ELSEVIER

Materials Science and Engineering B96 (2002) 132–136

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Si and H adsorption on the silicon terminated β-SiC(001) surface: an ab initio study

Alessandra Catellani [a,*], Laurent Pizzagalli [b], Giuali Galli [c]

[a] *CNR-MASPEC, Parco Area delle Scienze, 37a, 43010 Parma, Italy*
[b] *Laboratoire de Métallurgie Physique, SP2MI, BP 30179, F-86962 Futuroscope Chasseneuil cedex, France*
[c] *Lawrence Livermore National Laboratory, PO Box 808, Livermore, CA 94550, USA*

Abstract

We review some recent results on the stoichiometric silicon terminated SiC(001) surface: in particular, we discuss the effect of strain on the clean surface, and the subsequent adsorption of Si and H atoms, by means of first principles molecular dynamics simulations. The structural modifications induced by hydrogenation on the stable reconstruction for the clean SiC surface compare fairly well with recent experimental data. © 2002 Elsevier Science B.V. All rights reserved.

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

---

1. Introduction

Silicon carbide is a promising material for high power and high frequency applications and biological sensors [1]; although not the most stable, the cubic polytype (β-SiC) is expected to present higher electron mobilities than the most stable hexagonal polytypes. Furthermore, β-SiC is a potential substrate for nitride growth, since its lattice mismatch with several nitrides is fairly small and its elastic and thermal properties are close to those of nitride materials. For similar reasons, it has been recently proposed that β-SiC might be a promising substrate for diamond growth [2,3]. The different reconstructions of β-SiC surfaces have been widely studied in the last 10 years [4], the characterization and understanding of growth mechanisms on the substrate being prerequisites for industrial applications [1]. Still, a number of key questions on the stable geometry of stoichiometric [5–11], and non-stoichiometric [12–17] surface reconstructions remain unanswered.

The silicon terminated SiC(001) surface (Si–SiC(001)) is particularly interesting as several reconstructions have been found to occur at this surface, depending on the fractional Si coverage, and also because it is more appealing for potential technological applications. Furthermore, controversies are still open on the most stable geometry, both from the experimental and theoretical point of view.

At the stoichiometric ($\theta_{si} = 1$) surface, dimerization of surface Si atoms induces a $p(2 \times 1)$ periodicity: an early structural analysis [18] of the $p(2 \times 1)$ LEED pattern has led to a buckled-dimer model similar to that of Si(001). This model is not confirmed by ab initio calculations [5,19,20], reporting instead unbuckled dimers much longer than those of Si(001); moreover recent ARUPS data [8] are consistent with a weak bonding of unbuckled Si dimers. Core level photoemission spectroscopy [21,22] suggests that the stable reconstruction for the clean stoichiometric Si–SiC(001) surface should be the $c(4 \times 2)$ geometry, $p(2 \times 1)$ occurring only in the presence of defects. Indeed, STM images [9] have revealed a $c(4 \times 2)$ reconstruction for the clean surface, while the $p(2 \times 1)$ pattern appears in areas of missing dimers. The model which has been proposed on the basis of STM experiments for the $c(4 \times 2)$-SiC(001) reconstruction is as well different from the $c(4 \times 2)$ of Si(001) [23], involving alternating symmetric dimers (AUDD) with different heights [5,9,24], instead of buckled dimers.

Finally, relying upon total energy arguments, the Missing Row Asymmetric Dimer (MRAD) [7] model was proposed for the $c(4 \times 2)$ reconstruction of Si–SiC(001). In this model, asymmetric ad-dimers are on

---

[*] Corresponding author. Tel.: +39-521-268-200; fax: +39-521-269-206

E-mail address: catellani@maspec.bo.cnr.it (A. Catellani).

PII: S0921-5107(02)00303-3

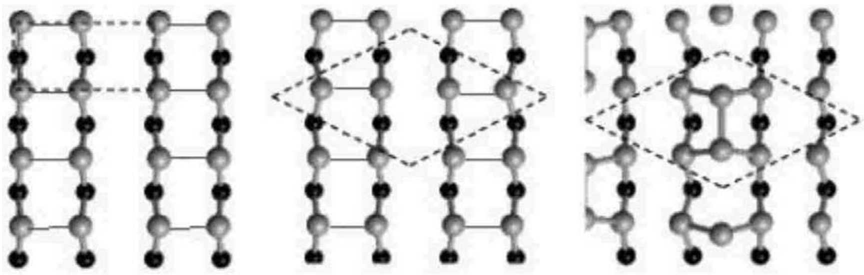

Fig. 1. Top view of the clean (left) and hydrogenated atomic structures for Si–SiC(001) surface. Black (grey) spheres represent C (Si) atoms. Small light grey spheres are the hydrogen atoms. Only two outermost planes are shown.

top of a full Si-dimerized surface (Fig. 1, right panel), providing a total Si coverage of $\theta_{\mathrm{si}} = 1.5$. The stability of this reconstruction was discussed within the grand canonical scheme, and it was shown that MRAD is indeed the most stable structure, at the chosen value of the silicon chemical potential. However, there is no consensus on the formation energies of these surfaces, since different calculations [7,25,26] predict different values, the error being as large as the energy gain of the MRAD model over AUDD. Most importantly, there is at present no experimental evidence [10,11,22,28,29] of a coverage larger than one, for the $c(4 \times 2)$ reconstruction.

In the present paper, in order to shed light on some of these issues, we review some recent ab initio results on the (001) stoichiometric silicon terminated surface of the cubic SiC polytype, including the study of adsorbates. Our results are discussed in comparison with other theoretical and experimental data. As adsorbates, we have explicitly considered silicon atoms or dimers, which are known to induce large order reconstructions and extended nanostructures [14–17,30–33]. Furthermore, we have studied the modifications induced by hydrogenation: 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 [34,35]. Hydrogen passivation of silicon carbide surfaces has been less investigated so far, though the number of studies devoted to this topic has considerably increased [36,37].

2. Method

We performed density functional calculations in the local density approximation at zero temperature. The ionic interactions are represented by non-local norm-conserving pseudopotentials for Si (s and p non-locality) and C (s non-locality) [38]. The relaxed atomic structures have been obtained using a $p(4 \times 4)$ symmetric supercell with 16 atoms per layer, 11 layers and a 10 Å vacuum region, i.e. 176 atoms, plus adatoms [5]. We used a plane-wave basis with energy cutoffs of 39 Ry for the wave functions and 154 Ry for the charge density. The k-point integration was performed using the Γ point of the supercell, which corresponds to three-inequivalent k points in the Brillouin zone for the $c(4 \times 2)$ cell. Such sampling has proved to be sufficient to get good relaxed structures and energies [5].

Convergence was considered achieved for forces ≤ 0.002 eV Å^{-1}. The STM images are calculated within the Tersoff–Hamann approximation [39].

3. The clean surface

With the technique described above, we have shown [5] that, at the LDA lattice parameter (4.3 Å), the stable reconstruction for the stoichiometric Si-terminated surface ($\theta_{\mathrm{si}} = 1$) is a $p(2 \times 1)$ dimer row geometry, with flat weak dimers (bond length ~ 2.6 Å, see Fig. 1 left panel). Our results are in agreement with other ab initio calculations [8,19,40]. In particular, it has been shown that increasing the number of k-points gives slightly larger bond-lengths, which vary from 2.58 up to 2.63 Å when including three to eight k-points [5]. This $p(2 \times 1)$ reconstruction lays only a few meV per atom lower than the ideal surface: the extremely flat potential energy surface of this system is a signature of its unique elastic characteristics, and a probable reason for the open controversies on the surface geometry. The calculated surface energy is 2.7 eV per atom [5], close to the formation energy of a Si–C bond, indicating the quasi-ideal character of the reconstructed surface.

Recently we proposed [5] that the tensile stress is responsible for the AUDD $c(4 \times 2)$ reconstruction observed via STM on clean, nominally stoichiometric Si–SiC(001) surfaces. Our calculations for SiC slabs under stress revealed that if the Si-surface is under a compressive stress, Si atoms tend to occupy ideal positions, and no reconstruction takes place. On the contrary, when applying either a uniform tensile stress or a uniaxial tensile stress along the dimers, a change in the surface reconstruction is observed, in particular a symmetry breaking leading to a $c(4 \times 2)$ pattern. The reconstruction is characterized by alternating unbuckled short and long dimers, with the short dimers having a smaller z component than the long ones (AUDD [9], see Fig. 1, central panel). The dimer bond lengths and the difference in z coordinates between long and short dimers depend on the applied stress (The dimer bond lengths are 2.54 and 2.62 Å with $\delta_z \simeq 0.04$ Å in the case of a uniform tensile stress ($\simeq 2\%$) [5].).

This structure is in good agreement with the AUDD originally proposed on the basis of STM measurements [9], where the authors postulated a height difference between dimers of $\delta_z \simeq 0.1$ Å. The calculated STM images [5,39] compare fairly well with the experimental ones. Furthermore, calculated [41,25] and experimental [21,22] core level shifts are in good agreement.

The surface states and the electronic structure of the $c(4 \times 2)$-AUDD surface are similar to those of the $p(2 \times 1)$. The AUDD surface is semiconducting, with an LDA surface band gap of $\simeq 0.2$ eV (for comparison, the $p(2 \times 1)$ reconstruction has an LDA energy gap of $\simeq 0.3$ eV). Close to the top of the valence band top are two groups of four surface states with π character; these come from the small splitting of the bonding and antibonding π states, which takes place when the symmetry is lowered from $p(2 \times 1)$ to $c(4 \times 2)$ under tensile stress. Close to the conduction band bottom we find empty surface states with π_z^* and σ character. The surface states and the band structure are in quantitative and qualitative agreement with ARUPS data [29]. This comparison will be discussed in detail in a forthcoming publication [29].

4. H adsorption

The two models for the $c(4 \times 2)$ reconstruction (AUDD and MRAD), one terminated by flat long dimers, bonded to C atoms in the underlayer, and the other with buckled, short, staggered dimers, bonded to Si atoms, should present completely different electronic properties, and surface reactivity. In order to shed light on these topics, and in view of experimental results that have recently been performed on the hydrogenated surface [36,37], we have studied in detail the structural modifications induced by hydrogen adsorption on the $c(4 \times 2)$ AUDD reconstruction. STM images with large doses of deposited hydrogen [36,37] have shown that a monohydride phase is preferentially obtained on the Si–SiC(001) surface. In our calculations, 1 Ml of H atoms were distributed on the two surfaces of the slab, at an initial distance of $\simeq 2$ Å, and both the ionic and electronic degrees of freedom of the system were relaxed, to ground state. The converged geometry of the system is represented in Fig. 2. According to our simulations, the AUDD geometry is removed, in favor of a $p(2 \times 1)$ geometry, with short (2.39 Å) flat dimers. The hydrogen atoms relax to an H–Si distance of $\simeq 1.5$ Å, in a monohydride symmetric configuration that allows saturation of each Si dangling bond.

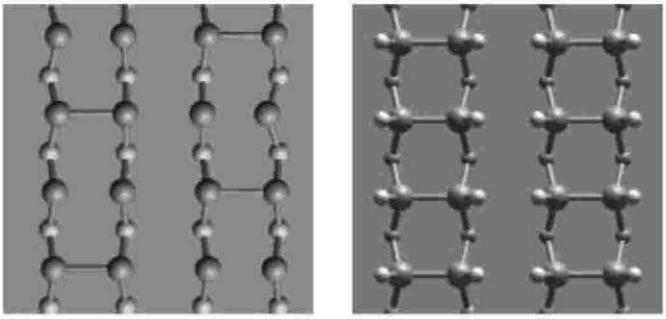
Fig. 2. STM calculated images for filled states ($V_{\text{tip}} = -\text{IV}$) for the clean (left) and hydrogenated (right) Si–SiC(001) surface. The atomic structure is superimposed, to help localization.

These results are in remarkable agreement with the experimental observation of a $p(2 \times 1)$ reconstruction [37], and with the disappearance of surface-related peaks in the measured DOS [36,37]. Indeed, the calculated LDA band gap opens to $\simeq 1.4$ eV, almost one order of magnitude wider than the clean AUDD surface band gap.

In order to get a thorough comparison with experiment, we have calculated STM images for the hydrogenated surface: in Fig. 3, we present our results for constant current filled states images for both the clean (left) and hydrogenated (right) surfaces, obtained at the same tip voltage (1 V). The filled states image of the clean surface shows spots localized on the Si atoms belonging to up dimers, while in the empty states images (not shown) down dimers appear brighter. Since H adsorption removes the AUDD reconstruction with different Si-dimers heights and leads to a $p(2 \times 1)$ geometry, the corresponding image for the hydrogenated surface presents spots of equal brightness. The current intensity is largely reduced (more than one order of magnitude), in comparison with the clean AUDD surface. This is a further point of agreement with experiment, where the hydrogenated portions of the surface appear darker than the clean ones [36].

This result, together with the experimental observation of a reversible appearance of the $c(4 \times 2)$ pattern upon H desorption [37] strongly favors the AUDD model over the MRAD one. Indeed, there is no possible way to obtain a $p(2 \times 1)$ reconstruction upon H adsorption in the MRAD model, unless removing the outermost layer of Si ad-dimers.

5. Si adsorption

For completeness, and in view of other open controversies on the enriched Si–SiC(001) surfaces, we have

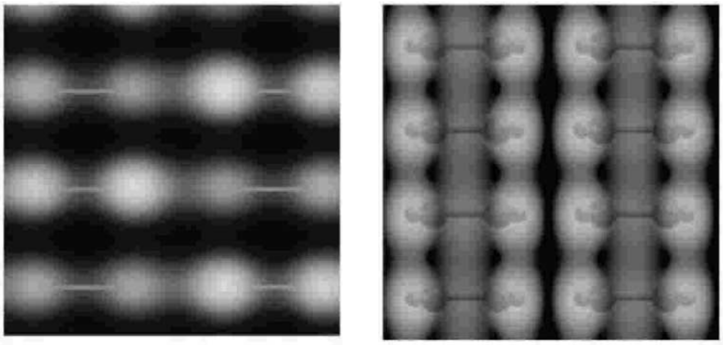

Fig. 3. Top view of the relaxed atomic structures for Si–SiC(001) surface. Black (grey) spheres C (Si) atoms. Only two outermost planes are shown,

Table 1
Calculated structural parameters for ad-dimers at silicon terminated β-SiC(001) surface

	CGG-1[a]	CGG-2[b]	LKP-1[c]	LKP-2[d]	LKP-3[e]	SF[f]
	$\theta_{si} = 1/16$	$\theta_{si} = 1.33$	$\theta_{si} = 1.5$	$\theta_{si} = 1.8$	$\theta_{si} = 2$	$\theta_{si} = 2$
Si–Si (Å)	2.28	2.24	2.30	2.25	2.24	2.31
δ_z (Å)	0.38	0.50	0.54	0.54	0.50	0.58

[a] [41].
[b] [12].
[c] [7].
[d] [47].
[e] [13].
[f] [26,27].

also considered the adsorption of Si adatoms and ad-dimers [41]. In these simulations, the $p(2 \times 1)$ surface has always been used as the starting point, in view of the extremely poor stability of the AUDD geometry, upon adsorption or contamination.

In particular, we considered a Si ad atom and optimized two different surface geometries, with the adatom between and on top of dimer rows, respectively. The configuration of minimum energy [41] corresponds to the adatom located between rows, at 0.9 Å from the surface and forming four long (2.50 Å), equivalent backbonds with the surface atoms, at variance with Si/Si(001) [42,43] and C/Si(001) [44–46], where it has been shown that an adatom privileges a specific row, forming only three backbonds: two with atoms of the first surface layer and one with an atom of the second surface layer.

Finally we studied Si ad-dimers. We have considered an ad-dimer between rows and optimized the total energy for geometries parallel and perpendicular to the $p(2 \times 1)$ dimer rows. We have found that the perpendicular ad-dimer has a total energy about 0.6 eV lower than the parallel one. The stable geometry of the ad-dimer is buckled ($\simeq 0.5$ Å), and with a bond length much smaller than those of surface dimers, 2.28 Å [41].

We wish to point out, at this point, that notwithstanding the discrepancies among the several proposed models for further order reconstructions [8,12–17,31–33,47–49], the add-unit in any of the observed coverages seems to be a buckled ad-dimer perpendicular to the dimers on the underlying Si surface. Indeed, calculations have shown that a single parallel ad-dimer is energetically much less favored than a perpendicular one [41], for Si–SiC(001). The geometry of the ad-unit also comes out similar in the different calculations (see Table 1).

6. Conclusions

To conclude, we have performed first principles calculations on the adsorption of selected atomic species on the clean stoichiometric Si–SiC(001). In particular, we have studied the effect of H passivation on the Si terminated $c(4 \times 2)$ β-SiC(001) surface. The monohydride phase obtained, removes the $c(4 \times 2)$ pattern, and leads to a $p(2 \times 1)$ reconstruction, with flat, short silicon dimers. The electronic and structural properties of this hydride phase are in good agreement with recent experimental results, and strongly favor the AUDD model for this surface.

Acknowledgements

We are indebted to P. Soukiassian, for helpful discussion. Computing facilities of IDRIS (CNRS, France) and CSCS (Manno, Switzerland) are acknowledged. The work was partially performed under INFM contract PRA-1MESS, and the auspices of the US Department of Energy by University of California Lawrence Livermore National Laboratory (contract No. W-7405-Eng-48). Two of us (Alessandra Catellani and Laurent Pizzagalli) are grateful to Lawrence Livermore National Laboratory for hospitality and financial support.

References

[1] M.A. Capano, R.J. Trew, Mater. Res. Soc. Bull. 22 (1997) 19.
[2] Y.G. Gogotsi, M. Yoshimura, Nature 385 (1997) 513.
[3] Y.G. Gogotsi, J.D. Jeon, M.J. McNallan, J. Mater. Chem. 7 (1997) 1841.
[4] V.M. Bermudez, Phys. Stat. Sol. (b) 202 (1997) 447.
[5] A. Catellani, G. Galli, F. Gygi, F. Pellacini, Phys. Rev. B57 (1998) 12255.
[6] G. Galli, L. Pizzagalli, A. Catellani, F. Gygi, A. Baratoff, Appl. Surf. Sci. 162–163 (2000) 1.
[7] W. Lu, P. Krüger, J. Pollmann, Phys. Rev. Lett. 81 (1998) 2292.
[8] P. Käckell, F. Bechstedt, H. Hüscken, B. Schröter, W. Richter, Surf. Sci. 391 (1997) L1183.
[9] P. Soukiassian, F. Semond, L. Douillard, A. Mayne, G. Dujardin, L. Pizzagalli, C. Joachim, Phys. Rev. Lett. 78 (1997) 907.
[10] L. Duda, L.S.O. Johansson, B. Rehil, H.W. Yeom, S. Hara, S. Yoshida, Surf. Sci. 439 (1999) 199.
[11] L. Duda, L.S.O. Johansson, B. Rehil, H.W. Yeom, S. Hara, S. Yoshida, Phys. Rev. B61 (2000) R2460.
[12] L. Pizzagalli, A. Catellani, G. Galli, F. Gygi, A. Baratoff, Phys. Rev. B60 (1999) R5129.
[13] W. Lu, P. Krüger, J. Pollmann, Phys. Rev. B60 (1999) 2495.
[14] F. Semond, P. Soukiassian, A. Mayne, G. Dujardin, L. Douillard, C. Jaussaud, Phys. Rev. Lett. 77 (1996) 2013.
[15] S. Hara, S. Misawa, S. Yoshida, Y. Aoyagi, Phys. Rev. B50 (1994) 4548.
[16] S. Hara, et al., Surf. Sci. 357–358 (1996) 436.
[17] S. Hara, et al., Surf. Sci. 421 (1999) L143.
[18] J.M. Powers, A. Wander, M.A. Van Hove, G.A. Somorjai, Surf. Sci. Lett. 260 (1992) L7.
[19] M. Sabisch, P. Krüger, A. Mazur, M. Rohlfing, J. Pollmann, Phys. Rev. B53 (1996) 13121.
[20] A. Catellani, G. Galli, F. Gygi, Phys. Rev. Lett. 77 (1996) 5090.
[21] M. Shek, Surf. Sci. 349 (1996) 317.
[22] V.Yu Aristov, H. Enriquez, V. Derycke, P. Soukiassian, G. Le Lay, C. Grupp, A. Taleb-Ibrahimi, Phys. Rev. B60 (1999) 16553.
[23] A. Ramstad, G. Brocks, P.J. Kelly, Phys. Rev. B51 (1995) 14504.
[24] L. Pizzagalli, C. Joachim, A. Mayne, G. Dujardin, F. Semond, L. Douillard, P. Soukiassian, Thin Solid Films 318 (1998) 136.
[25] A. Catellani, G. Galli, unpublished results.
[26] S.A. Shevlin, A.J. Fisher, Phys. Rev. B62 (2000) 6904.
[27] S.A. Shevlin, A.J. Fisher, Appl. Surf. Sci. 162–163 (2000) 94; S.A. Shevlin, A.J. Fisher, E. Hernandez, Phys. Rev. B63 (2001) 195306.
[28] P. Soukiassian, V. Aristov, L. Douillard, F. Semond, A. Mayne, G. Dujardin, L. Pizzagalli, C. Joachim, B. Delley, E. Wimmer, Phys. Rev. Lett. 82 (1999) 3721.
[29] Y. Aristov, P. Soukiassian, A. Catellani, R. Di Felice, G. Galli, submitted for publication.
[30] V.Yu Aristov, L. Douillard, O. Fauchoux, P. Soukiassian, Phys. Rev. Lett. 79 (1997) 3700.
[31] L. Douillard, V.Y. Aristov, F. Semond, P. Soukiassian, Surf. Sci. Lett. 401 (1998) L395.
[32] J. Kitamura, et al., unpublished.
[33] P. Soukiassian, F. Semond, A. Mayne, G. Dujardin, Phys. Rev. Lett. 79 (1997) 2498.
[34] H.N. Waltenburg, J.T. Yates, Jr, Chem. Rev. 95 (1995) 1589.
[35] E. Pehlke, Phys. Rev. B62 (2000) 12932.
[36] V. Derycke, P. Fonteneau, N.P. Pham, P. Soukiassian, Phys. Rev. B63 (2001) R201305.
[37] S.M. Widstrand, L.S.O. Johansson, K.O. Magnusson, M.I. Larsson, H.W. Yeom, S. Hara, S. Yoshida, Surf. Sci. 47 (2001) 247.
[38] D. Hamann, Phys. Rev. B40 (1989) 2980.
[39] J. Tersoff, D.R. Hamann, Phys. Rev. B31 (1985) 805.
[40] H. Yan, X. Hu, H. Jónsson, Surf. Sci. 316 (1994) 181.
[41] A. Catellani, G. Galli, F. Gygi, Appl. Phys. Lett. 72 (1998) 1902.
[42] Q.M. Zhang, C. Roland, P. Boguslawski, J. Bernholc, Phys. Rev. Lett. 75 (1995) 101.
[43] G. Brocks, P.J. Kelly, Phys. Rev. Lett. 76 (1996) 2362.
[44] C.L. Liu, L.J. Borucki, T. Merchant, M. Stoker, A. Korkin, Appl. Phys. Lett. 76 (2000) 885.
[45] C.L. Liu, L.J. Borucki, T. Merchant, M. Stoker, A. Korkin, Phys. Rev. B62 (2000) 5021.
[46] G. Cicero, A. Catellani, Appl. Phys. Lett. 78 (2001) 2312.
[47] W. Lu, P. Kruger, J. Pollmann, Phys. Rev. B61 (2000) 2680.
[48] S. Hara, et al., Surf. Sci. Lett. L231 (1990) 196.
[49] S. Hara, Y. Aoyagi, M. Kawai, S. Misawa, E. Sakuma, S. Yoshida, Surf. Sci. 273 (1992) 437.