Hydrogen induced surface metallization of $\beta$-SiC(100)-(3 $\times$ 2) revisited by DFT calculations

R. Di Felice*, C. M. Bertoni, C. A. Pignedoli†

INFM-National Research Center on nanoStructures and bioSystems at Surfaces ($S^3$),
Dipartimento di Fisica, Università di Modena e Reggio Emilia,
Via Campi 213/A, 41100 Modena, Italy

A. Catellani
CNR-IMEM, Parco Area delle Scienze 37a, 43010 Parma, Italy, and INFM-S3

(Dated: June 13, 2018)

Abstract

Recent experiments on the silicon terminated 3 $\times$ 2 SiC(100) surface indicated an unexpected metallic character upon hydrogen adsorption. This effect was attributed to the bonding of hydrogen to a row of Si atoms and to the stabilization of a neighboring dangling bond row. Here, on the basis of Density-Functional calculations, we show that multiple-layer adsorption of H at the reconstructed surface is compatible with a different geometry: besides saturating the topmost Si dangling bonds, H atoms are adsorbed at rather unusual sites, i.e. stable bridge positions above third-layer Si dimers. The results thus suggest an alternative interpretation for the electronic structure of the metallic surface.

PACS numbers: 68.35.Md, 68.55.Ac, 81.15.Aa

* rosa@unimore.it
† Present Address: IBM Corporation, Zurich Research Laboratory, Saumerstrasse 4, Rueschlikon, Switzerland
The silicon terminated $\beta$-SiC(100)-$3 \times 2$ surface is constituted of extra Si-dimers on top of silicon terminated layers $[1, 2, 3]$. A recent experimental investigation $[4, 5, 6]$ has shown a surprising property: the transition from a semiconducting to a metallic surface induced by hydrogen chemisorption. In general semiconductor surfaces undergo reconstruction, relaxation or dimerization just to eliminate the presence of partially occupied surface bands within the gap. Furthermore, hydrogen chemisorption on the reconstructed surfaces can modify or even quench the reconstruction by passivating the surface, often removing all the surface states from the gap. For this system, instead, the experiments have been interpreted in terms of an opposite effect, i.e. the existence of a band of unsaturated dangling bonds (DBs) on a row of Si atoms, induced by the adsorption of H atoms along a neighboring row of other Si atoms. On the basis of their observations, Derycke et al. $[5]$ pointed out the possibility of engineering, at the atomic level, the structural and electric properties of surfaces using the reconstruction geometry as a template $[5]$.

The interest in this silicon terminated, overstoichiometric $\beta$-SiC(100) surface is linked to the problem of the epitaxial production of silicon carbide, with a high technological impact $[7]$. The presence of excess Si atoms allows the system to stabilize the subsurface planes by the creation of multiple Si-dimer layers that are responsible for different possible reconstructions. Among them, the observed $3 \times 2$ periodicity is obtained with a complex layering of dimers of different lengths. The stable geometry of this reconstruction is still intensely debated: here, we do not enter this controversy, but rather focus on the mechanisms of H adsorption, assuming for the clean surface the model proposed by Lu et al. $[3]$, consistently with the choice adopted for the interpretation of the experimental H-induced metallization $[5]$. As indicated in Fig. 1a, this clean $3 \times 2$ surface is characterized by a coverage of 1 monolayer (ML) extra silicon atoms on top of the bulk-like Si-terminated SiC(100) face. Of this extra ML, $\frac{2}{3}$ ML Si atoms are accomodated at the first adlayer forming a couple of flat dimers in each periodicity unit. The remaining $\frac{1}{3}$ ML Si atoms are accomodated on top of them forming a second adlayer of buckled dimers. The Si-rich SiC(100)-(3 × 2) surface thus exposes 3 outermost Si layers, starting from the vacuum, with coverages of $\frac{1}{3}$ ML, $\frac{2}{3}$ ML, and 1 ML on the first, second, and third layer respectively. This structure, called Two-Adlayer Asymmetric-Dimer Model (TAADM) $[3, 8, 9]$, was proposed among several possible $3 \times 2$ geometries on the basis of total-energy calculations including a detailed investigation of the electronic structure and optical properties. In particular, in this configuration the tilting of the upper dimers ($\text{Si}_D-\text{Si}'_D$) is responsible for the existence of a gap between two surface bands, $\pi$-bonding (filled) and $\pi^*$-antibonding (empty) on the $\text{Si}_D-\text{Si}'_D$ dimers. The two second-layer dimers ($\text{Si}_d-\text{Si}'_d$) have
FIG. 1: Side view of the outermost layers for the 3×2 model reconstruction adopted in the present work: black (gray) spheres represent C (Si) atoms, smaller white spheres indicate H atoms. (a) The clean reconstructed TAADM SiC(100) surface. (b) The 2H2H\textsubscript{u} model for the hydrogenated surface, proposed on the basis of the recent experiments \cite{5,6}. (c) The equilibrium adsorption geometry 2H2H\textsubscript{r} obtained by relaxing the system starting from the experimental 2H2H\textsubscript{u} model. A 2×2 replica of the unit surface cell is shown.

a short length, and weaker silicon dimers are present at the third layer (Si\textsubscript{b}−Si\textsubscript{b}'). Let us call the latter as Si atoms in the channel.

H atoms can be bonded to the atoms of the external Si\textsubscript{D}−Si\textsubscript{D}' dimers by weakening the strength of such bonds and eliminating the buckling \cite{10,11}. A further supply of hydrogen could result in the di-hydrogenation of the Si atoms of the external dimers or in the chemisorption of H on Si atoms in the channel. Derycke \textit{et al}. \cite{5} suggested that only one Si atom of each channel dimer is bonded to H, giving rise to a structure with a row of unsaturated Si DBs (black sticks in Fig. 1b) in the [0\textbar 1\textbar 1] direction at the third surface layer.

To test this model, with the specific aim of interpreting the origin of metallicity in terms of surface bands, we performed first-principle calculations based on the Density Functional formalism. The surfaces were simulated by repeated supercells. The unit supercell contained a slab with eight (or sixteen \cite{12}) atomic layers, and 13 Å of vacuum to inhibit the interaction between neighboring replicas. The bottom of the slab was terminated by a H layer saturating C DBs, the top of the slab contained the extra adlayers of Si and H atoms. All the investigated geometries were relaxed with
respect to both ionic and electronic degrees of freedom [13], to find the local minima starting from our initial conditions. The atomic species were described by ultrasoft pseudopotentials [14], the electronic wavefunctions were expanded in plane waves with a kinetic energy cutoff of 22 Ry. Brillouin Zone (BZ) sums were performed at three special Monkhorst-Pack $\mathbf{k}$ points in the irreducible wedge of the two-dimensional (2D) BZ [15]. The PBE exchange-correlation functional was used [16]. We checked our results by performing test calculations in the local spin density approximation.

We compared different patterns and amounts of hydrogenation of the TAADM surface starting from different trial geometries. In the following, the structures are labeled according to the H content and adsorption layer: thus, $nH$ indicates a hydrogenated surface with $n$ H atoms per unit cell adsorbed on top of the outermost Si dimers of the $3 \times 2$ reconstruction; $nHmH$ indicates a hydrogenated surface with $n$ and $m$ H atoms per unit cell adsorbed on top and in the third layer channel, respectively. (i) $2H$ and $4H$ are characterized by the adsorption of H only on top of the outermost Si dimers, with one and two H atoms for each top Si atom, respectively; (ii) $3H$ has two H atoms attached to $\text{Si}_D$ and only one H atom attached to $\text{Si}'_D$ on each top dimer; (iii) $2H2H$ includes H atoms at the outermost Si dimers as in configuration $2H$, plus two H atoms per cell at the $\text{Si}'_b$ atoms in the channel, with one H atom for each $\text{Si}_b-\text{Si}'_b$ dimer (Fig. 1b,c) placed at an initial H-Si$_b$ distance (structure $2H2H_u$ in Fig. 1b) typical of the H-Si single bond, $\sim1.5$ Å; (iv) $2H1H$ ($3H1H$) can be obtained from $2H2H$ by removing (transferring to the outermost dimers) half of the H atoms from the channel. In agreement with previously published results [10, 11], the $2H$ and $4H$ structures are semiconducting: The outermost Si dimers are elongated from 2.30 Å to 2.42 Å in the $2H$ geometry and are broken in the $4H$ one (Si-Si distance 3.16 Å). A similar effect occurs at Si dimers of Si(100) [17]. The electronic structure in these cases exhibits surface bands that partially overlap the upper and lower edges of the bulk gap. The occupied and unoccupied bands remain well separated, preserving the semiconducting behavior as in the case of the partial or full hydrogenation of the Si(100) surface.

Assuming a uniform flux of atomic H, the adsorption of H atoms on the Si atoms of the weak dimers in the channel is probable. This gives rise to the most interesting case of the $2H2H_r$ structure. The starting configuration $2H2H_u$ for this surface, suggested on experimental basis [5], results unstable: the H atoms bonded to $\text{Si}_b$ atoms (Fig. 1b) move spontaneously to reach an equilibrium location bridging $\text{Si}_b$ and $\text{Si}'_b$ sites ($2H2H_r$, Fig. 1c). This migration was also obtained through extended calculations, with full atomic relaxation, performed with a larger supercell ob-
tained by doubling the $3 \times 2$ cell, to test that our results are not affected by the specific choice of periodic boundary conditions. In this migration, the H-Si$'_b$ distance increases from 1.5 Å to 1.68 Å and becomes equal to the H-Si$_b$ distance. The Si$_b$–H–Si$'_b$ angle becomes 133°. In the relaxed geometry of Fig. 1c, the topmost Si$_D$–Si$'_D$ dimers are 2.36 Å long (stretched by 5% with respect to the clean TAADM surface) and flat, and the H-Si$_D$ = H-Si$'_D$ distance is 1.5 Å. A full account of the energetics for the hydrogenated SiC(100)-(3 $\times$ 2) surface is beyond the scope of our work. However, let us point out some considerations. Structures 2H, 2H1H, 2H2H$_r$, differ from each other for the successive addition of one H atom in the channel: therefore, they can be used to estimate the energy gain upon subsurface hydrogenation. Our results indicate that, in H-rich conditions, there is an energy gain of 1.1 eV for the addition of one H atom per cell to the structure 2H to obtain 2H1H (the total energies of two structures with a different H content are compared by adding to the energy of the H-deficient surface the local-spin-density free-atom chemical potential for H, consistently with the use of dissociated hydrogen in the experiments [5]). A further energy gain of 0.7 eV is realized by adding a second H atom per cell in the channel and forming the equilibrium structure 2H2H$_r$. The latter configuration is unfavorable by 0.5 (0.28) eV/H-atom with respect to the iso-stoichiometric configuration 4H (3H1H) where a higher H content is located at the outermost dimers. The formation of a hydrogenated surface with the same periodicity and H content in the various layers as in 2H2H$_r$, as revealed by Derycke and coworkers [5], is most likely induced by kinetic conditions attained with a uniform exposure to atomic hydrogen [18].

In agreement with the experiments, the 2H2H$_r$ surface, iso-stoichiometric with the claimed measured one [5], exhibits a metallic character [19]. However, our relaxed geometry is consistent with an alternative interpretation for the electronic structure, not based on a DB band. Whereas the H atoms adsorb on top of the first-layer Si dimers in a rather conventional arrangement that realizes the saturation of surface DBs, the fingerprint of this bizarre hydrogenated surface is the presence of deep subsurface H adatoms. Additionally, the unusual site selected by such adatoms is mainly responsible for the modification of the surface bandstructure in the energy range of the bulk bandgap. The H-Si$_b$ bonding scenario [5] would imply saturation of a third-layer Si row (Si$'_b$) and depletion of the other (Si$_b$), thus explaining the metallization in terms of a DB band. Instead, the unusual bridge location for H induces a non-bonding rehybridization of the third-layer Si dimers with a consequent upward energy shift and surface-to-bulk charge transfer, as detailed below.

The bandstructure of the 2H2H$_r$ surface is shown in Fig. 2. The bands are plotted along the edges of the irreducible part of the $3 \times 2$ 2D BZ. The shaded gray areas represent the projected
FIG. 2: Computed bandstructure of the hydrogenated $2H2H_r$ $\beta$-SiC(100)-$3 \times 2$ surface. Gray zones mark the projected bulk bandstructure. The 1.47 eV bandgap compares reasonably well with the bulk DFT value of 1.38 eV (affected by the renowned DFT underestimation, in this case 40%). We find that a few bands appear within the bandgap range, but they do not have a DB character, as inferred from the wavefunction analysis discussed below. Two occupied surface bands A and B are present in a small region of the 2D BZ slightly above the occupied PBBS continuum. Separated from B by a small energy gap ($\simeq 0.6$ eV), other surface bands are revealed: They are partially occupied. Band C lays in the upper region of the bulk bandgap. The Fermi level is well inside the conduction band, and crosses also other surface bands (D) in a small region of the 2D BZ. This is consistent with the observation of a negative band bending at the surface, as observed by STM [5].

The shape of the charge density distribution associated to the most relevant electron states is shown in Fig. 3. Figure 3a represents the band B at the $M$ point: This is a state localized at the subsurface H atoms ($s$-like shape) and at the $Si_d-Si_b$ ($Si'_d-Si'_b$) backbonds. Band A is given by similar orbitals. Bands A and B derive from a couple of similar bands of the clean TAADM SiC(100)-(3 $\times$ 2) surface, where the backbonds are instead hybridized with the $\sigma$-bonding contribution of the channel Si dimers: They remain just above the PBBS continuum. The metallic behavior of the $2H2H_r$ surface stems both from the minimum of the conduction band, which is occupied in the range of band bending, and from the surface bands C and D. The charge density for the state in Fig. 3b (explanation in the caption) clearly indicates a non-bonding character be-
FIG. 3: Isosurface plots of fully and partially occupied surface states for the hydrogenated 3×2 structure 2H2H$_r$ (side views). Black, gray, white spheres represent C, Si, H atoms, respectively. (a) Filled B band at $\overline{M}$. (b) Surface state at $\overline{M}$ close to the D band, identified as a gray dot in Figure 2, almost at $E_f$. (c) C band at $\overline{M}$. (d) D band at $\overline{M}$. In (c) and (d), the left (right) panels show views along the $[0\overline{1}1]$ ($[0\overline{1}1]$) direction, slightly tilted.

tween H and Si$_b$ ($\text{Si}_b$). It is originated from one of the surface bands of the TAADM structure with $\sigma$-bonding character on the channel Si$_b$-Si$_b$ dimers: the dimer bonding characteristic (clean surface) is transformed into the non-bonding characteristic (hydrogenated surface), with a consequent upward energy shift, upon subsurface H adsorption. In Figs. 3c and 3d we show two other partially occupied surface states at $\overline{M}$, belonging to bands C and D, respectively (black spots at $\overline{M}$ in Fig. 2). The dominant feature of the states in Figs. 3c and 3d is the identical antibonding character along $[0\overline{1}1]$ on second-layer Si dimers (right panels), and a charge component also on first-layer Si dimers. The difference between the two bands is evident only along the $[011]$ direction (left panels, bonding and antibonding nature for Figs. 3c and 3d, respectively). Of the three occupied surface bands that are present at the top of the valence continuum in the clean surface [3], one due to $\pi$-bonding states on the outermost dimers is shifted well into the occupied bulk continuum, whereas the other two are split into bands A and B that remain occupied, and C and D that are partially occupied because, reaching energies degenerate with the bottom conduction continuum, give origin to charge transfer to bulk states. Summarizing the above description, our results indicate that no metallic DB band localized on third-layer Si atoms exists in the bandgap. The only
electron states that can be found within the bandgap and possess a charge component on the third layer, have a clear non-bonding Si-H-Si character. The strongest metallic contribution is due to the filling of the PBBS continuum, and by the presence of partially filled surface states which stem from the Si$_b$-Si'$_b$ dimers (bonding) and finally assume a non-bonding Si$_b$-H-Si'$_b$ character. We note that, whereas on one hand the partial filling of the bulk conduction band may be affected by the DFT underestimation of energy gaps, the scenario denoted here suggests a very common and well documented situation in surface/interface science, characterized by the attainment of a two-dimensional electron gas induced by band-bending effects [20].

We estimate that of the extra 2 electrons due to third-layer hydrogen, $\simeq 0.66$ electrons are present in the upper surface band C, while the remaining 1.33 electrons per $3 \times 2$ cell are in the bottom of the conduction band and in small portions of the surface bands near the Fermi level (D). This geometry (non-bonding bridge position) is rather unusual, yet compatible with other investigations. In fact, a similar H coordination was obtained for bulk SiC, in the case of interstitial hydrogen in the neighborhood of a carbon vacancy, where the H atom position is equidistant from two neighboring Si atoms [21]. Our calculations clearly indicate that the same ligand geometry is assumed by the H atoms in the third layer at this unconventional hydrogenated SiC(100)-$3 \times 2$ surface, where no preferential bond is created with one of the two neighboring Si$_b$ and Si'$_b$ atoms.

For completeness, in order to include in our investigation a truly non-symmetric condition for sub-surface H adsorption, we have also considered a geometry were the two H atoms are not in the channel Si$_b$-Si'$_b$, but at interstitial bulklike positions inside the building blocks of the surface reconstruction. Such a configuration, whose computed bandstructure reveals a semiconducting character, is a local minimum of the total energy surface: the energy is 0.42 eV per cell [18] higher than that of the structure $2H2H_r$. We also computed the bandstructure for the asymmetric configuration $2H2H_u$ [5] without relaxing the ionic degrees of freedom: the outcome does not reveal a dangling-bond band in the gap.

In conclusion, our first-principle calculations enable us to support the metallic character of the hydrogenated $\beta$-SiC(100)-(3$\times$2) surface [5]. We propose an alternative explanation of the bandstructure, which is not compatible with the formation of a DB band induced by inequivalence of Si atoms at the broken third-layer Si dimers. (a) The periodicity is preserved upon hydrogen chemisorption. (b) H atoms chemisorb preferably on the outermost dimers and this does not change the semiconductor character of the surface; the separation between surface filled and empty bands increases. (c) Although not energetically preferred, equilibrium structures with H atoms in
the subsurface channel can be found as local minima of the potential energy surface. Third-layer H adsorption gives an energy gain with respect to low-coverage regimes, but does not result in additional covalent bonds. Instead, a channel H atom chooses a bridge position at the middle of the two neighboring Si\(_b\) and Si\(_{\prime b}\) atoms, depleting the third-layer Si dimers of bonding charge. (d) These rehybridization effects are translated into energy shifts well into the conduction band of the orbitals originally localized at the channel Si dimers, that simultaneously change their nature from \(\sigma\)-bonding to non-bonding. (e) The Fermi level is in a region where both surface and bulk bands are responsible for conduction.

This work was funded by INFM through the Parallel Computing Initiative and by MIUR-IT through FIRB-NOMADE.

[1] V. Bermudez, phys. ptat. pol. (b) 202, 447 (1997), and references therein.
[2] A. Catellani and G. Galli, Prog. Surf. Sci. 69, 101 (2002), and references therein.
[3] W. Lu, P. Krüger, and J. Pollmann, Phys. Rev. B 60, 2495 (1999).
[4] V. M. Bermudez, Nature Materials 2, 218 (2003).
[5] V. Derycke, P. G. Soukiassian, F. Amy, Y. J. Chabal, M. D. D’Angelo, H. B. Enriquez, and M. G. Silly, Nature Materials 2, 253 (2003).
[6] F. Amy and Y. J. Chabal, J. Chem. Phys. 119, 6201 (2003).
[7] F. Semond, P. Soukiassian, A. Mayne, G. Dujardin, L. Douillard, and C. Jaussaud, Phys. Rev. Lett. 77, 2013 (1996).
[8] W. Lu, W. G. Schmidt, E. L. Briggs, and J. Bernholc, Phys. Rev. Lett. 85, 4381 (2000).
[9] M. D’Angelo, H. Enriquez, V. Yu. Aristov, P. Soukiassian, G. Renaud, A. Barbier, M. Noblet, S. Chiang, and F. Semond, Phys. Rev. B 68, 165321 (2003).
[10] L. Pizzagalli and A. Catellani, Surf. Sci. 494, 53 (2001).
[11] V. Derycke, P. Fonteneau, N. P. Pham, and P. Soukiassian, Phys. Rev. B 63, 201305 (2001).
[12] The energetics obtained from the calculations with a 8 atomic layers are in agreement with those obtained with 16 layers. The thicker slab describes correctly the relative energy of the surface bands with respect to the projected bulk bandstructure and is used for the computation and discussion of the electronic properties in this work. The thinner slab is used to evaluate the relative energy of the several computed geometries.
The energetics and electronic structure of the most relevant surfaces were refined by using a finer grid of \( k \) points: six for the clean; twelve for \( 2H2H \) and \( 3H1H \).

A full account of the reaction kinetics would require the computation of several geometries to describe the potential energy surface, and also the inclusion of zero-point energies in the energetics estimates. This is beyond the scope of this investigation, which is instead devoted to the electronic properties.

The other iso-stoichiometric surfaces investigated here, \textit{i.e.} \( 4H \) and \( 3H1H \), are semiconducting. We find metallic surfaces only for different H contents (\( 3H \) and \( 2H1H \), incompatible with the experimentally suggested hydrogenation amount), as expected on the basis of electron counting.