse and J. Joubert, *Phys. Rev. B*, 1999, **59**, 1758.

34 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188.

35 J. C. Garcia, D. B. de Lima, L. V. C. Assali and J. F. Justo, *J. Phys. Chem. C*, 2011, **115**, 13242.

36 Y. Ding and Y. Wang, *Appl. Phys. Lett.*, 2012, **100**, 083102.

37 W. Wei, Y. Dai, B. Huanga and T. Jacob, *Phys. Chem. Chem. Phys.*, 2013, **15**, 8789.

38 L. Hu, and J. Zhao and J. Yang, *J. Phys.: Condens. Matter*, 2014, **26**, 335302.

39 M. Niu, D. Cheng and D. Cao, *Sci. Rep.*, 2014, **4**, 4810.

40 O. D. Restrepo, R. Mishra, J. E. Goldberger and W. Windl, *J. Appl. Phys.*, 2014, **115**, 033711.

41 Our first principles calculation show that Si_3N_4 is stable material with a negative heat for formation of -7.49 eV while Ge_3N_4 is unstable with a positive heat for formation of 0.13 eV.

42 H. Shu, S. Wang, Y. Li, J. Yip and J. Wang, *J. Chem. Phys.*, 2014, **141**, 064707.

43 R. J. Baierle, M. J. Caldas, E. Molinari and S. Ossicini, *Solid State Commun.*, 1997, **102**, 545.

44 G. Alla, C. Delerue and M. Lannoo, *Phys. Rev. Lett.*, 1996, **76**, 2961.

45 Q. Wu, X. Wang, T. A. Niehaus and R. Zhang, *J. Phys. Chem. C*, 2014, **118**, 20070.

46 X. Pi, Z. Ni, Y. Liu, Z. Ruan, M. Xu and D. Yang, *Phys. Chem. Chem. Phys.*, 2015, **17**, 4146.