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Role of hydrogen adsorption on the carbon terminated β-SiC(100)-c(2 × 2) surface structure: a theoretical approach

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Abstract

The role of hydrogen adsorption on different clean surface models for the carbon terminated β-SiC(100)-c(2 × 2) surface structure is investigated through the use of *ab initio* calculations. The structural and electronic effect of hydrogen atoms bonded to carbon and/or silicon dimers is specifically considered and compared with the results for a clean surface model. The presence of adsorbed hydrogen atoms affects the atomic equilibrium positions, as well as electronic properties, of the atoms of the clean structure. These last properties are altered in different directions if the adsorption occurs in one or the other of the two investigated models. The changes in both structural and electronic properties were evaluated and compared with those of the clean surface. From our obtained results, a possible metallization, as a result of hydrogen adsorption, is theoretically postulated to occur in a similar way to what occurs with the silicon terminated β-SiC(100)(3 × 2) surface.

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

1. Introduction

Silicon carbide, as a result of its great potential for technological applications in several devices, has attracted much experimental and theoretical attention. The study of the structural and electronic properties of its surfaces is of particular importance, and the cubic 3C-SiC(100) and hexagonal 6H-SiC(0001) polytypes are the most important ones. Great effort from both experimental and theoretical sides has been put forth to determine the structure of the cubic surfaces, as a result of a large variety of reconstructions [1–3], which can be either Si or C terminated [4–8]. A lot of experimental work has been done on the (2 × 1) and (3 × 2) Si-terminated β-SiC(100) surfaces [9–13] and also on the c(2 × 2) carbon terminated surface [12, 14, 17]. This last phase has structural characteristics that were initially considered to be dependent on the preparation process, where the presence or absence of hydrogen was believed to play an important role [12, 15]. Of particular importance were the dimer-row (DR), staggered-dimer (SD) and bridging-dimer (BD) models [16]. The controversy about the most stable β-SiC(100) clean structure appears to have been reconciled [16, 17], although there are still small differences in the energies associated with the different equilibrium positions for different models [16]. This small difference in energy for the clean surface models provides justification for considering the hydrogen adsorption effects in different models for the carbon terminated β-SiC(100) surface.

The semiconductor surfaces are known to be susceptible to chemical passivation via the use of an atom, like hydrogen, to remove dangling bonds [18, 19]. These surfaces usually become saturated by the presence of a monovalent atom and, as a consequence, the surface states are removed from the gap [20]. However, it was reported that such hydrogen adsorption may also lead to metallization under certain conditions [13]. This experimental observation for the β-SiC(100)(3 × 2) surface has motivated theoretical calculations for interpreting this unusual phenomenon [21–23]. These results have suggested the possibility of exploring

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a similar phenomenon coming from hydrogen adsorbed on other β-SiC(100) reconstructed surfaces, such as the carbon terminated β-SiC(100)-c(2 × 2). A comparison has also been made between these calculations and previous theoretical calculations [24, 25] of hydrogen bonded to such a surface.

In this paper the results of *ab initio* theoretical calculations on the effects of hydrogen adsorption in different models for the carbon terminated β-SiC(100)-c(2 × 2) surface are presented. This is done both for the SD and for the BD models. The possibility of hydrogen adsorption on the most external carbon and/or silicon atoms is investigated by considering different quantities of hydrogen. Section 2 presents the theoretical methods employed in the calculations and section 3 contains the results obtained and a comparative discussion. The final section of the paper summarizes the conclusions.

2. Theoretical model and methodology

The geometry optimization and the calculation of energies and electronic properties were performed by using the density-functional theory (DFT) [26, 27] within the generalized gradient approximation (GGA) and parametrization as proposed by Perdew–Burke–Ernzerhof (PBE) [28, 29] for the exchange–correlation term. The valence electrons were treated with the Troullier–Martins pseudopotential [30] and the electronic wavefunctions expanded using an atomic orbital basis set with polarized functions (DZP) [31]. The atomic positions were relaxed until the Hellmann–Feynman [32] forces were minimized at a point where the forces had become smaller than 0.05 eV Å^{-1}. For this work, we have used the SIESTA code [33], using the slab supercell methodology, with six special k-points in the Brillouin-zone sampling, within the Monkhorst–Pack [34] scheme. The unit cell has a total of 44 atoms, distributed in nine layers, with an alternate composition of C and Si atoms. Of these, the first six layers are free to relax. Below the other three layers, which are kept fixed, there is an additional tenth layer with eight hydrogen atoms in order to passivate the dangling carbon bonds. The plot of the density of states (DOS) was obtained via convolution of the Gaussian functions with a dispersion of 0.2 eV.

3. Results and discussion

3.1. Structural aspects

The carbon terminated β-SiC(100)-c(2 × 2) surface was previously believed to occur as two different structures. Bermudez and Kaplan [8] have proposed a staggered carbon dimer model (SD), which is schematically represented in figure 1(a). From LEED experimental results, Powers *et al* [12] have additionally proposed a bridging carbon model (BD), which is schematically shown in figure 1(b). They have also suggested the possibility that the structure would be dependent on the preparation route, either using a C_2H_4 atmosphere or by silicon sublimation. Later, Yeom *et al* [17] verified that the BD model is experimentally consistent, regardless of the sample preparation route. Both model surfaces (SD and BD) were considered in this work, either in a clean form or with hydrogen adsorbed in different quantities.

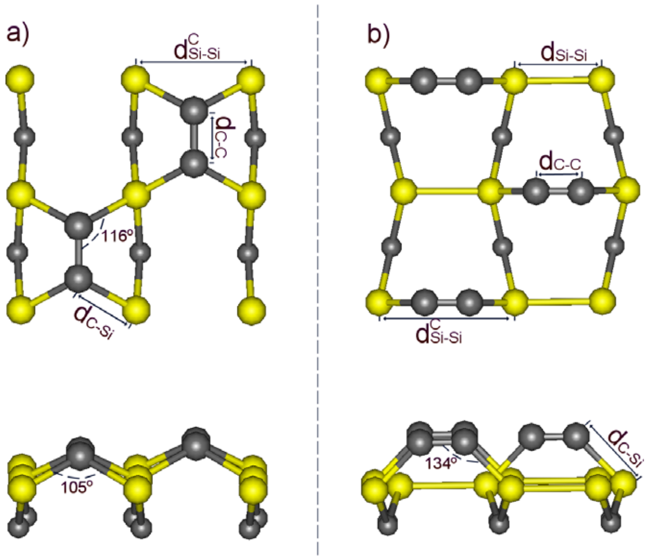

Figure 1. The structure of the SD (a) and BD (b) models for the β-SiC(100)c(2 × 2) clean surface. In both cases, the upper figure corresponds to a top view, while a side view is represented by the lower one. The C atoms are represented by dark circles (black in colour) and silicon atoms by light grey (yellow in colour). Smaller dark circles represent carbon atoms of the third layer. Values of angles are those resulting from calculations of this work.

In the SD case, hydrogenation would be possible only with the carbon dimers. However, for the BD model, hydrogenation could occur either partially (just on carbon atoms) or totally, i.e., on both chemical species (C and Si). The SD hydrogenated surface, with hydrogen adsorbed to the two carbon dimers, is schematically represented in figure 2(a), this particular phase being indicated by SD-4(H–C). The partially BD hydrogenated phase, represented in figure 2(b), is denoted as BD-4(H–C), corresponding to hydrogen atoms bonded just to the two carbon dimers. Finally, the BD totally hydrogenated phase, with hydrogen atoms bonded either to C and Si atoms, is denoted as BD-4(H–C)2(H–Si) and is schematically represented in figure 3.

The theoretically optimized lattice parameter for the bulk SiC was found to be 4.45 Å, while the experimental value quoted in reference [14] is 4.36 Å, which corresponds to a 2% difference. The calculated structural results for the carbon terminated β-SiC(100)-c(2 × 2) clean surface for the SD model are shown in table 1 with corresponding distances indicated in figure 1(a). This work can be compared with the experimental results of Powers *et al* [12] and also with the theoretical calculations by Käckell *et al* [25], Catellani and Galli [15] and Sabisch *et al* [2]. These last studies were performed using the LDA approach. This work's results indicate a higher d_{C-C} value compared to the other theoretical calculations, but it is known that the LDA approach leads to smaller bonding lengths compared to the results obtained using a GGA calculation. The value obtained in this work for the C–C distance of the dimer, 1.41 Å, suggests a double bonding for the carbon dimers, a

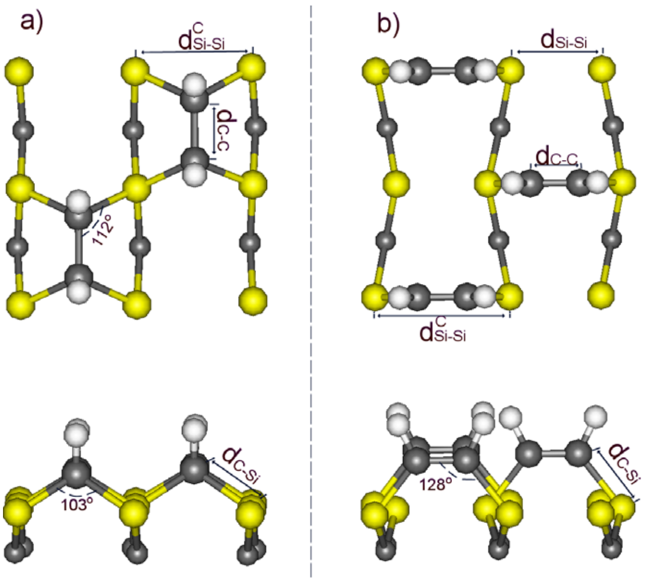

Figure 2. The structure of the SD (a), SD-4(H–C), and BD (b), BD-4(H–C), models for the β-SiC(100)c(2 × 2) surface with hydrogen atoms adsorbed to the carbon dimers. In both cases, the upper figure corresponds to a top view, while a side view is represented by the lower one. The C atoms are represented by dark circles (black in colour) and silicon atoms by light grey (yellow in colour). Smaller dark circles represent carbon atoms of the third layer. Hydrogen atoms are represented as small white circles.

Table 1. Distances according to figure 1(a) for the SD model. In this case there are no adsorbed hydrogen atoms. The index a refers to the surface obtained by Powers *et al* [12] using silicon sublimation. The index b corresponds to the case the same authors claim to be obtained in a C_2H_4 atmosphere.

	This work	Exp [12]	LDA [25]	LDA [15]	LDA [2]
d_{C-C} (Å)	1.41	1.32^a; 1, 46^b	1.38	1.37	1.36
d_{C-Si} (Å)	1.94	—	1.91	1.96	1.93
d^C_{Si-Si} (Å)	3.09	—	3.06	—	—

value that coincides with the results obtained by Frauenheim *et al* [35] for carbon dimers in a (100) diamond surface.

Calculations were also performed for the BD model of a clean surface. These results are summarized in table 2. The calculated values for d_{C-C} and d_{C-Si} agree very well with the experimental results of Yeom *et al* [17] and are 5% smaller than the results of Powers *et al* [12]. In this model, the carbon dimer makes a triple bond. There is a more pronounced discrepancy between the calculated and experimental results for d_{Si-Si}, despite the fact that the present results give values that are higher than previous LDA calculations.

As already noted, the possibility of hydrogen adsorption was also considered at the positions shown in figure 2 for both models, SD (a) and BD (b). The calculated distances are shown in table 3. These results can be compared with those of Käckell *et al* [25]. The hydrogen relaxes the surface's structure and changes the C–C bond of the carbon dimers from double to single in the SD model and from triple to double in the BD model. There is also an increase in the Si–C bond length as a result of the hydrogen adsorption.

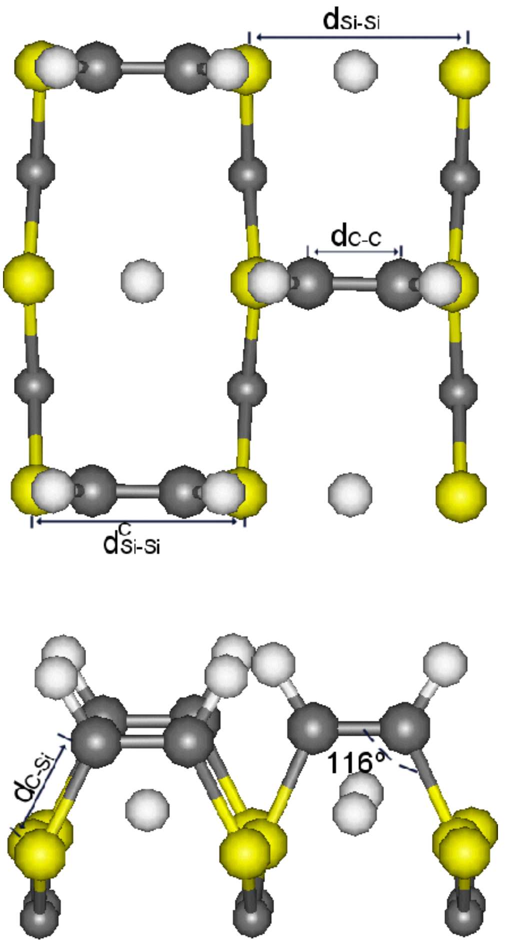

Figure 3. Equilibrium positions of the hydrogen atoms adsorbed to either carbon as silicon dimers in the BD model (BD-4(H–C)2(H–Si)). As before, the upper figure corresponds to a top view, while a side view is represented by the lower one. The C atoms are represented by dark circles (black in colour) and silicon atoms by light grey (yellow in colour). Smaller dark circles represent carbon atoms of the third layer. Hydrogen atoms are represented as small white circles.

The results obtained for the BD totally hydrogenated model (BD-4(H–C)2(H–Si)) are presented in table 4, where distances between pairs of atoms are noted, together with experimental results by Powers *et al* [12]. It is worth mentioning and specifically comparing one particular aspect of the results of Powers *et al*: the C–C distance of the carbon dimers in the clean (BD) and totally hydrogenated BD models. According to those authors, in the clean surface, this distance would be 1.31 Å, corresponding to a carbon double bond. In the case of the model with adsorbed hydrogen, resulting from the preparation involving exposure to C_2H_4, this distance would be even smaller, 1.25 Å. It seems to us that hydrogen adsorption would cause an expansion in the dimer distance for carbon and/or silicon dimers. This can also cause a change in the bonding and/or saturation of possible dangling bonds. In the case of the C–C distance [37], this is exactly what was obtained in the present calculations, with the C–C distance being 1.26 Å in the clean model, and becoming 1.38 or 1.37 Å

Table 2. Distances and angles according to figure 1(b) for the BD model. In this case there are no adsorbed hydrogen atoms.

	This work	LDA [25]	LDA [15]	LDA [2]	LDA [36]	LDA [3]	GGA [3]	Exp [12]	Exp [17]
$d_{\mathrm{C-C}}$ (Å)	1.26	1.23	1.23	1.22	1.30	1.22	1.23	1.31	1.22 ± 0.05
$d_{\mathrm{C-Si}}$ (Å)	1.86	1.82	1.81	1.83	1.90	1.82	1.85	1.93	1.84 ± 0.02
$d^{\mathrm{C}}_{\mathrm{Si-Si}}$ (Å)	3.85	—	—	—	—	—	—	3.47	—
$d_{\mathrm{Si-Si}}$ (Å)	2.46	2.38	2.37	2.40	2.38	2.39	2.42	2.71	2.70 ± 0.1
C–C–Si (deg)	134	—	—	—	—	—		124	—

Table 3. Distances according to figures 2(a) and (b) for the BD-4(H–C) and SD-4(H–C) models. In this case there are hydrogen atoms bonded to carbon atoms.

	$d_{\mathrm{C-C}}$ (Å)		$d^{\mathrm{C}}_{\mathrm{Si-Si}}$ (Å)		$d_{\mathrm{C-Si}}$ (Å)		$d_{\mathrm{Si-Si}}$ (Å)
	SD-4(H–C)	BD-4(H–C)	SD-4(H–C)	BD-4(H–C)	SD-4(H–C)	BD-4(H–C)	BD-4(H–C)
This work	1.64	1.38	3.09	3.76	1.97	1.93	2.55
LDA [25]	1.61	1.35	3.06	—	1.95	1.89	2.48

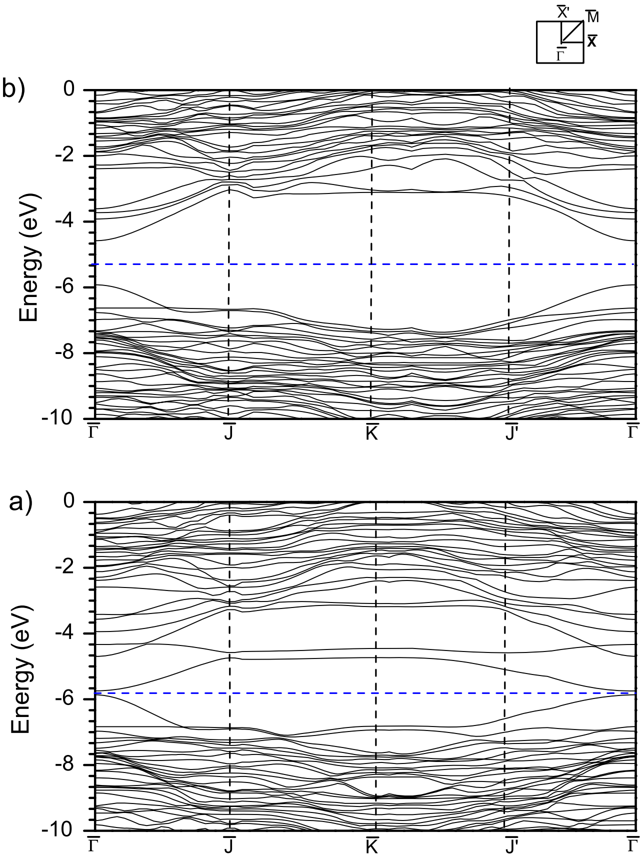

Figure 4. Band structure along symmetry directions in the Brillouin zone for the clean SD model (a) and SD-4(H–C) (b). In case (a), the gap is 0.12 eV and in (b) it is 1.34 eV. The Fermi level is indicated by the horizontal dotted line.

in the partially and totally hydrogenated models, respectively. A similar theoretical result was obtained by Käckell *et al* [25], with this distance changing from 1.23 to 1.35 Å, for the clean versus partially hydrogenated surfaces. In contrast to our results, Käckell *et al* could not obtain a stable totally hydrogenated phase.

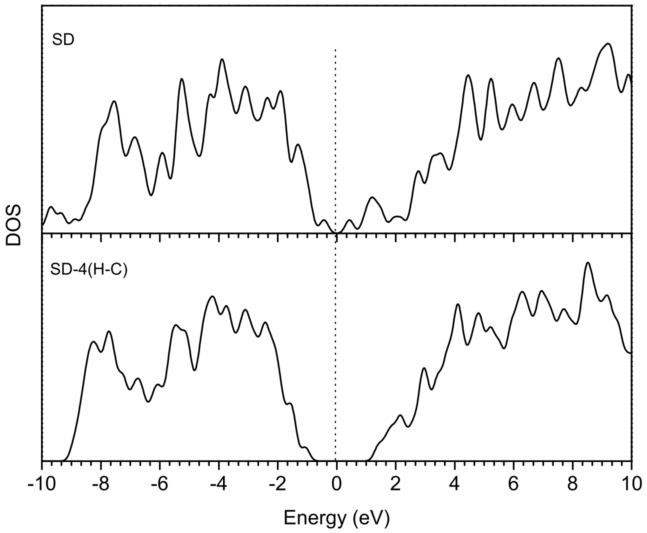

Figure 5. Density of states for the clean surface and also for the SD-4(H–C) model.

Table 4. Distances and angles according to figure 3 for the BD-4(H–C)2(H–Si) model. In this case there are hydrogen atoms bonded both to carbon and to Si atoms.

	$d_{\mathrm{C-C}}$ (Å)	$d_{\mathrm{C-Si}}$ (Å)	$d^{\mathrm{C}}_{\mathrm{Si-Si}}$ (Å)	$d_{\mathrm{Si-Si}}$ (Å)	C–C–Si (deg)
This work	1.37	1.89	3.04	3.39	116
Exp. [12]	1.25	1.86	3.09	3.09	119

3.2. Electronic features

The energy bands were calculated along symmetry directions within the Brillouin zone. In figure 4, the calculated energy bands and Fermi level positions are shown for the clean SD model and for the SD-4(H–C). For the same two cases, the density of states (DOS) is depicted in figure 5.

Assuming the clean carbon terminated β-SiC(100)-c(2 × 2) surface has an SD structure, its band structure, shown in figure 4(a), suggests a typical semiconductor behaviour, with an energy *gap* of 0.12 eV localized at the $\bar{\Gamma}$ point.

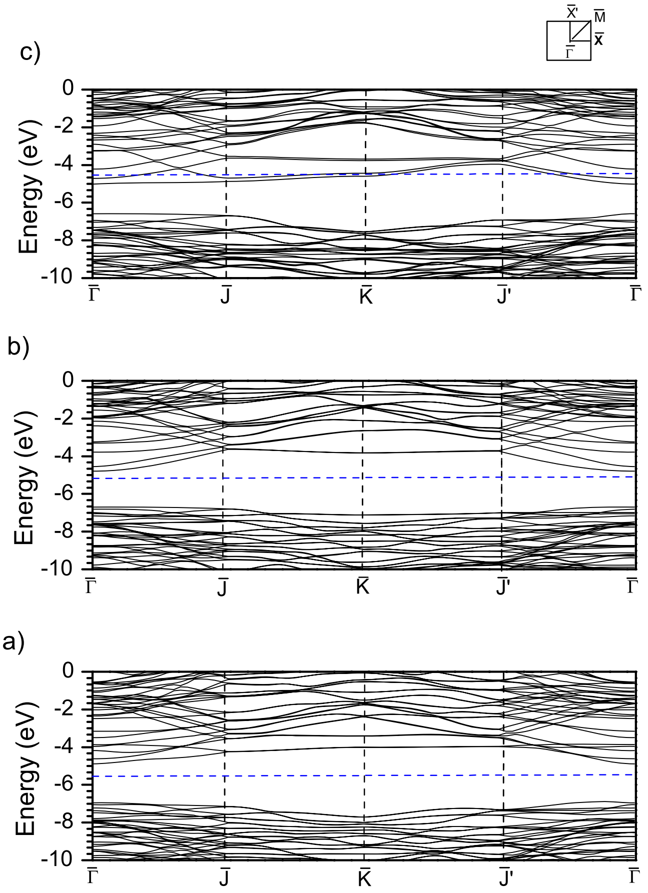

Figure 6. Band structure along symmetry directions in the Brillouin zone for the clean BD model (a), BD-4(H–C) (b) and BD-4(H–C)2(H–Si) (c). In case (a), the gap is 2.08 eV, in (b) it is 1.90 eV while in (c) a metallic behaviour can be seen. The Fermi level is indicated by the horizontal dotted line.

Hydrogen adsorption in the carbon dimers of the clean surface causes a widening among the bands closer to the *gap* region present in the clean system, as shown in figure 4(b). This behaviour was also observed by Käckell [25] in the present case, with the resulting *gap* increasing to 1.34 eV. The Fermi level for this model (SD-4(H–C)) was found to be equal to −5.29 eV.

In figure 5, the DOSs for both the clean and hydrogenated systems are presented. As can be seen, the peaks close to the *gap* in the clean system completely disappear as a result of the hydrogen adsorption, so it is possible to conclude that, besides a change in the interatomic distances, the hydrogen adsorption over the carbon dimers increases the energy difference between the highest occupied state and the lowest unoccupied one, giving a semiconductor character to the system. This is the typical behaviour when the surface adsorbs a monovalent atom, known as its passivation.

In figure 6, similar to the previous case, the energy bands and Fermi level for the models BD (clean), BD-4(H–C) and BD-4(H–C)2(H–Si) are represented, while figure 7 shows the corresponding DOS.

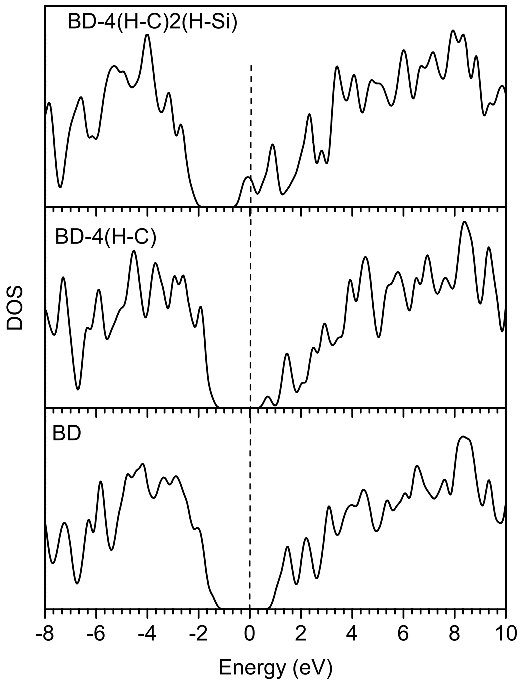

Figure 7. Density of states for the clean surface and also for the models BD-4(H–C) and BD-4(H–C)2(H–Si) which correspond to different quantities of adsorbed hydrogen.

When a carbon terminated β-SiC(100)-c(2×2) surface is considered to have a BD structure with or without hydrogen adsorbed to its dimers, the calculated band structures are as shown in figure 6(a) for a clean surface, as shown in 6(b) when the hydrogen atoms are adsorbed just to the carbon dimers and as shown in 6(c) when adsorption is either to carbon and silicon dimers. The clean surface exhibits semiconductor behaviour, with a *gap* of 2.08 eV and a Fermi level at −5.48 eV. Subsequent adsorption of hydrogen to the carbon dimers modifies the band structure, with the bands just above and just below the Fermi level becoming closer. This behaviour is in the opposite direction of what occurs for the SD model. The *gap* is now 1.90 eV, with the Fermi level located at −5.20 eV. Additional hydrogen adsorption, saturating the system, causes the appearance of bands crossing the Fermi level and overlapping with the bottom of the conduction band, as shown in figure 6(c). This additional hydrogen atom is bonded to two silicon atoms, forming an angular Si–H–Si bond. It is also possible to see, via comparison between figures 6(b) and (c), the occurrence of a 'split' of some bands, clearly visible in the region close to the point M̄. In this case there is no gap, which corresponds to a clear metallic behaviour.

Similar to what was done for the SD model, figure 7 represents the DOS for the BD, BD-4(H–C) and BD-4(H–C)2(H–Si) models. Contrary to the tendency observed in the SD model, states closer to the Fermi level appear when adsorption just to the carbon dimers of the clean surface is considered (see the states around 0.66 eV). Further adsorption (model BD-4(H–C)2(H–Si)) leads to the appearance of states at and above the Fermi level, as shown in figure 7. This is in clear contradiction to what was observed for the SD model and also to the 'normal' behaviour for this kind of adsorption, where the tendency is to 'clean the *gap*' by removal of the

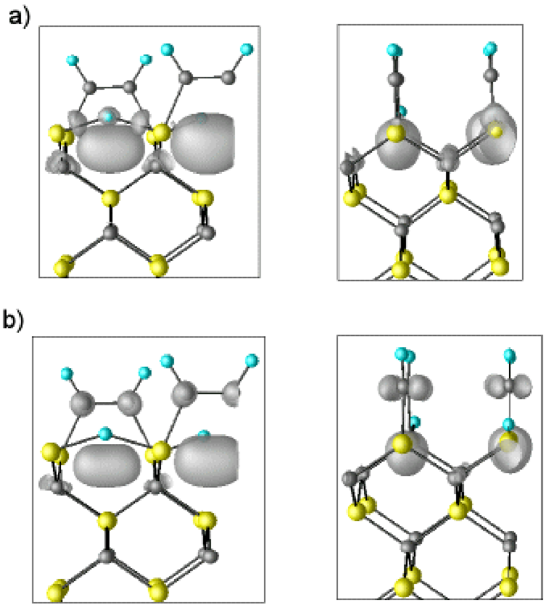

Figure 8. Electronic charge density for the highest occupied and lowest unoccupied states for an energy range as follows: (a) HOMO (between −5.40 and −4.53 eV); (b) LUMO (between −3.76 and −4.53 eV).

dangling bonds. However, this behaviour of our calculated results is similar to that observed for the silicon terminated β-SiC(100)(3 × 2) [13, 23].

The electronic charge density for the highest occupied molecular orbitals (HOMO) and for the lowest unoccupied molecular orbitals (LUMO) was plotted in figure 8. The energy range was 0.87 eV and 0.77 eV, respectively below and above the Fermi level. It is possible then to observe that the levels associated with the ones in the vicinity of the HOMO are localized in the vicinity of the silicon atoms and the hydrogen atoms bonded to them. On the other hand, for levels in the vicinity of the LUMO, it is possible to associate electronic levels with silicon and carbon atoms. This localization associated with the surface atoms is consistent with the results in figure 7, suggesting a metallization process with LUMO levels being accessed from the HOMO levels.

It is well known that the band-gap energy calculated by GGA/LDA-DFT is underestimated, compared with experimental determinations. Nevertheless, it appears that this fact is not responsible, in the present calculation, for the metallization. This more plausibly appears to be associated with the hydrogen adsorption at specific bridge sites (Si–H–Si), which creates electronic states at the Fermi level, similarly to what has been identified in another SiC surface [21–23].

4. Summary and conclusions

The changes in the structural and electronic properties resulting from hydrogen adsorption in two models for the carbon terminated β-SiC(100)-c(2 × 2) surface were obtained by using DFT calculations. For the clean models, the results of this work are comparable with previous experimental and theoretical conclusions available in the literature. From the performed calculations, it is possible to conclude that the presence of hydrogen affects the final structural characteristics of the surface and also is reflected in the electronic properties. Hydrogen adsorption on carbon dimers changes the respective chemical bonds, allowing surface relaxation. Hydrogen deposition on carbon dimers in the case of the SD model results in a typical electronic behaviour caused by adsorption of a monovalent atom, i.e., the dangling bonds are passivated. An opposite behaviour is found when adsorption is on the dimers in the BD model. In this case, adsorption exclusively on the carbon dimers reduces the *gap* compared with that of the clean model. Additional adsorption to the silicon dimers leads to a metallic behaviour. Hydrogen bonded to a Si dimer was found to be theoretically stable with the current calculations, which is contradictory to previous theoretical calculations [25]. This work shows that in such circumstances hydrogen can occupy a bridge position in the angular Si–H–Si bonds on the second layer, resulting in a half-filled band at the Fermi level, which overlaps with the bottom of the conduction band.

Acknowledgments

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