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Surface Science 494 (2001) 53–59

SURFACE SCIENCE

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Ab initio calculations of the H-induced surface restructuring on β-SiC(0 0 1)-(3 × 2)

L. Pizzagalli [a,*], A. Catellani [b]

[a] *Laboratoire de Métallurgie Physique, SP2MI, BP 30179, F-86962 Futuroscope Chasseneuil Cedex, France*
[b] *CNR-MASPEC, Parco Area delle Scienze, 37a, 43010 Parma, Italy*

Received 10 March 2001; accepted for publication 30 July 2001

Abstract

The effect of H passivation on the β-SiC(0 0 1)-(3 × 2) surface has been investigated for different hydrogen coverages with first principles pseudopotential calculations. Monohydride configurations result in symmetric Si addimers, while an asymmetric canted geometry is stabilized for dihydride coverages. Energy comparisons in the grand-canonical frame indicate that the occurrence of the actual hydride geometry strongly depends on the experimental conditions. On the basis of calculated images, we predict that dihydride or monohydride configurations could be discriminated with STM investigations. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silicon carbide; Density functional calculations; Chemisorption; Surface relaxation and reconstruction; Hydrogen atom

The passivation with hydrogen is an important process to reduce the chemical activity of surfaces exposing dangling bonds. This mechanism has been largely studied over the past 10 years for silicon surfaces and is still the subject of research [1,2]. On the Si(0 0 1) surface, complete monohydride (2 × 1), mixed monohydride and dihydride (3 × 1), and disordered dihydride and trihydride (1 × 1) configurations have been observed [3,4]. Which reconstruction occurs depends on the deposition temperature and on the level of hydrogen exposure. Hydrogen passivation of silicon carbide surfaces has been less investigated so far, though the number of studies devoted to this material has considerably increased [5], due to its unique and promising properties [6]. It has been reported that hydrogen passivation at room temperature of the silicon terminated (3 × 2) reconstructed β-SiC(0 0 1) surface leads to the formation of a (3 × 1) reconstruction [7–9]. Additional H exposure results in a (1 × 1) surface [9]. These transformations seem reversible, the (3 × 2) being recovered by annealing from either the (3 × 1) or the (1 × 1) reconstructions [7,9]. Recent results however indicate the persistence of the (3 × 2) reconstruction after H adsorption [10]. In addition, all experimental investigations agree that the surface passivation is obtained only with pre-dissociated hydrogen molecules. As far as we know, no theoretical studies of the hydrogenation effect are available, except an empirical quantum chemistry prediction of a monohydride (2 × 1) surface [11], never observed though.

* Corresponding author. Tel.: +33-549-496-833; fax: +33-549-496-692.
E-mail address: laurent.pizzagalli@univ-poitiers.fr (L. Pizzagalli).

0039-6028/01/$ - see front matter
PII: S0039-6028(01)01482-0

In this letter, we investigate the effect of the adsorption of hydrogen on the (3×2) reconstructed β-SiC(0 0 1) surface, for different H coverages. The structure modifications occurring on the surface dimers are described. A grand-canonical analysis of the energetics of the adsorption mechanism is also presented. Finally, scanning tunneling microscopy (STM) images versus H coverage are calculated.

The choice of the structural model for the clean (3×2) surface is still subject of debate. Indeed, as many as four different structural models have been proposed in the literature. No one is fully supported by all experiments and calculations, though. There is a general agreement that (i) the (3×2) reconstruction occurs with excess Si adsorbed on top of the Si-terminated (2×1) or c(4×2) surface, (ii) it seems to be the last stage before self-limitation of the growth [12], and (iii) it includes Si dimers as structural basis. However, discrepancies remain about the coverage of the excess Si atoms. To our knowledge, the only reported investigations of the coverage conclude to a measured value close to 1/3 ML [13,14]. Two structural models comply with this requirement (Fig. 1). The ADD model (also called ADDR or SDR model), originally proposed by Hara et al. [13], has been found to be energetically not favored by all first principles calculations [15–18]. Yan et al. [19] proposed the ALT model (also called ADR), which is supported by STM investigations [20] and several calculations [15–17,21]. This model however is incompatible with LEED measurements [22]. Two other structural models, with different excess Si coverages, have also been proposed. The DDR model (Fig. 1) is obtained for a coverage of 2/3 ML: although supported by several experiments [8,23], it is ruled out by ab initio calculations [16–18,21]. Finally, another model, TAAD (Fig. 1), has been proposed as the most stable configuration by Lu et al. [18] via total energy arguments. This model presents an excess Si coverage of 1 ML but seems supported by recent optical anisotropy measurements [24]. The model is built in close connection to the MRAD proposed geometry for the c(4×2) reconstruction, which is not supported by experimental evidences, up to now. The overlayer structure in TAAD still maintains a fractional coverage of 1/3 excess Si atoms, and then resembles the ALT configuration.

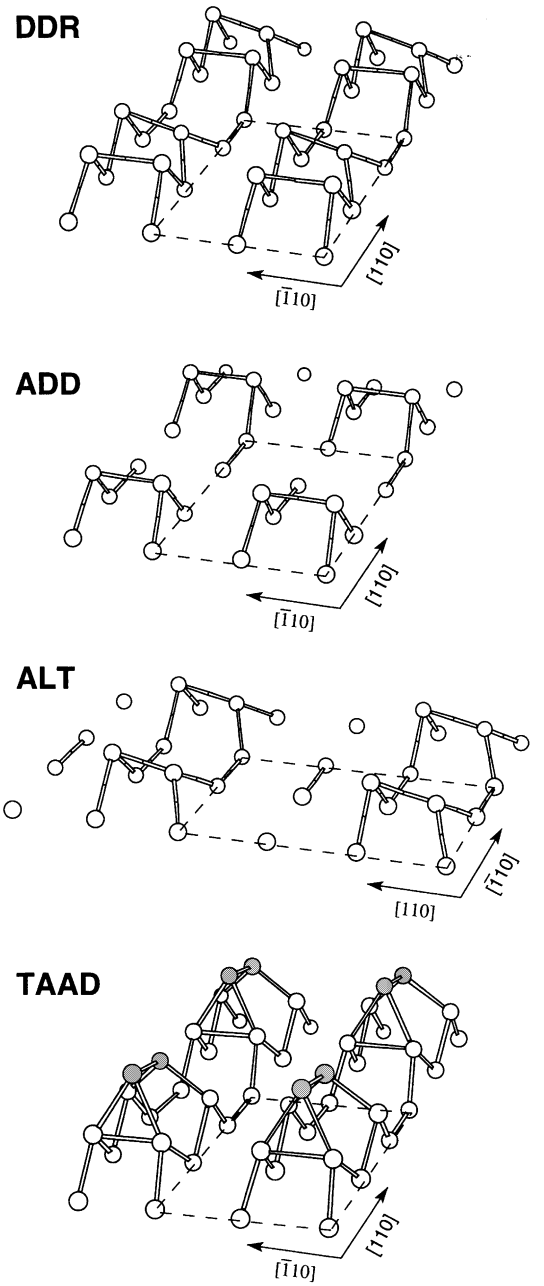

Fig. 1. Geometries of the different proposed (3×2) models for the clean surface [16]. Only the excess Si addimers and the underlying Si layer are represented. Note the presence of an extra adlayer for the TAAD model (grey balls).

New additional measurements, especially of the coverage, would be necessary for an unambiguous determination of the (3×2) structure. It has been speculated that a precise characterization of the H-covered surface could be meaningful to this purpose. Thus it would be desirable to investigate H adsorption for all the four proposed models. Such study might however be not conclusive, since a large number of configurations, with varying H and Si coverages, would lead to the comparison of very similar energies. In this paper, we do not focus on the determination of the clean (3×2) structure via H adsorption. Rather, we concentrate on the effect of hydrogen interaction with the excess Si dimers, considering one unique structural model compatible with a persisting (3×2) reconstruction upon H adsorption, as observed in recent experiments [10]. Indeed, all the proposed models but ADD present Si addimers with similar buckling and bond lengths [16–18,21] perpendicular to the underlying dimers. Here we concentrate on the ALT model. Although it is inadequate regarding LEED, this model is supported by many experimental and theoretical experiments. A major advantage is its low Si coverage which allows to consider a restricted set of H-adsorbed configurations. Because of the similarity of Si-overlayer geometries in the proposed models, especially with the outermost overlayer of TAAD, we expect that our results should be not specific on the chosen (3×2) structure.

We performed density functional calculations in the local density approximation at zero temperature. The ionic interactions are represented by nonlocal norm-conserving pseudopotentials for Si (s and p nonlocality) and C (s nonlocality) [25]. The relaxed atomic structure have been obtained using a (6×4) supercell with eight atomic layers and a 10 Å vacuum region, i.e. 200 atoms for one surface fully covered with hydrogen [16]. The bottom layers were frozen in the p(2×1) configuration determined earlier [26]. We used a plane-wave basis with energy cutoffs of 36 Ry for the wave functions and 130 Ry for the charge density. The k-point sampling was done at the Γ point, corresponding to four inequivalent k points in the Brillouin zone for the (3×2) cell. Such sampling has proved to be sufficient to get good relaxed structures and energies [16,17]. The STM images are calculated within the Tersoff–Hamann approximation [27].

The relaxed geometry of the ALT model is represented in Fig. 1. This structure includes Si dimers on top (Si addimers) and also Si dimers in the underlying Si layer (Si underdimers). We considered three different atomic configurations, corresponding to an increasing H coverage. The first one, M1, is the monohydride phase with one H for each Si of the addimers, i.e. two H atoms by (3×2) cell. The second one, M2, is also a monohydride phase, but includes additional hydrogen atoms decorating the Si underdimers, i.e. four H atoms by (3×2) cell. Last, the dihydride D configuration shows a surface with a total of six H atoms by (3×2) cell, with four H on the addimers and two H on the Si underdimers. The geometries obtained for the Si addimers in all cases are represented in Fig. 2. The clean surface shows asymmetric, strongly bonded, and significantly buckled addimers. One of the backbond lengths is larger than the other to accommodate buckling. The hydrogen adsorption in the monohydride phases M1 or M2 drastically changes the structure of the addimer, although preserving a (3×2) surface periodicity. The buckling is removed and the Si addimer becomes symmetric. The bond is slightly weakened with a length of 2.33 Å. This value is lower than the one calculated by Northrup for the monohydride (2×1) phase of Si(0 0 1)–H (2.4 Å) [28], since the reduced lattice parameter of SiC compared to Si allows the two Si adatoms to get closer without large backbonds distortion. M2 configuration differs from M1 only for the hydrogenation of the symmetric Si underdimers (see Fig. 1). It results in a strengthening of the underdimer bond, with a bond length decreasing from 2.62 to 2.35 Å. This last result may be compared with theoretical investigations of the monohydride (2×1) β-SiC(0 0 1)–H surface, i.e. without the Si addimers. We found that the bond length is slightly lower than the value computed with an empirical quantum chemistry method (2.48 Å [11]), but very close to the first principle determination (2.39 Å [29]). For the dihydride phase D, we found that a symmetric SiH_2 geometry is unstable, and that the system relaxes to a canted

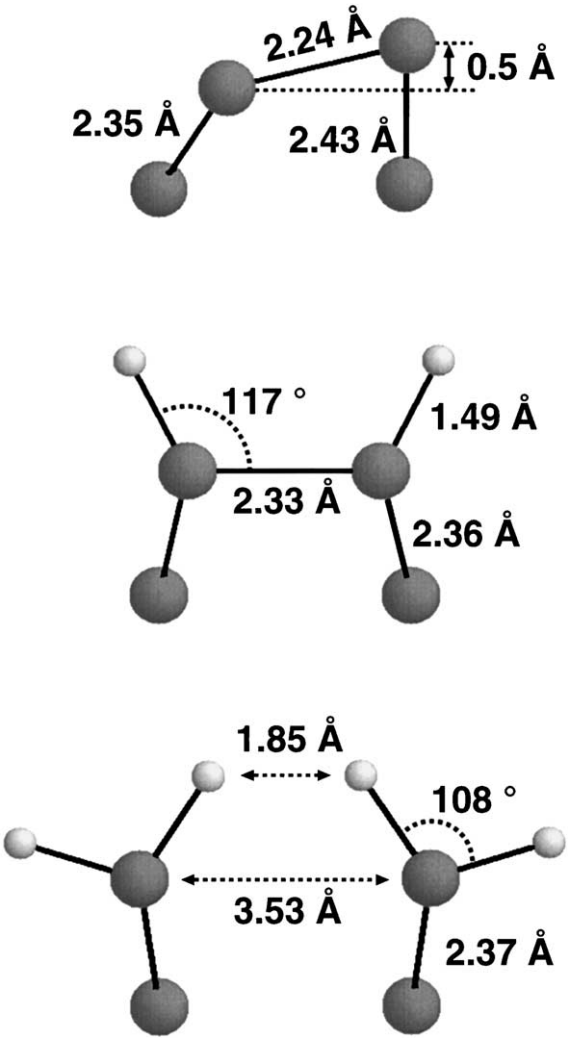

Fig. 2. Side view of the relaxed geometries of the Si addimer for the clean surface (top), the monohydride phase M1 or M2 (middle), and the dihydride phase D (bottom). Si (H) atoms are represented by grey (white) balls.

configuration (Fig. 2). A nonsymmetric canted structure is also energetically favored in the case of the dihydride Si(0 0 1)–H surface, due to repulsive steric interactions between neighboring hydrogen atoms [28]. This effect is even more dramatic for SiC, due to the reduced lattice parameter. However, there is a major difference with the surface obtained for the dihydride Si(0 0 1)–H. Here, the backbonds are not distorted in the same, but in opposite direction. The configuration then retains the same peculiar mirror symmetry of the hydride Si dimers, and the same (3×2) surface periodicity. The situation is supposed to be specific to configurations where there is enough space around the addimer for accommodating this distortion. Hence, it should occur for the ALT and TAAD models. For the DDR (or ADD) model, where addimers are contiguous along the addimer bond direction, dihydride adsorption would lead to a different, more symmetric (3×1) pattern, with SiH_2 groups either symmetric or canted in the same direction.

Energy comparison of structures including a variable number of H atoms are done using a grand-canonical analysis. We considered an isolated system composed of the surface and a gas, in equilibrium with a thermostat. We compare the free energies $F = U + E^{zpe} - n\mu$. U is the first principles zero temperature calculated energy of the configuration, E^{zpe} is the zero-point energy of the surface, n is the number of adsorbed H atoms, and μ is the chemical potential. We assumed that only Si–H vibrational modes contribute significantly to E^{zpe}, thus $E^{zpe} = 0.21n$ eV [28]. We are then left with the evaluation of the chemical potential. At equilibrium, the chemical potential of the adsorbed H atoms μ is related to the gas chemical potential in a simple way. If we consider an atomic hydrogen gas, $\mu = \mu_H$, whereas for a molecular hydrogen gas we get $2\mu = \mu_{H_2}$. The canonical chemical potentials μ_H and μ_{H_2} can be calculated considering a perfect gas at a given pressure and temperature. Since exact conditions during hydrogenation are not precisely known, it is better to consider a possible range for the chemical potential. A good maximum for μ_{H_2} is obtained from a zero temperature ab initio calculation of an isolated H_2 molecule, using the same supercell and cutoff to get convergence error cancellation. We obtained $\mu_{H_2}(\max) = -30.481$ eV, by including the zero-point energy correction of H_2 (0.272 eV). [1] $\mu_H(\max) = -13.003$ eV is obtained from the H_2 calculation using the experi-

[1] Note that a slightly higher chemical potential maximum could be obtained by considering high pressure conditions. However, the pressure effect is almost negligible in normal conditions.

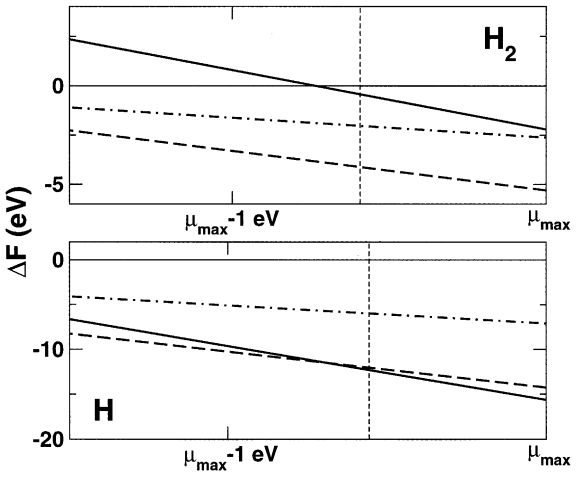

Fig. 3. Free energy comparison of the different H-passivated surfaces in equilibrium with a molecular (top) or atomic (bottom) hydrogen gas, versus the H chemical potential. The clean surface is the energy reference (—). The three configurations are represented: M1 (–·–·–·), M2 (– – –) and D (—). For reference, the vertical dashed line marks the chemical potentials calculated for a temperature of 300 K and a pressure of 10^{-4} Torr.

mental H_2 atomization energy value 4.747 eV [30]. The results are represented in Fig. 3. First, we consider the hydrogenation with molecular hydrogen H_2. In that case, the configuration M2, i.e. a monohydride surface fully covered with H, is the most stable structure for a large range of chemical potential. The situation is more complex in the case of exposure to atomic hydrogen. The most stable configurations depends on the chemical potential value (Fig. 3). If $\mu \approx \mu_{max}$, the dihydride D phase is favored whereas for lower μ, the monohydride M2 phase is stabilized. Experimentally, atomic hydrogen gas deposition is done by cracking molecular hydrogen gas with a filament. Assuming a negligible radiative heating of the surface by the filament, and deposition done at RT ($T = 300$ K) with an hydrogen partial pressure $P = 10^{-4}$ Torr at the surface vicinity, we determined the chemical potential within the perfect gas theory. It corresponds approximately to the transition between M2 and D configurations (Fig. 3). Small variations of temperature and pressure around this reference state are then expected to change the passivated structure. If the partial gas pressure is raised, the chemical potential increases favoring the dihydride D configuration. Our results indicate that the hydride configuration of the surface is very sensitive to the preparation conditions, which could explain why different reconstructions are observed [7–10].

In order to get a thorough comparison with experiments, we have calculated the filled and empty states STM images for the different configurations (Fig. 4). The filled states image of the clean surface shows well-defined spots encompassing the Si addimers, brighter on the upper Si adatoms. Similar, although symmetric patterns are visible for monohydride M1 and M2 configurations, since H adsorption removes the Si-addimers buckling. For the D geometry, two smaller blobs are distinguishable, one for each SiH_2 unit, instead of only one oval spot. In this case, asymmetric spots are observed, due to the peculiar relaxed structure obtained for the dihydride configuration.

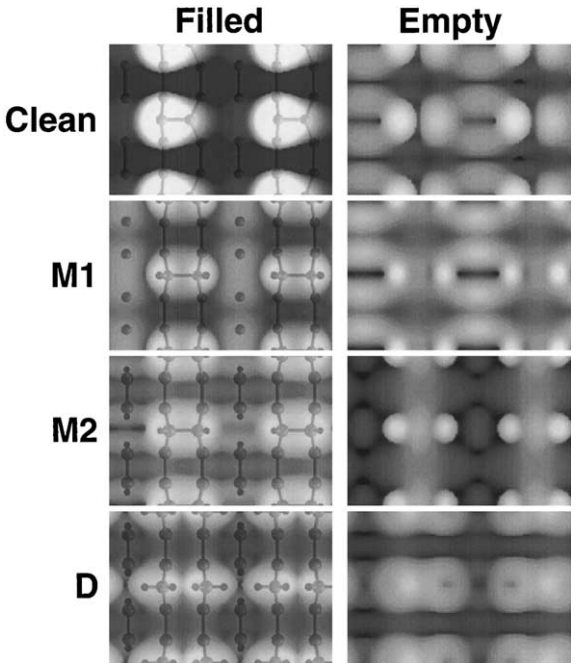

Fig. 4. Filled (left) and empty (right) states STM images for the clean surface and the three passivated configurations M1, M2 and D. The voltage is 1 V (–1 V) in all cases for probing the empty (filled) states; only the empty states image of the clean surface is obtained with 0.7 V, to enhance contrast. The geometry is projected on the image, to help localization.

Empty states images are less contrasted. For the clean surface, the structure of the addimers is resolved, and we observed one small separate spot centered on each adatom. Similar features are obtained for the monohydride M1 and M2 configurations. The H passivation of the underdimers in the M2 geometry leads to a current reduction, which results in an enhanced contrast of the adatoms blobs. The increased brightness of the spots in the reconstructed empty states image and the persistence of a (3×2) reconstruction are found in nice agreement with newest experimental results on the hydrogenation of Si–SiC(0 0 1) [10]. The complete passivation of the adatoms in the dihydride case leads to a poorly contrasted 'peanut'-like spot. Interestingly, the addimer asymmetry seems indistinguishable in the image. Useful insights for the analysis of STM investigations can be deduced from our calculations. First, it will be difficult to distinguish the monohydride phase from the clean surface with filled states images, since H-passivated and clean addimers appear very similar. Monohydride H passivation could however be recognized in the empty states images as a contrast enhancement of the spots observed for each Si adatom. For the dihydride phase, significant information should come from filled states images, where the dihydride passivation would change the Si addimers appearance from one large oval blob to two almost circular separate spots.

To conclude, we have performed first principles calculations of the effect of H passivation on the Si terminated (3×2) β-SiC(0 0 1) surface, for different H coverages. Monohydride phases include symmetric Si addimers with a dimer bond length of 2.33 Å. For the dihydride coverage, we found that a structure with symmetric SiH_2 unit is unstable and relaxes to a canted configuration due to steric repulsive H–H interaction. Grand-canonical energy comparisons have been done considering surface exposition to both molecular and atomic hydrogen. We found that both monohydride or dihydride configurations could be obtained with exposure to atomic hydrogen, depending on the (P,T) experimental conditions. The electronic and structural properties obtained for the monohydride phase seem to be in nice agreement with newest, yet unpublished experimental results, predicting the persistence of the (3×2) reconstruction upon H adsorption on low coverage Si–SiC(0 0 1) surfaces. Another geometry should be favored in the case of addimers contiguous in the addimer bond direction: additional calculations and experimental data are demanded to shed some light on this particular point.

Acknowledgements

We are indebted to P. Soukiassian, for sharing with us results before publication. Computing facilities of IDRIS (CNRS, France) and CSCS (Manno, Switzerland) are acknowledged. Work partially supported by INFM-PRA:1MESS.

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