Missing-Row Asymmetric-Dimer Reconstruction of SiC(001)-$c(4 \times 2)$

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A new reconstruction model for the cubic SiC(001)-$c(4 \times 2)$ surface is suggested on the basis of *ab initio* pseudopotential total energy and grand canonical potential calculations. Our results clearly favor an adatom structure with half a monolayer of Si atoms adsorbed at the Si-terminated surface. The adatoms form a missing-row reconstruction with strong asymmetric dimers whose bond length is 2.3 Å. The model exhibits a semiconducting surface and it is in good accord with recent experimental data. The previously suggested alternatively up- and down-dimer model turns out to be neither a stable nor a metastable structure. [S0031-9007(98)07081-1]

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The paramount technological potential of SiC for high-power, high-temperature, and high-frequency electronic devices has led to very strong current interest in its bulk and surface properties both in experiment [1] and theory [2]. Among the numerous polytype surfaces, cubic β-SiC(001) has attracted particular attention. A whole variety of (1×1), (2×1), $c(4 \times 2)$, (3×2), and (5×2) reconstructions has been observed in experiment, critically depending on the actual growth and surface preparation conditions (cf. Ref. [1]). Here we address the $c(4 \times 2)$ and (2×1) reconstructions. A number of these has been investigated by low-energy electron diffraction (LEED) [3–5], Auger electron spectroscopy [3–6], scanning tunneling microscopy (STM) [7–10], and *ab initio* calculations [11–14]. There is very good general agreement between experiment [5,7] and theory [11–13] concerning the reconstruction of the C-terminated surface which is characterized by very strong symmetric C dimers. For the Si-terminated surface, on the contrary, there is conflicting evidence both from experiment and theory concerning qualitative features, as well as, quantitative details of the reconstruction.

Based on the results of their recent STM study, Soukiassian *et al.* [9] have suggested an alternatively up- and down-dimer (AUDD) model for the SiC(001)-$c(4 \times 2)$ surface. In this model, both the up and down dimers are assumed to be symmetric. The down dimers are relaxed perpendicular to the surface towards the substrate by about 0.1 Å while the up dimers remain within the ideal surface plane. More recently, the same group [10] has observed a reversible phase transition at 400 °C between the room-temperature $c(4 \times 2)$ and a high-temperature (2×1) reconstruction. The room-temperature $c(4 \times 2)$ surface was found to be semiconducting with a gap of about 1.7 eV while the high-temperature (2×1) surface was found to be metallic. The reconstruction of these surfaces has been studied by Douillard *et al.* [15] employing cluster calculations which, however, do not account for the long-range symmetry of the surface, as usual. These calculations were based on five-dimer clusters. The results seem to support the AUDD model. The (2×1) surface has been investigated by Powers *et al.* [16] using LEED. These authors arrived at a reconstruction model with rows of buckled Si dimers with a dimer-bond length of 2.31 Å, very similar to the reconstruction of Si(001)-(2×1). In the interpretation of the above mentioned experimental data it was assumed that the $c(4 \times 2)$ and (2×1) reconstructions occur at the *clean* surface and originate from a strong dimerization of neighboring Si surface-layer atoms. This interpretation contradicts the results of *ab initio* calculations [11–14] which do not find any significant dimer formation at the clean surfaces. In addition, the theoretical results for the *clean* $c(4 \times 2)$ and (2×1) surfaces indicate that the electronic structure of both surface reconstructions is very similar (cf. Ref. [14]). In particular, they do not give any indication of the former being semiconducting and the latter being metallic. These results cannot be reconciled with the above mentioned experimental findings [10]. Finally, we mention that two Si $2p$ core-level shifts of about -0.5 and -1.4 eV have been observed at the $c(4 \times 2)$ surface by Shek [17] using soft x-ray photoemission and LEED. Based on this finding, the author has suggested that the surface is terminated by two Si layers rather than by only one.

To resolve the issues raised above, we have investigated seven structural models of the Si-terminated SiC(001) surface by *ab initio* pseudopotential total energy and grand canonical potential calculations. On the basis of our results we arrive at the conclusion that this surface is characterized by an entirely different reconstruction which we label as the missing-row asymmetric-dimer (MRAD) model.

Our calculations have been carried out in the same way as described at length in Ref. [11]. The wave functions are expanded in terms of linear combinations of Gaussian orbitals with s, p, d, and s^* symmetry. We employ supercells with six atomic and six vacuum layers with $c(4 \times 2)$ surface unit cells in each case and hydrogen saturation of the dangling bonds at the bottom of the slabs is used. Supercell convergence has been checked by carrying out test calculations with thicker slabs. The Brillouin-zone summations have been carried out convergently using four special $\mathbf{k}_{\parallel}$ points in the irreducible part of the $c(4 \times 2)$ zone. To eliminate the forces, we have relaxed all atomic positions in the first three substrate layers and in the adlayer.

First, we have investigated the ideal (1×1) and reconstructed (2×1) and $c(4 \times 2)$ configurations of the *clean* Si-terminated surface. Next, we have optimized the structure of half a monolayer of Si adsorbed at this surface in a (2×1) and two $c(4 \times 2)$ configurations. Finally, we have also considered a full monolayer of Si atoms adsorbed at the surface. We have explored the nonstoichiometric surfaces, as well, since they very well could occur in the various growth and preparation modes employed in the experiment (cf. Refs. [1,3–10,16,17]). To be able to meaningfully compare structures with different stoichiometries we have calculated the grand canonical potential or formation energy as a function of the atomic chemical potential of Si for each case [18,19]. The results are shown in Fig. 1.

The clean Si-terminated surface is characterized by a Si coverage of $\Theta_{\mathrm{Si}} = 0$. Our optimal structure differs from that of the ideal SiC(001)-(1×1) surface only in that neighboring Si surface atoms slightly move towards each other to a distance of 2.73 Å. This leads to a (2×1) reconstruction. *No Si dimers are formed at this surface* in striking contrast to the case of the Si(001)-(2×1) surface [20], as was discussed in detail in Ref. [11].

The $c(4 \times 2)$ AUDD model [9] is based on the assumption that there are two different kinds of symmetric Si dimers at the surface having alternating height with respect to the substrate. The down dimers are supposed to reside 0.1 Å lower than the up dimers which remain within the ideal surface plane. For this configuration, we find a total energy which is 30 meV *higher* than that of our optimal (2×1) reconstruction and it is also higher than the total energy of the ideal (1×1) surface. When we allow the atoms in the topmost three layers of our slabs to move freely the system relaxes back to the (2×1) reconstruction. This indicates that the AUDD model for the $c(4 \times 2)$ reconstruction is neither stable nor metastable. The electronic properties of the AUDD model, in particular, turn out to be almost identical to those of the optimized (2×1) reconstruction [11,12], a result which is in contrast to the experimental observations [10].

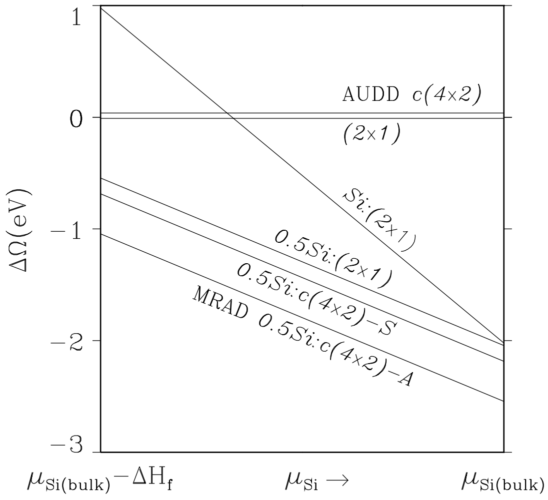
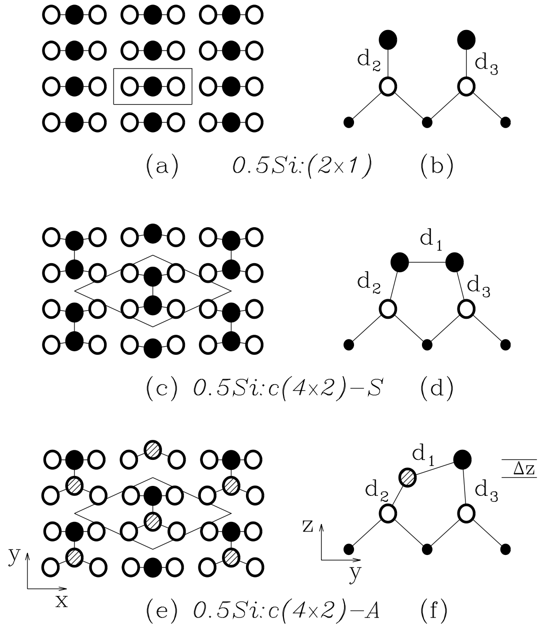


FIG. 1. Formation energy vs Si chemical potential for clean and nonstoichiometric Si-terminated SiC(001) surfaces. The chemical potential of Si varies between $\mu_{\mathrm{Si(bulk)}} - \Delta H_f \leq \mu_{\mathrm{Si}} \leq \mu_{\mathrm{Si(bulk)}}$ and $\Delta H_f = 0.72$ eV.

The structural models discussed above are based on the assumption that the observed (2×1) and $c(4 \times 2)$ reconstructions occur at the *clean* Si-terminated SiC surface. However, measurements of Si to C Auger peak ratios and of photoemission cross sections for SiC(001) show that these reconstructions could very well be related to additional Si adatoms at the surface, as pointed out by Dayan [3] and by Shek [17], respectively. We, therefore, suggest an alternative model for the $c(4 \times 2)$ reconstruction which is compatible with measured STM images [9] and other experimental data [4,17]. We have considered half a monolayer of Si atoms adsorbed at the Si-terminated surface. We label this case by $\Theta_{\mathrm{Si}} = 0.5$. Depending on the symmetry imposed in the optimization, a (2×1) or two different $c(4 \times 2)$ structures are obtained. Top and side views of the resulting configurations, which we label 0.5Si:(2×1) and 0.5Si:$c(4 \times 2)$ for obvious reasons, are shown in Fig. 2 where the structural parameters are defined as well. Their optimal values are summarized in Table I. In these three cases the Si adatoms form missing-row structures. The 0.5Si:(2×1) configuration [see Figs. 2(a) and 2(b)] turns out to be metastable (see also Fig. 1). The calculated bond lengths of this structure indicate that the bonding character of the Si surface atoms becomes stronger due to adsorption of half a monolayer of Si. Interestingly enough, our calculations reveal that the energy of the surface can be lowered by *dimerization* of neighboring Si atoms in the adatom rows forming $c(4 \times 2)$ or $p(2 \times 2)$ reconstructions. Here, we focus on the $c(4 \times 2)$ structure. If C_{2v} symmetry is retained during optimization, the system shows a symmetric dimer structure [see Figs. 2(c) and 2(d)] which we label 0.5Si:$c(4 \times 2)$-S. In this structure, the Si adlayer atoms have formed symmetric Si dimers with a bond length of 2.32 Å. If the C_{2v} symmetry is relaxed during optimization, the system shows an asymmetric-dimer reconstruction [see Figs. 2(e) and 2(f)] which we label 0.5Si:$c(4 \times 2)$-A. In this structure, the Si adlayer atoms form asymmetric Si dimers with a bond length of 2.30 Å. This is our new missing-row asymmetric-dimer model.

The comparison of the formation energies for all investigated configurations (see Fig. 1) clearly reveals that the three half monolayer structures are the most favorable with the MRAD model being the most stable,



(a) $0.5Si{:}(2\times1)$ (b)

(c) $0.5Si{:}c(4\times2)\text{-}S$ (d)

(e) $0.5Si{:}c(4\times2)\text{-}A$ (f)

FIG. 2. Top and side views of the three different half-monolayer missing-row structures of the Si-terminated SiC(001) surface considered. Si adatoms are represented by solid and shaded circles while the Si substrate-surface layer atoms are represented by open circles. The small dots in the side views represent C atoms in the second layer. The unit cells for the different structures are indicated.

in particular. Its total energy is 360 meV lower than that of the 0.5Si:$c(4\times2)$-S and 540 meV lower than that of the 0.5Si:(2×1) structure per $c(4\times2)$ unit cell. We note, in particular, that the Si:(2×1) structure containing a full monolayer of Si adatoms turns out to be a *metastable* structure, only, with respect to the boundary conditions. Its reconstruction results from a movement of the Si adatoms towards each other. The resulting surface-bond length of 2.54 Å is in very good accord with previous results [11,12]. Carrying out structure optimizations employing larger unit cells, we have found that a (3×2) reconstruction of the surface is the most stable structure for a coverage of $\Theta_{\text{Si}} = 1$. We note, however, that in this structure 1/3 of a monolayer is adsorbed in the uppermost and 2/3 of a monolayer is adsorbed in a second adlayer (next to the substrate surface) [21] .

Concerning the electronic structure, we restrict ourselves to the MRAD model which is energetically most favorable. A small section of its surface-band structure is shown in Fig. 3. We observe four salient bands of surface states. Clearly, there is no overlap between the highest occupied (D_{up}) and the lowest empty (D_{down}) band. The D_{up} and D_{down} states are localized mainly at the up and down atoms of the dimers, respectively, as can clearly be seen from a Mulliken analysis. The surface is semiconducting in agreement with experiment [10]. Our calculated band gap of 1.1 eV is somewhat smaller than the measured gap of 1.7 eV as usual in local density approximation calculations. An occupied surface state band centered at 1.3 eV below the Fermi level (E_F) has been observed [10]. From the measured bulk gap of 2.41 and the Fermi energy of 0.4 eV below conduction-band minimum [22] it follows that this surface-state band locates at 0.7 eV above valence-band maximum. In our calculations, the occupied D_{up} band is located near 0.2 eV above valence-band maximum.

TABLE I. Bond lengths (in Å) for the investigated half-monolayer structures (see Fig. 2).

Structure	d_1	d_2	d_3	Δz
0.5Si:(2×1)		2.37	2.37	0
0.5Si:$c(2\times1)$-S	2.32	2.37	2.37	0
0.5Si:$c(2\times1)$-A	2.30	2.35	2.42	0.54

We have mentioned already that a reversible phase transition between the semiconducting $c(4\times2)$ and the metallic (2×1) surface has been observed [10]. Aristov *et al.* [10] assumed that these two structures have the same surface stoichiometry. Nevertheless, their electronic properties were found to be drastically different. Therefore, we have also calculated the surface-band structure of the 0.5Si:(2×1) structure and we find that it is totally different from that of our MRAD model indeed. It has a band gap of only 0.2 eV and, in addition, the strongly dispersing empty surface-state band in the gap-energy region is partially lower than the measured Fermi energy [22] in the n-type sample. This may be the reason why a metallic (2×1) surface has been observed in experiment. We expect that a semiconducting 0.5Si:(2×1) surface with a small gap would be observed if the doping of the SiC sample were changed from n to p type. Such experiments would be most useful, as well, to find out whether the (2×1) reconstruction of SiC(001) is stabilized by the occupation of the lowest surface conduction band at 0.2 eV due to n doping.

To relate our results to the published STM data [9], we have calculated STM images for our MRAD model within the Tersoff-Hamann approach [23]. The calculated STM image for the filled D_{up} surface state is shown in Fig. 4(a) in comparison with the respective experimental STM image [9] in Fig. 4(b). Only the dimer-up atoms are visible and the MRAD structure can clearly be resolved.

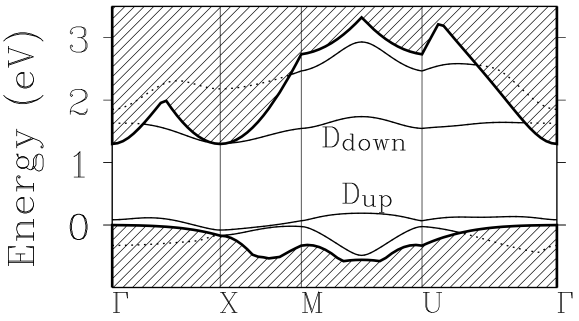


FIG. 3. Surface-band structure of our MRAD model.

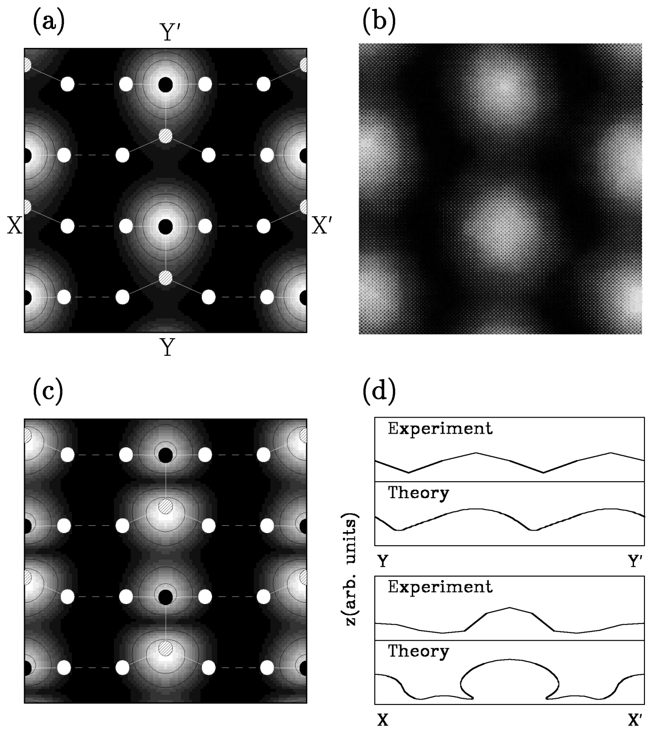


FIG. 4. Calculated filled- and empty-state STM images, (a) and (c), of our MRAD model in comparison with the filled-state STM image (b) from experiment [9]. The atomic configuration is indicated in (a) and (c) [cf. Fig. 2(e)]. (d) Shows a comparison of calculated and measured [9] height profiles along the Y, Y' and X, X' lines [indicated in (a)] parallel and perpendicular to the dimer rows, respectively.

Figure 4(c) shows the calculated image of the empty D_{down} state. This STM image shows twice as many spots as that of the filled state. They belong to the dimer-up and dimer-down atoms, as can clearly be seen from the surface structure shown in Figs. 4(a) and 4(c), as well. The D_{down} band mainly originates from the dangling bonds at the down atoms which reside 0.54 Å lower than the up atoms (see Table I). Therefore, both the up and down atoms in the dimers are visible in the empty-state image. The figure also reveals that the MRAD structure is not as clearly visible in the empty-state image as it is in the filled-state image. Figure 4(d) shows respective measured and calculated height profiles for the filled-state image along the Y, Y' and X, X' lines, indicated in Fig. 4(a). Our calculated STM images and height profiles along the Y, Y' and X, X' lines are in good agreement with experiment.

Finally, we would like to point out that the reconstruction behavior of the SiC(001) surface discussed above is obviously very different from that of the Si(001) surface [20]. This fact originates from the ionicity of SiC, the disparity of the covalent radii of C and Si and the difference in bond-bending forces around C and Si atoms, respectively, as discussed in Refs. [2] and [24].

In summary, we have investigated several (2×1) and $c(4 \times 2)$ reconstructions of the Si-terminated β-SiC(001) surface. Our results do not support the previously suggested AUDD model [9]. Instead, our newly suggested missing-row asymmetric-dimer model has been found to be the most favorable model for the reconstruction of this surface. The MRAD model has a semiconducting surface in agreement with experiment and it shows strong asymmetric surface dimers with a bond length of 2.30 Å. It easily explains, in addition, why more than one Si $2p$ core-level shift has been observed. Finally, our calculated STM images and height profiles are in very gratifying agreement with experiment.

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