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# *Ab initio* electronic and structural properties of clean and hydrogen saturated $\beta$ -SiC(100)(3 × 2) surfaces

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## Abstract

This paper deals with *ab initio* calculations relating to the atomic and electronic structure of the  $\beta$ -SiC(100)(3 × 2)–H surface. The results lead to the interpretation that electronic states associated with H atoms are responsible for a metallic behaviour, when saturation in the H deposition on the clean  $\beta$ -SiC(100)(3 × 2) is effected, a feature observed experimentally by Derycke *et al.* Although confirming the experimentally observed electronic behaviour, the present results differ as regards the H atom positions. Atomic structural properties were calculated and compared with previous ones available in the literature.

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

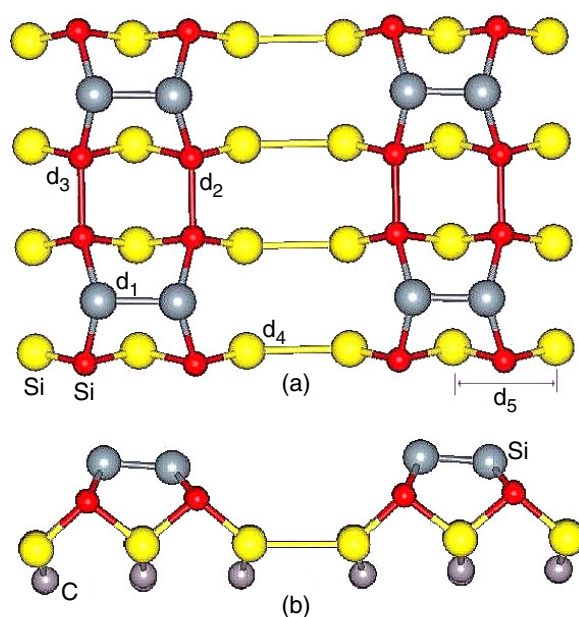
## 1. Introduction

Semiconductor surfaces are known to be susceptible to chemical passivation by the use of hydrogen. The production of a surface from the bulk condition, e.g. by cleavage, leads to the formation of dangling bonds [1, 2] which are saturated by the presence of a monovalent atom. So, hydrogen adsorption has always been expected to cause removal of surface states [3], and remove pre-adsorbed hydrogen leading to metallization [4].

Recently, a paper was published giving results that apparently correspond to a behaviour that could be termed ‘the other way around’, i.e., ‘the first observation of surface metallization induced by atomic hydrogen’ was reported [5]. These results refer to a silicon-rich single domain of a cubic  $\beta$ -SiC(100) film, grown on a silicon substrate. SiC is a wide bandgap semiconductor which, as a result of its characteristics, has important technological applications in a variety of areas such as microelectronics, voltage, temperature and frequency high

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**Figure 1.** Structure of the silicon-rich  $\beta$ -SiC(100)(3  $\times$  2) clean surface: (a) top view; (b) side view, with C atoms (not shown in (a)) on the fourth layer. The values for  $d_2$  and  $d_3$  can differ according to the model adopted.

resistance electronic devices, matrix composites and biocompatibility applications [6–17]. This importance justifies the experimental and theoretical interest in the  $\beta$ -SiC(100)(3  $\times$  2) surface [17, 18].

Figure 1 shows the structure of the Si-rich  $\beta$ -SiC(100)(3  $\times$  2) surface, after Si deposition and the necessary treatments for establishing the 3  $\times$  2 long range order. In the top layer there are rows of asymmetric Si dimers resting on similar dimers in the second layer, these rotated by  $\pi/2$  relative to previous ones. The dimers of these first two layers present two different bond lengths, represented by  $d_1$  and  $d_2/d_3$  in the figure. The dimers of the first layer are perpendicular to the direction where there is a formation of rows [19]. The third layer is also a Si layer, corresponding to the top layer of the Si terminated  $\beta$ -SiC(100), with Si dimers forming a c(4  $\times$  2) reconstruction [20]. This Si-rich  $\beta$ -SiC(100)(3  $\times$  2) surface has a top layer with dangling bonds that can be saturated by the presence of a monovalent atom, like hydrogen, while the second and third layers present dimerization, which apparently prevents dangling bonds, for reasons not yet known [5].

The results of Derycke *et al* [5] were obtained from different techniques: scanning tunnelling microscopy (STM), scanning tunnelling spectroscopy (STS), ultraviolet photoemission spectroscopy (UPS) and infrared absorption spectroscopy (IRAS). The observed asymmetry in the spot intensity of the STM topographical images, associated with the tilted dimers of the first layer, disappears when the clean surface is exposed to atomic hydrogen (10 L H<sub>2</sub>), which led the earlier authors to interpret the adsorption sites of the H atoms as being on top of the Si–Si dimers of the first layer.

The initial patches, formed with the H deposition, increase as the H coverage reaches 20 L H<sub>2</sub>, until most of the surface presents them, leading to an even intensity for the bright spots. The earlier authors interpreted this as showing that, after H deposition, the dimers become symmetrical. The STS measurements suggest H adsorption as inducing a bandgap closure,

which was interpreted as evidence of surface metallization, an interpretation corroborated by UPS measurements. With these measurements, Derycke *et al* [5] found, for the clean case, a spectral peak (peak and maximum value at 2.8 and 1.9 eV, respectively, below the Fermi level) associated with a bulk structure, and another one, which is progressively quenched with H deposition, associated with a surface state. For the H saturated case another feature appears at the Fermi level, what has led the earlier authors to interpret it as a result of surface metallization.

The infrared absorption spectroscopy (IRAS) measurements performed by Derycke *et al* [5] indicated three bands at frequencies of 2118 cm<sup>-1</sup> (with an asymmetry at 2110 cm<sup>-1</sup>), 2140 and 2100 cm<sup>-1</sup>. The last one, observed both in p and s polarizations, was considered as not relevant for the SiC surface. The 2118 cm<sup>-1</sup> band was detected with a polarization in the plane perpendicular to the surface dimer rows, containing the dangling bonds. The frequency and polarization are in agreement with previous IRAS results obtained for monohydride termination of the top layer dimers (H–Si–Si–H) [21, 22]. The other band frequency (2140 cm<sup>-1</sup>), also detected with a polarization perpendicular to the dimer rows, is too high to be associated with a hydrogen structure, such as monohydrides or dihydrides on silicon surfaces [21, 22], even if a considerable strain were to be present. Derycke and co-workers [5], on the basis of previous IRAS results for  $\beta$ -SiC(111) and 6H-SiC(0001) systems [23], suggested that this could be associated with Si–H structures, with silicon atoms directly bonded to a carbon plane. So, the two bands frequencies and polarizations seem to indicate the presence of H atoms bonded to silicon atoms in the first and third surface layers.

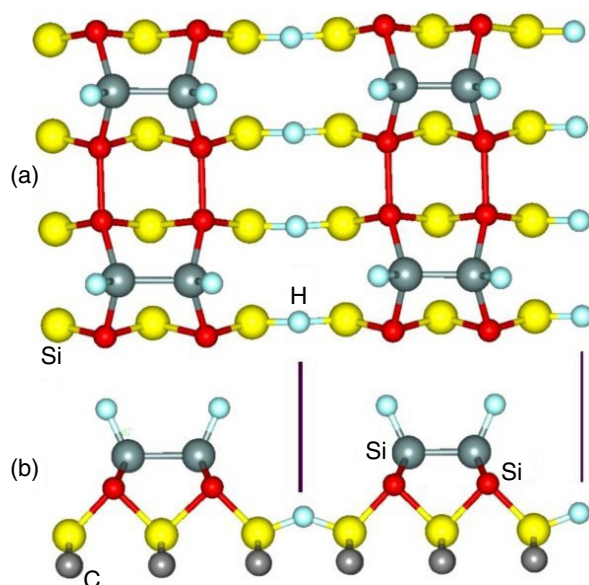
Motivated by the experimental results of Derycke *et al* [5], we have theoretically calculated structural and electronic properties of the  $\beta$ -SiC(100) surface, for three different systems. In section 2 we describe the method of calculation, for which the results are presented in section 3, together with a comparison with some other similar calculations and experimental data. The conclusions constitute section 4.

## 2. Methodology

In order to investigate the electronic and structural properties of the  $\beta$ -SiC(100) silicon-rich surface, we have considered three systems with different concentrations of hydrogen. The first system is just the  $\beta$ -SiC(100) silicon-rich surface, i.e., without hydrogen at the surface. This system is formed of 108 atoms in each supercell: 12 hydrogen atoms, 60 silicon atoms and 36 carbon atoms. We refer to this system here as the *clean* system. The second system, termed *hydrogenated*, corresponds to the previous one with addition of four more hydrogen atoms, these ones bound to the silicon atoms of the first layer. Finally, the *saturated* system, has an additional amount of hydrogen, now bound to the silicon dimers of the third layer.

The simulation process for calculating the properties of these systems consists of two steps. To save computational time, first the atomic positions and box size were let free for self-adjustment using a Monte Carlo simulation. At this stage we used a Tersoff [24] interatomic potential for SiC, while the potential for the SiH was the same one as was previously used for the a-SiNH system [25–27]. After convergence of this initial process, the results were used as input for the second step: an *ab initio* calculation.

For further geometry optimization and calculation of electronic properties, we adopted the density functional theory (DFT) [28, 29]. To determine the exchange–correlation energy, we adopted the procedure proposed by Perdew [30], within the approach of the local density approximation (LDA), with valence electrons treated with the Troullier–Martins pseudopotential [31], the electronic wavefunctions being expanded in an atomic orbital basis set.



**Figure 2.** Structure of the silicon-rich  $\beta$ -SiC(100)(3  $\times$  2) surface with hydrogen, for the *saturated* system, in a top view (a) and a side view (b). In the *hydrogenated* system the H atoms along the marked lines do not exist. In case (b), the C atoms (not shown in (a)) are below the third-layer Si atoms.

The ionic positions were relaxed, until a minimization of Hellmann–Feynman [32] forces was reached, down to a point where the forces had become smaller than  $0.05 \text{ eV \AA}^{-1}$ . For this work, we used the SIESTA code [33]. We adopted the supercell approach, with four special  $k$ -points in the Brillouin-zone sampling within the Monkhorst–Pack [34] scheme. Our model is a semi-infinite system: a slab of finite thickness, periodically reproduced in the direction perpendicular to the surface with a vacuum layer of thickness 1.4 times the slab height, separating adjacent slabs. The density of states (DOS) was obtained by convolution with Gaussian functions, centred at the Kohn–Sham one-electron energy level.

### 3. Results

Initially we explored the *clean* structure, as shown in figure 1 in top and side views. Figure 2 shows the atomic positions for the  $\beta$ -SiC(100) after hydrogen deposition and saturation. The *hydrogenated* system corresponds to the one without hydrogen atoms linked to the third layer of Si atoms or, in other words, resulting from the removal (in the *saturated* system) of the H atoms along the marked lines of figure 2. Table 1 presents the calculated structural parameters for each of the models explored, together with a comparison with a previous LDA theoretical calculation performed by Lu and co-workers [18] and experimental results obtained by D’angelo and co-workers [35], using grazing incidence x-ray diffraction. In the same table there are results from a paper by Tejada *et al* [36], this one using soft x-ray photoelectron diffraction.

The figures in table 1 deserve a brief comment, mostly concerning the results from the last two references [35, 36]. The values of interatomic distances, as presented in the text by D’Angelo and co-workers [35], can be calculated from the coordinates of table 2 included in that paper. In doing this, it was possible for us to obtain an adequate reproduction of the values for  $d_1$ ,  $d_4$  and  $d_5$  using the coordinates given by those authors [35]. However,

**Table 1.** Structural parameters corresponding to the ones shown in figure 1 for the three systems explored: *clean*, *hydrogenated* and *saturated*. A comparison with two previous works is also shown.

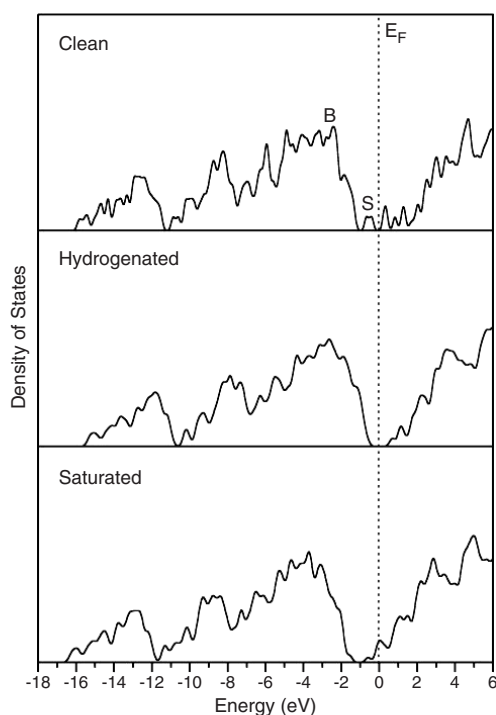
	$d_1$ (Å)	$d_2$ (Å)	$d_3$ (Å)	$d_4$ (Å)	$d_5$ (Å)	$\Theta$ (deg)
A (This work— <i>clean</i> )	2.36	2.48	2.51	2.52	3.60	5.38
B (Lu <i>et al</i> [18]— <i>clean</i> )	2.24	2.37	2.38	2.41	3.43 <sup>a</sup>	12.8
C (D'angelo <i>et al</i> [35]— <i>clean</i> )	2.78	3.48	3.48	2.38	3.43	5.34
D (Tejeda <i>et al</i> [36]— <i>clean</i> )	2.54	1.83	2.40	2.43	3.41	5.5
E (This work— <i>hydrogenated</i> )	2.44	2.56	2.56	2.52	3.61	
F (This work— <i>saturated</i> )	2.35	2.52	2.52	3.24	3.26	
Theo.–theo.: ratio (A/B)	1.053	1.046	1.055	1.046	1.049	0.420
Theo.–exp.: ratio (A/C)	0.849	0.713	0.721	1.059	1.049	1.007
Theo.–exp.: ratio (A/D)	0.929	1.355	1.046	1.037	1.056	0.978

<sup>a</sup> Value indirectly determined from the reference data.

adopting the same procedure, it was not possible for us to obtain the same values as quoted by those authors as regards distances  $d_2$  and  $d_3$ . The figures presented by them for  $d_2$  and  $d_3$  do not match the ones calculated from their own coordinates, respectively, 2.41 and 2.27 Å. On the other hand, our structural results are within 5% of the results calculated by Lu and co-workers [18], as well as with the more recent experimental results of Tejeda *et al* [36]. In this last reference, there is a significant difference between  $d_2$  and  $d_3$  (31%). Lu and co-workers [18] find just a 0.5% difference between the two distances, while our results indicate 1.2%. The last column of table 1 contains the value of the angle formed by the tilted most external Si dimers for the clean system. Derycke and co-workers [5] mentioned an asymmetry in the positions of these Si atoms, a feature also mentioned in connection with other experimental measurements [19, 35, 36] and even obtained by theoretical calculations [18]. Our results significantly differ from the previous theoretical calculation [18], though agreeing very well with the experimental results.

Figure 3 presents the electronic densities of states for the three calculated models. As can be seen, for the *clean* system we can associate peak B with valence states and the S one with surface states (dangling bonds located at the top dimers). These S states, as well those just above the Fermi level, are localized states. As is usual in the LDA approximation, the gap is underestimated, which causes these states to be closer than what would be expected. As experimentally observed by Derycke *et al* [5], the peak S completely disappears as a result of hydrogen deposition. In our calculations this is reflected in the disappearance of peak S, with hydrogen passivating the dangling bonds, as can be seen in figure 3, for the density of states of the *hydrogenated* system. The *clean* and *hydrogenated* cases present no states at the Fermi level. An additional amount of hydrogen leads to the *saturated* system, for which the presence of electronic states at the Fermi level can be observed, i.e., corresponding to a conductor behaviour.

Derycke *et al* [5] interpreted their results from observing a metallic behaviour as a result of H saturation, due to hydrogen termination of the Si third layer, leading to a breaking of the Si dimers. This formation, according to those authors, would result in a Si–H oriented bond with the H atoms resting asymmetrically on the Si atoms. This would lead to a Si atom with a dangling bond, which would be responsible for the surface metallization. We have however found, with the calculations performed, the hydrogen atom located at the centre of the silicon dimer, i.e., in a symmetry preserving position, as can be seen in figure 2. The two silicon atoms are bridged by one hydrogen atom, with the Si–H bond length of 1.71 Å, forming an angle of 141.1°. The Si–Si distance has increased (from 2.52 to 3.24 Å) its length due to the breaking



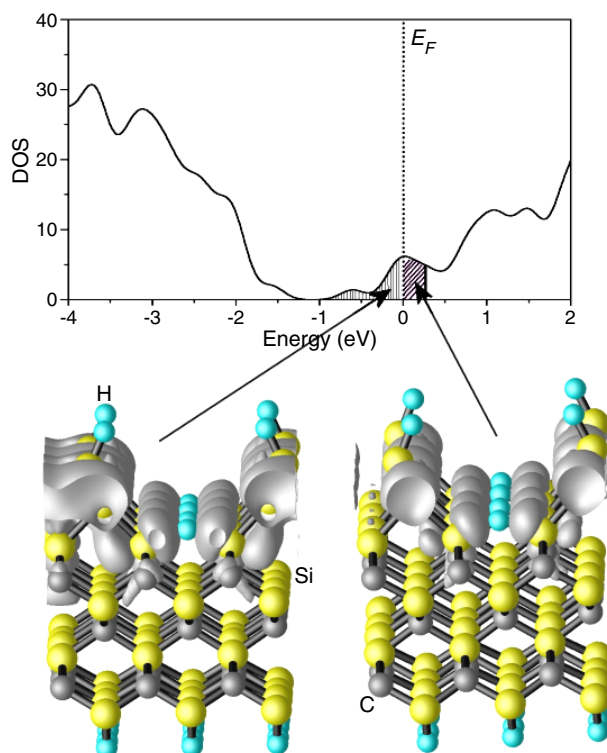
**Figure 3.** Densities of electronic states for the three calculated models.

of the Si–Si strained bond. This behaviour, which could be termed a three-centre–two-electron bonding, is a common feature in a-Si:H systems and C vacancies in c-SiC.

Gali *et al* [37] have investigated the occurrence of an overcoordinated hydrogen in a carbon vacancy in c-SiC, finding an angle of  $156^\circ$  between the bonds. Sriraman *et al* [38] observed a hydrogen induced crystallization of hydrogenated amorphous silicon films treated with  $H_2$  plasma. The crystallization occurs on insertion of a hydrogen atom into a long Si–Si bond, which leads the system to relax. Tuttle *et al* [39] reported a study of hydrogen in a-Si, using the DFT LDA, where they report the Si–H distance as being  $1.66 \text{ \AA}$  and an angle of  $163.9^\circ$ . Their results for the Si–H–Si bond length and angle are very close to ours, differing, respectively, by 3% and 14%. As a result of a different environment, the more pronounced difference in angle should be expected. We think that the mechanism of breaking the Si–Si strained bond and capture of hydrogen, in order to form a Si–H–Si bond, is similar to the one discussed by Gali, Sriraman and Tuttle. This possibility appears to us to be the most plausible one.

From our results, the electronic states associated with the Si–H–Si system are located at the Fermi level, being just partially occupied, as can be seen in figure 3, if we compare the *hydrogenated* and *saturated* systems. In figure 4, we can observe that a hydrogen induced band and the bottom of the conduction one are formed by states that are associated with the additional hydrogen atoms of the *saturated* phase. This situation, within the perspective of the energy band scheme, can be interpreted as the hydrogen causing the appearance of electronic states about 1.5 eV above the top of the valence band. The band resulting from these states merges with those at the bottom of the conduction band, moving the Fermi energy to a higher value. This is an interpretation that should be considered within the limits of the DFT calculations, a method intrinsically related to the fundamental state. Certainly the conduction mechanism





**Figure 4.** Density of the electronic charge corresponding to the energy bands indicated by arrows for the *saturated* model.

is a consequence of a complex transition from localized states to the continuum, as already pointed out by Derycke [5] and Wilson [3]. These states appear to be weakly correlated, being localized in the hydrogen atoms which are 3.19 Å apart. Our interpretation is that the hydrogen induced band, at the Fermi level, introduces some electron states at the bottom of the conduction band, thus suggesting an n-type conduction process.

#### 4. Conclusions

In this work, we have been able to calculate the electronic and structural properties of the  $\beta$ -SiC(100)(3 × 2) surface, under three different conditions, according to the amount of deposited hydrogen. The results give support to the conclusion that neither the *clean* nor the *hydrogenated* phases present states at the Fermi level, while the *saturated* phase is in fact a conducting one. The structural results, on the other hand, are comparable, for the *clean* phase, with previous calculations [18, 35, 36].

In the *saturated* case we have found the hydrogen atom located symmetrically between the silicon atoms of the third layer, forming a ‘two-electron—three-centre’ bond.

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