Boron and nitrogen impurities in SiC nanoribbons: an ab initio investigation

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Abstract

Using ab initio calculations based on density-functional theory we have performed a theoretical investigation of substitutional boron and nitrogen impurities in silicon carbide (SiC) nanoribbons. We have considered hydrogen terminated SiC ribbons with zigzag and armchair edges. In both systems we verify that the boron and nitrogen atoms energetically prefer to be localized at the edges of the nanoribbons. However, while boron preferentially substitutes a silicon atom, nitrogen prefers to occupy a carbon site. In addition, our electronic-structure calculations indicate that (i) substitutional boron and nitrogen impurities do not affect the semiconducting character of the armchair SiC nanoribbons, and (ii) the half-metallic behavior of the zigzag nanoribbons is maintained in the presence of substitutional boron impurities. In contrast, nitrogen atoms occupying edge carbon sites transform half-metallic zigzag nanoribbons into metallic systems.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Silicon carbide (SiC) nanostructures have attracted much interest in recent years because they combine the excellent properties of SiC bulk [1–3] (wide band gap, high thermal conductivity, high breakdown electric field, thermal stability, high electronic mobility, and others) with quantum-size effects. This combination makes SiC nanostructures interesting materials for nanotechnology applications and nanoscale engineering [4].

Recently, increasing attention has been paid to the planar structures of SiC. Although silicon prefers sp³ instead of sp² hybridization, SiC nanoribbons (SiCNRs) have been successfully synthesized [5] and first-principles calculations have shown that SiC has a stable two-dimensional honeycomb structure, similar to graphene [6–8]. In addition, recent ab initio studies revealed that the monolayer SiC sheet is semiconducting with a band gap of about 2.55 eV [6–8], while armchair SiCNRs are nonmagnetic semiconductors (with a wide band gap for all widths) [9, 10], and zigzag SiCNRs narrower than 4 nm present half-metallic behavior without applied external electric field or chemical modifications [9–11]. This feature makes narrow zigzag SiCNRs promising candidates for spintronic applications.

The great potential of SiC nanoribbons for future applications in spintronics stimulates detailed studies of the effects of impurities and defects in their electronic properties. In particular, the case of SiC nanoribbons doped with boron and nitrogen atoms is an important issue to investigate, since B and N are common contaminants in SiC bulk, acting as p- and n-type dopants, respectively. Moreover, it is well known that substitutional boron and nitrogen impurities in zigzag graphene nanoribbons break the spin degeneracy of the transmittance channels, and transform metallic nanoribbons into semiconducting systems [12–15].

In this work we have performed a theoretical investigation, using ab initio calculations based on density-functional theory, of substitutional boron and nitrogen impurities in armchair and zigzag SiC nanoribbons. Our results indicate that the boron and nitrogen atoms energetically prefer to be localized at the edges of both nanoribbons. However, while boron preferentially substitutes a silicon atom, nitrogen prefers to occupy a carbon site. In addition, we verify that substitutional B and N impurities do not affect the semiconducting character of armchair SiCNRs, although the spin degeneracy of the band structure is broken. On the other hand, we observe different effects of these impurities on the half-metallic behavior of
Figure 1. Structural models of (a) 4-ZSiCNR and (b) 7-ASiCNR, indicating the substitutional sites investigated. Odd (even) numbers correspond to Si (C) sites.

2. Method of calculation

The ab initio calculations presented in this work were carried out within the framework of density-functional theory (DFT) [16], using the SIESTA code [17]. We employed the generalized gradient approximation as implemented by Perdew, Burke and Ernzerhof (GGA-PBE) [18] for the exchange-correlation functional, and norm-conserving fully separable pseudopotentials [19] to treat the electron–ion interactions. The Kohn–Sham orbitals were expanded in a linear combination of numerical pseudoatomic orbitals [20] using a split-valence double-zeta basis set with polarization functions (DZP) [21].

We have considered hydrogen-passivated zigzag and armchair SiCNRs with widths $W = 4$ (4-ZSiCNR) and $W = 7$ (7-ASiCNR), respectively. The 4-ZSiCNR and 7-ASiCNR structures were modeled within the supercell approach with 40 and 54 atoms (including hydrogen atoms) in the unit cell, respectively. The structural models of 4-ZSiCNR and 7-ASiCNR, indicating the substitutional sites investigated, are shown in figure 1. A vacuum region of about 20 Å along the nonperiodic directions was employed to avoid interactions between two neighboring ribbons. All the atomic positions were relaxed during the geometry optimization until the Hellman–Feynman forces were below 0.01 eV Å$^{-1}$. The Brillouin zone was sampled using the Monkhorst–Pack scheme [22] with a $11 \times 1 \times 1$ grid for the total-energy calculations and a $120 \times 1 \times 1$ mesh for the electronic-structure calculations. The convergence of our total-energy results with respect to the number of $k$-points was verified.

In each system the energetic stability of the impurities was determined by comparing their formation energies [23, 24]

$$\Omega = E_T - \sum_i N_i \mu_i,$$

where $E_T$ is the total energy of the structure, $\mu_i$ is the chemical potential of the atomic species $i$, and $N_i$ is the number of $i$ atoms in the structure. The chemical potentials of Si and C are restricted to the ranges

$$-\Delta H(\text{SiC}) + \mu_{\text{Si}}^{\text{bulk}} \leq \mu_{\text{Si}} \leq \mu_{\text{Si}}^{\text{bulk}},$$

and

$$-\Delta H(\text{SiC}) + \mu_{\text{C}}^{\text{bulk}} \leq \mu_{\text{C}} \leq \mu_{\text{C}}^{\text{bulk}},$$

where $\Delta H(\text{SiC})$ is the SiC formation heat.

The (relative) formation energies presented in this work were calculated assuming the Si/C stoichiometric condition

$$\mu_{\text{C, Si}} = \mu_{\text{C, Si}}^{\text{bulk}} - \frac{1}{2} \Delta H(\text{SiC}).$$

3. Results and discussion

Initially we examined the equilibrium geometries and the electronic structures of pristine 4-ZSiCNR and 7-ASiCNR. We found optimized Si–C bond lengths from 1.77 to 1.84 Å in 4-ZSiCNR, and from 1.75 to 1.81 Å in 7-ASiCNR. In both systems, the Si–H and C–H bond lengths were about 1.52 and 1.11 Å, respectively. These values are in good agreement with previous calculations for SiC nanoribbons [10], sheets [6] and nanotubes [25, 26]. By analyzing the electronic structure in figure 2 we observed that pristine 4-ZSiCNR (figure 2(a)) presents a half-metallic behavior, with a semiconducting spin-up channel (band gap of 0.22 eV at the $\Gamma$ point) and a metallic

zigzag SiCNRs: the half-metallicity of the nanoribbons is maintained in the presence of substitutional B impurities, whereas zigzag SiCNRs become metallic when doped with N atoms.

1 According to [9, 10] the width $W$ of a SiCNR is defined as the number of zigzag chains across the ribbon width for ZSiCNRs, or the number of dimer lines for ASiCNRs.
spin-down channel. On the other hand, pristine 7-ASiCNR
(figure 2(b)) is a semiconductor with a direct band gap of
2.22 eV (at the Γ point) for both spin-up and spin-down
channels.

Considering one B or N atom per supercell we investigated
eight substitutional sites (sites labeled from 1 to 8 in figure 1)
in both 4-ZSiCNR and 7-ASiCNR. In B-doped nanoribbons (B/4-
ZSiCNR and B/7-ASiCNR) the formation energy of each B
configuration was compared with that of the B\textsubscript{Si} configuration:
\[ \Delta \Omega_{\text{B}} = \Omega(\text{B}_{\text{Si}}) - \Omega(\text{B}_{\text{Si}}) . \]

Table 1. Relative formation energies (in eV) of substitutional B
(ΔΩ\textsubscript{B}) and N (ΔΩ\textsubscript{N}) impurities in 4-ZSiCNR and 7-ASiCNR. ΔΩ\textsubscript{B}
and ΔΩ\textsubscript{N} are given by equations (5) and (6). The occupation sites
indicated in figure 1.

| Sites       | 4-ZSiCNR | 7-ASiCNR |
|-------------|----------|----------|
| Si\textsubscript{i} | 0.00     | 1.90     |
| C\textsubscript{2}  | 1.16     | 1.35     |
| Si\textsubscript{5} | 0.61     | 3.88     |
| C\textsubscript{4}  | 2.01     | 1.37     |
| Si\textsubscript{8} | 1.24     | 4.30     |
| C\textsubscript{6}  | 2.30     | 0.74     |
| Si\textsubscript{1} | 1.22     | 2.61     |
| C\textsubscript{8}  | 1.95     | 0.00     |

Here \( i \in \{1, \ldots, 8\} \), \( A \in \{\text{Si, C}\} \) and \( \text{B}_{\text{Si}} \) denotes the
configuration in which B substitutes Si at the site \( i \). In the
N/4-ZSiCNR and N/7-ASiCNR systems, we compared each
N\textsubscript{A} configuration with that of the N\textsubscript{Si} configuration using
\[ \Delta \Omega_{\text{N}} = \Omega(\text{N}_{\text{Si}}) - \Omega(\text{N}_{\text{Si}}) . \]

Our results for the relative formation energies \( \Delta \Omega_{\text{B}} \) and \( \Delta \Omega_{\text{N}} \)
are summarized in table 1. In this case, positive values of \( \Delta \Omega_{\text{B}} \)
(\( \Delta \Omega_{\text{N}} \)) indicate that \( \text{B}_{\text{Si}} \) (\( \text{N}_{\text{Si}} \)) is energetically more favorable
than \( \text{B}_{\text{Si}} \) (\( \text{N}_{\text{Si}} \)).

As can be seen in table 1, \( \text{B}_{\text{Si}} \) and \( \text{N}_{\text{Si}} \) are the most
favorable configurations in both 4-ZSiCNR and 7-ASiCNR.
This indicates that the B and N atoms energetically prefer
to be localized at the edges of the nanoribbons. However,
while B preferentially occupies a Si site, N prefers to substitute
a C atom. Among the B\textsubscript{C} configurations, \( \text{B}_{\text{Si}} \) are the most
stable in 4-ZSiCNR and 7-ASiCNR, respectively.
However, at the Si/C stoichiometric condition, \( \text{B}_{\text{Si}} \) is energetically less favorable than \( \text{B}_{\text{Si}} \) by 1.16 (0.89) eV in
4-ZSiCNR (7-ASiCNR). Extending the calculations of the
formation energies \( \Omega(\text{B}_{\text{C}}) \), \( \Omega(\text{B}_{\text{Si}}) \) and \( \Omega(\text{B}_{\text{Si}}) \) to different
values of \( \mu_\text{C} \) and \( \mu_\text{Si} \), we verify that \( \Omega(\text{B}_{\text{Si}}) < \Omega(\text{B}_{\text{Si}}) \) and
\( \Omega(\text{B}_{\text{Si}}) > \Omega(\text{B}_{\text{Si}}) \) within the limits given by the expressions (2)
and (3) with \( \Delta H(\text{SiC}) = 0.72 \text{ eV} \).\(^2\) These results indicate
that B\textsubscript{C} is not expected to occur in either armchair or zigzag
SiCNRs. Performing the same analysis for N impurities, we
observe that \( \text{N}_{\text{Si}} \) is the most likely configuration among the N\textsubscript{Si}
configurations in both 4-ZSiCNR and 7-ASiCNR, but \( \text{N}_{\text{Si}} \) is
less favorable than \( \text{N}_{\text{Si}} \) within the allowed ranges for \( \mu_\text{C} \) and
\( \mu_\text{Si} \) (expressions (2) and (3)). Thus, it is not expected that N
atoms occupy Si sites in SiCNRs.

The energetic preference of the B (N) atoms for Si (C) sites
at the stoichiometric condition has been also observed in SiC
nanotubes [27] and nanowires [28]. In these nanostructures,
like in SiCNRs, the formation of \( \text{N}_{\text{Si}} \) is not expected to occur.
Nevertheless, in SiC nanotubes and nanowires B\textsubscript{C} becomes

\(^2\) Note that the calculations of \( \Delta \Omega_{\text{B}} \) and \( \Delta \Omega_{\text{N}} \) at the Si/C stoichiometric
condition do not depend on the value of \( \Delta H(\text{SiC}) \). For example, using
equations (1) and (4) we obtain
\[ \Delta \Omega_{\text{B}} = \Omega(\text{B}_{\text{Si}}) - \Omega(\text{B}_{\text{Si}}) = E_T(\text{B}_{\text{Si}}) - E_T(\text{B}_{\text{Si}}) + \mu_\text{C}^{\text{bulk}} - \mu_\text{Si}^{\text{bulk}} \]

at the stoichiometric condition.
more likely than $B_{\text{Si}}$ at the limit $\mu_{\text{Si}} = \mu_{\text{Si}}^{\text{bulk}}$ and $\mu_{\text{C}} = \mu_{\text{C}}^{\text{bulk}} - \Delta H (\text{SiC})$ [27, 28].

We next examined the equilibrium geometries of the most likely configurations ($B_{1}\text{Si}$ and $N_{8}\text{C}$) in 4-ZSiCNR and 7-ASiCNR. The variations in the Si–C bond lengths with respect to the pristine structures were less than 0.03 Å in the $B_{1}\text{Si}/4$-ZSiCNR, $N_{8}\text{C}/4$-ZSiCNR and $B_{1}\text{Si}/7$-ASiCNR systems, and less than 0.05 Å in $N_{8}\text{C}/7$-ASiCNR. As depicted in figure 3, we found (i) B–C and B–H bond lengths of 1.57 and 1.24 Å (1.54 and 1.24 Å), respectively, in the $B_{1}\text{Si}/4$-ZSiCNR ($B_{1}\text{Si}/7$-ASiCNR) system, and (ii) N–Si and N–H bond lengths of 1.75 and 1.03Å, respectively, in $N_{8}\text{C}/4$-ZSiCNR. In the $N_{8}\text{C}/7$-ASiCNR structure, besides the N–Si bond lengths of 1.72 and 1.80 Å, we also observed that the Si$_{1}$ atom (see figure 1(b)) moves upward (along the $z$ direction) by 0.28 Å with respect to the pristine 7-ASiCNR, while the hydrogen atom bonded to Si$_{1}$ is displaced by 0.77 Å in the opposite direction. A similar behavior is found in $N_{8}\text{C}/7$-ASiCNR (the second most stable configuration for N/7-ASiCNR), where the Si$_{1}$ and H atoms are displaced by 0.25 and 0.87 Å, respectively. By constraining the relaxation of the $N_{8}\text{C}/7$-ASiCNR and $N_{8}\text{C}/7$-ASiCNR systems along the $z$ direction (the atoms are free to relax in the $x$ and $y$ directions), we verify that their total energies are increased by 0.60 and 0.62 eV, respectively, in comparison with the fully relaxed structures. Even so, $N_{8}\text{C}$ remains the most favorable configuration for N/7-ASiCNR.

Figures 4 and 5 display the electronic band structures and the projected density of states (PDOS) of $B_{1}\text{Si}/4$-ZSiCNR, $N_{8}\text{C}/4$-ZSiCNR, $B_{1}\text{Si}/7$-ASiCNR, and $N_{8}\text{C}/7$-ASiCNR. In figure 4(a) we observe that the $B_{1}\text{Si}/4$-ZSiCNR system presents half-metallic characteristics: the spin-up channel is semiconducting, with a direct band gap of 1.30 eV at the $\Gamma$ point, and the spin-down channel is metallic, with an energy band crossing the Fermi level ($E_{F}$) near to the X point. This result indicates that one substitutional B impurity per supercell does not affect the half-metallic behavior of 4-ZSiCNR. The PDOS of the $B_{1}\text{Si}/4$-ZSiCNR system (figure 5(a)) reveals that the partially occupied spin-down electronic state, as well as the highest-occupied spin-up state, is composed of C 2p and Si 3d orbitals, without contributions from $B_{1}\text{Si}$. The B 2p orbitals are localized below ($E_{F} - 0.5$ eV) and above ($E_{F} + 0.9$ eV).

As depicted in figures 4(b) and 5(b), the $N_{8}\text{C}/4$-ZSiCNR system is metallic, with degenerate spin-up and spin-down channels. The partially occupied state comes mainly from the Si 3p orbitals localized along the zigzag edge opposite to $N_{8}\text{C}$. The occupied state situated between 1.2 and 1.4 eV below the Fermi level is mostly composed of C 2p and Si 3d orbitals, without contributions from $B_{1}\text{Si}$. The B 2p orbitals are localized below ($E_{F} - 0.5$ eV) and above ($E_{F} + 0.9$ eV).
Figures 4(c) and (d) show that the semiconducting character of pristine 7-ASiCNR is maintained in the presence of substitutional B and N impurities, but the spin degeneracy of the band structure is broken. The $B_{1}^{1}/7$-ASiCNR system (figure 4(c)) presents a direct band gap of 2.17 eV (at the $\Gamma$ point) for the spin-up channel and an indirect band gap of 0.39 eV for the spin-down channel. We found an unoccupied spin-down state lying between 0.1 and 0.3 eV above the Fermi level. This state consists mainly of B 2p, C 2p, Si 3p and Si 3d orbitals (figure 5(c)). In $N_{8}^{8}/7$-ASiCNR (figure 4(d)), both spin-up and spin-down channels exhibit semiconducting characteristics, with direct band gaps of 1.34 eV (at the X point) and 2.15 eV (at the $\Gamma$ point), respectively. The highest-occupied spin-up state is very localized and lies at around 0.6 eV below the Fermi level. The PDOS of $N_{8}^{8}/7$-ASiCNR (figure 5(d)) indicates that this state is mainly composed of Si 3p, Si 3d and N 2p orbitals, and of the 2p orbitals of the inner C atoms. We verified that the C 2p orbitals localized along the edges do not contribute to this electronic state.

4. Conclusions

In summary, we performed a theoretical investigation, using *ab initio* calculations, of substitutional B and N impurities...
in SiCNRs. In both ASiCNRs and ZSiCNRs we found an energetic preference for B and N atoms occupying edge sites. However, we verified that B preferentially substitutes a Si atom, whereas N prefers to occupy a C site. We also observed that the formation of B\(_2\)C and N\(_2\)Si is not expected to occur in SiCNRs. In addition, our electronic-structure calculations revealed that B and N impurities have different effects on the electronic character of SiCNRs. We observed that (i) substitutional B and N impurities do not affect the semiconducting behavior of ASiCNRs, and (ii) the half-metallicity of ZSiCNRs is maintained in the presence of substitutional B atoms. In contrast, we verified that half-metallic ZSiCNRs become metallic when doped with N atoms.

These results suggest that the electronic properties of SiCNRs can be controlled by B- and N-doping processes.

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**References**

[1] Choyke W J, Matsunami H and Pensl G (ed) 2004 *Silicon Carbide: Recent Major Advances* (Berlin: Springer)

[2] Madar R 2004 *Nature* 430 974

[3] Masri P 2002 *Surf. Sci. Rep.* 48 1

[4] Mélinon P, Masenelli B, Tournus F and Perez A 2007 *Nature Mater.* 6 479

[5] Zhang H, Ding W, He K and Li M 2010 *Nanoscale Res. Lett.* 5 1264

[6] Sahin H, Cahangirov S, Topsakal M, Bekaroglu E, Akturk E, Senger R T and Ciraci S 2009 *Phys. Rev. B* 80 155453

[7] Yu M, Jayanthi C S and Wu S Y 2010 *Phys. Rev. B* 82 075407

[8] Bekaroglu E, Topsakal M, Cahangirov S and Ciraci S 2010 *Phys. Rev. B* 81 075433

[9] Sun L, Li Y, Li Z, Li Q, Zhou Z, Chen Z, Yang J and Hou J G 2008 *J. Chem. Phys.* 129 174114

[10] Zhang J-M, Zheng F-L, Zhang Y and Ji V 2010 *J. Mater. Sci.* 45 3259

[11] Lou P and Lee J Y 2009 *J. Phys. Chem. C* 113 12637

[12] Martins T B, Miwa R H, Silva A J R and Fazzio A 2007 *Phys. Rev. Lett.* 98 196803

[13] Martins T B, Silva A J R, Miwa R H and Fazzio A 2008 *Nanoscale Res. Lett.* 8 2293

[14] Rocha A R, Martins T B, Fazzio A and Silva A J R 2010 *Nanotechnology* 21 345202

[15] Sodi F C, Csányi G, Piscanec S and Ferrari A C 2008 *Phys. Rev. B* 77 165427

[16] Hohenberg P and Kohn W 1964 *Phys. Rev.* 136 B864

[17] Soler J M, Artacho E, Gale J D, García A, Juncosa J, Ordejón P and Sánchez-Portal D 2002 *J. Phys.: Condens. Matter* 14 2745

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

[19] Troullier N and Martins J L 1991 *Phys. Rev. B* 43 1993

[20] Sankey O F and Niklewski D J 1989 *Phys. Rev. B* 40 3979

[21] Artacho E, Sánchez-Portal D, Ordejón P, García A and Soler J M 1999 *Phys. Status Solidi b* 215 809

[22] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* 13 5188

[23] Sabisch M, Krüger P and Pollmann J 1997 *Phys. Rev. B* 55 10561

[24] Northrup J E and Zhang S B 1993 *Phys. Rev. B* 47 6791

[25] Menon M, Richter E, Mavrodonakis A, Froudakis G and Andriotis A N 2004 *Phys. Rev. B* 69 115322

[26] Zhao M W, Xia Y, Zhang R Q and Lee S-T 2005 *J. Chem. Phys.* 122 214707

[27] Gali A 2006 *Phys. Rev. B* 73 245415

[28] Oliveira I S S and Miwa R H 2009 *Phys. Rev. B* 79 085427