Hydrogen-Induced Surface Metallization of β-SiC(100)-(3×2) Revisited by Density Functional Theory Calculations

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(Received 30 September 2004; published 23 March 2005)

Recent experiments on the silicon terminated $(3 \times 2) - \mathrm{SiC}(100)$ 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: in addition to 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.

DOI: 10.1103/PhysRevLett.94.116103 PACS numbers: 68.35.Md, 68.55.Ac, 81.15.Aa

The silicon terminated β-SiC(100)-(3×2) surface is constituted of extra Si dimers on top of silicon terminated layers [1–3]. A recent experimental investigation [4–6] has shown a surprising property: the transition from a semiconducting to a metallic surface induced by hydrogen chemisorption. In general semiconductors 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 β-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 3×2 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 same model [3] adopted for the interpretation of the experimental H-induced metallization [5]. As indicated in Fig. 1(a), this clean 3×2 surface is characterized by a coverage of 1 monolayer (ML) extra silicon atoms on top of the bulklike Si-terminated SiC(100) face. Of this extra ML, $\frac{2}{3}$ ML Si atoms are accommodated at the first adlayer forming a couple of flat dimers in each periodicity unit. The remaining $\frac{1}{3}$ ML Si atoms are accommodated on top of them forming a second adlayer of buckled dimers. This structure, called two-adlayer asymmetric-dimer model (TAADM) [3,8,9], was proposed among several possible 3×2 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 (Si_D-Si'_D) is responsible

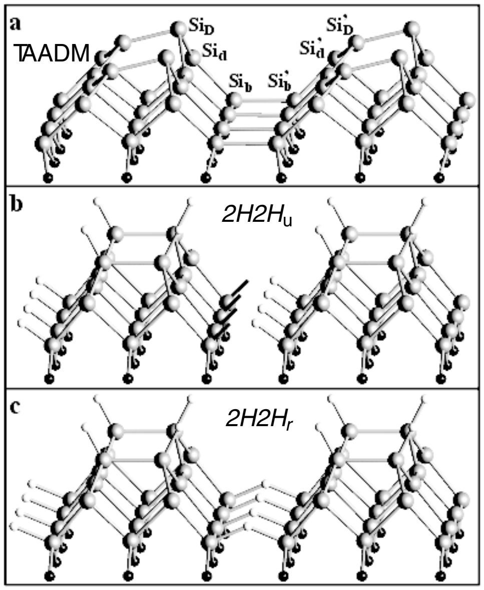

FIG. 1. Side view of the outermost layers for the 3×2 model reconstruction adopted in the present work: black (gray) spheres represent C (Si) atoms, smaller white spheres indicate H atoms. (a) The clean reconstructed TAADM SiC(100) surface. (b) The $2H2H_u$ model for the hydrogenated surface, proposed on the basis of the recent experiments [5,6]. (c) The equilibrium adsorption geometry $2H2H_r$ obtained by relaxing the system starting from the experimental $2H2H_u$ model. A 2×2 replica of the unit surface cell is shown.

for the existence of a gap between two surface bands, π-bonding (filled) and π^*-antibonding (empty) on the Si_D-Si'_D dimers. The 2nd-layer dimers (Si_d-Si'_d) have a short length, and weaker silicon dimers are present at the third layer (Si_b-Si'_b). Let us call the latter *Si atoms in the channel*.

H atoms can be bonded to the external Si_D-Si'_D dimers by weakening the strength of such bonds and eliminating the buckling [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 *et al.* [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. 1(b)] in the $[0\bar{1}1]$ direction at the third surface layer.

To test this model and interpret 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 [12]) atomic layers, and 13 Å of vacuum. 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 wave functions were expanded in plane waves with a kinetic energy cutoff of 22 Ry. Brillouin zone (BZ) sums were performed at three special Monkhorst-Pack **k** points in the irreducible wedge of the two-dimensional (2D) BZ [15]. The PBE exchange-correlation functional [16] was used. We checked our results by performing local-spin-density test calculations.

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; $nHmH$ 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 $4H$ contain H only on top of the outermost Si dimers, with one and 2 H atoms for each top Si atom, respectively; (ii) $3H$ has 2 H atoms attached to Si_D and only 1 H atom attached to Si'_D on each top dimer; (iii) $2H2H$ includes H atoms at the outermost Si dimers as in configuration $2H$, plus 2 H atoms per cell at the Si'_b atoms in the channel, with 1 H atom for each Si_b-Si'_b dimer [Figs. 1(b) and 1(c)] placed at an initial H-Si'_b distance [structure $2H2H_u$ in Fig. 1(b)] typical of the H-Si single bond, ~1.5 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 previous results [10,11], the $2H$ and $4H$ structures are semiconducting: the outermost Si dimers are elongated from 2.30 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 separated, preserving the semiconducting behavior as in the case of Si(100) hydrogenation.

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 Si'_b atoms [Fig. 1(b)] move spontaneously to reach an equilibrium location bridging Si_b and Si'_b sites [$2H2H_r$, Fig. 1(c)]. This migration was also obtained through extended calculations, with full atomic relaxation, performed with a larger supercell obtained by doubling the 3×2 cell, to test that our results are not affected by the choice of periodic boundary conditions. In this migration, the H-Si'_b distance increases from 1.5 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. 1(c), 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)-(3×2) 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 1 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 1 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 is unfavorable by 0.5(0.28) eV/H-atom with respect to the isostoichiometric 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 co-workers [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, isostoichiometric with the claimed measured one [5], is metallic [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 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 band structure around the bulk band gap. 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 nonbonding rehybridization of the third-layer Si dimers with a consequent upward energy shift and surface-to-bulk charge transfer.

The band structure of the $2H2H_r$ surface is plotted in Fig. 2 along the edges of the irreducible part of the 3×2 2D BZ. The 1.47 eV band gap compares reasonably well with the bulk density-functional theory (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 band gap range, but they do not have a DB character, as inferred from the wave function 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 lies in the upper region of the bulk band gap. The Fermi level is well inside the conduction band, and also crosses other surface bands (D) in a small region of the 2D BZ. This is consistent with a negative band bending at the surface, as observed by STM [5].

The shape of the charge density distribution for the most relevant electron states is shown in Fig. 3. Figure 3(a) represents the band B at $\bar{M}$: this is a s-like state localized at the subsurface H atoms 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 surface, where the backbonds are instead hybridized with the σ-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. 3(b) (explanation in the caption) clearly indicates a nonbonding character between H and Si_b' (Si_b). It is originated from one of the surface bands of the TAADM structure with σ-bonding character on the channel Si_b-Si_b' dimers: the dimer bonding characteristic (clean surface) is transformed into the nonbonding characteristic (hydrogenated surface), with a consequent upward energy shift. In Figs. 3(c) and 3(d) we show two other partially occupied surface states at $\bar{M}$, belonging to bands C and D, respectively. The dominant feature of the states in Figs. 3(c) and 3(d) is the identical antibonding character along $[0\bar{1}1]$ 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. 3(c) and 3(d), 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 π-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 PBBS continuum, they give origin to charge transfer to bulk states.

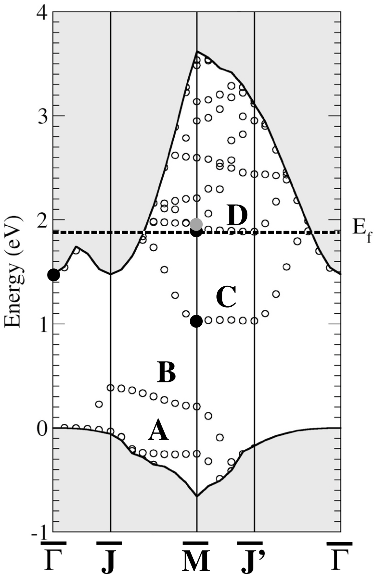

FIG. 2. Computed band structure of the hydrogenated $2H2H_r$ $\beta - \mathrm{SiC}(100) - (3 \times 2)$ surface. Gray zones mark the projected bulk band structure (PBBS).

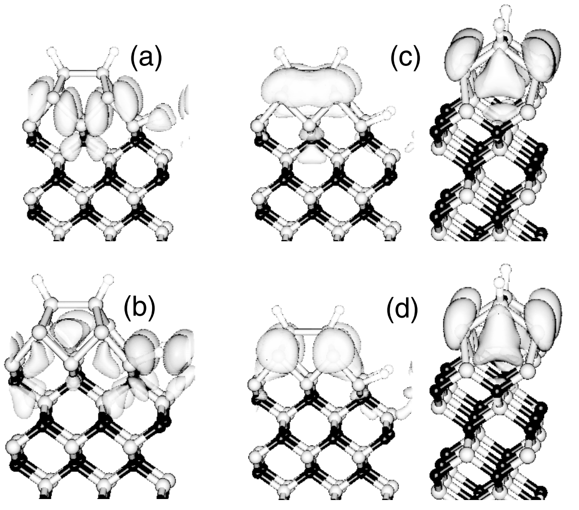

FIG. 3. Isosurface plots of fully and partially occupied surface states for the hydrogenated 3×2 structure $2H2H_r$ (side views). Black, gray, white spheres represent C, Si, H atoms, respectively. (a) Filled B band at $\bar{M}$. (b) Surface state at $\bar{M}$ close to the D band, identified as a gray dot in Fig. 2, almost at E_f. (c) C band at $\bar{M}$. (d) D band at $\bar{M}$ (black spot). In (c) and (d), the left (right) panels show views along the [011] ($[0\bar{1}\bar{1}]$) direction, slightly tilted.

Summarizing the above description, our results indicate that no metallic DB band localized on third-layer Si atoms exists in the band gap. The only electron states that can be found within the band gap and possess a charge component on the third layer, have a clear nonbonding 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 nonbonding 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 or 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 3×2 cell are in the bottom of the conduction band and in small portions of the surface bands near the Fermi level (D). This nonbonding bridge geometry is rather unusual, yet compatible with other investigations. A similar H coordination was obtained for bulk SiC: in the case of interstitial hydrogen in the neighborhood of a C vacancy, the H atom sits 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)-3×2 surface.

For completeness, in order to include in our investigation a truly nonsymmetric condition for subsurface H adsorption, we have also considered a geometry were the 2 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 band structure reveals a semiconducting character, is a local minimum of the total-energy surface, 0.42 eV/cell [18] higher than the structure $2H2H_r$. We also computed the band structure for the asymmetric configuration $2H2H_u$ [5] without relaxing the ionic degrees of freedom: the outcome does not reveal a DB band in the gap.

In conclusion, our calculations enable us to support the metallic character of the hydrogenated β-SiC(100)-(3×2) surface [5]. We propose an alternative explanation of the band structure, 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 H chemisorption. (b) H atoms chemisorb preferably on the outermost dimers maintaining 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 are viable. 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'_b atoms, depleting the third-layer Si dimers of bonding charge. (d) This rehybridization is 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 σ-bonding to nonbonding. (e) The Fermi level crosses both surface and bulk bands.

W. G. Schmidt is acknowledged for fruitful discussions and critical reading of the manuscript. This work was funded by INFM through the Parallel Computing Initiative and by MIUR-IT through FIRB-NOMADE.

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