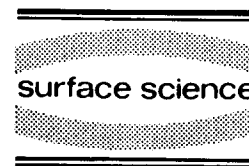




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Atomic structure of β -SiC(100) surfaces: a study using the Tersoff potential

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Abstract

Atomic structure of the β -SiC(100) surface is examined in a theoretical study using the empirical Tersoff potential. The surface energy is evaluated using several models of the atomic structure for three different surface compositions. The previously proposed Si dimer row structure of the (2×1) surface is supported by our calculations. For the (3×2) surface with excess silicon, we propose a new model, an alternate dimer row model, which we find to be energetically favored over the added dimer row model of Hara et al. [Surf. Sci. 231 (1990) L196]. Our calculations on the C-terminated $c(2 \times 2)$ surface favor the staggered dimer model of Bermudez and Kaplan [Phys. Rev. B 44 (1991) 11149] over the model of Powers et al. [Phys. Rev. B 44 (1991) 11159] placing C-dimers at Si bridge sites. However, the large charge transfer observed in tight-binding calculations of the latter model makes the empirical Tersoff potential less reliable for this surface.

1. Introduction

Silicon carbide (SiC) has received increasing attention for its important role as both a structural ceramic material and a wide band-gap semiconductor. Of its many polytypes, the cubic β -SiC has demonstrated its potential for use in high-temperature, high-frequency and high-power electronic devices [1]. Tremendous efforts have been devoted to growing large single crystal SiC wafers for this type of applications [2]. An understanding of the atomic structure of the single crystal surfaces is obviously very important in this

context. Furthermore, from a fundamental point of view, β -SiC is an interesting model system for comparative studies of group IV semiconductor materials, such as Si, Ge and diamond, as well as III-V materials such as GaAs.

β -SiC(100) surfaces have exhibited a variety of surface reconstructions depending on the concentrations of silicon and carbon on the surface [3]. For surfaces with excess Si coverage, (3×2) and occasionally also (5×2) LEED patterns have been observed. Upon annealing at about 1100°C, the LEED pattern becomes (2×1) and the surface is found to be terminated with a monolayer of silicon. At a higher temperature (around 1175°C) and/or with a longer annealing time, the surface LEED pattern transforms to $c(2 \times 2)$ [3,4]. Although this surface was initially thought to be

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Si-terminated [5], it has later been shown to be a C-terminated surface [3].

A great deal of experimental and theoretical work has been done to investigate the atomic structure corresponding to the various LEED patterns and progress has been made towards this understanding. Still, many details of these atomic configurations are subject to controversy. Moreover, in order to study dynamic surface processes and growth of β -SiC, there is a need to develop a large-scale simulation scheme which employs a suitable empirical interatomic potential. A crucial test of such an empirical potential is to examine whether it describes general features of the surface structure. So far, to the best of our knowledge, there have been no reports of such systematic studies in the literature for SiC.

In this paper, we present a computer simulation study of β -SiC(100) surfaces using the Tersoff potential. Our purpose is to check whether the Tersoff potential, which has performed well in describing the Si(100) surface and β -SiC bulk properties, can adequately reproduce the known aspects of the β -SiC(100) surface structure, and shed some light on those that are not as well known.

2. Calculations

The Tersoff potential was developed to model the structural properties and energetics of covalent systems [6]. It is based on the idea that in materials systems, bond order, or bond strength, depends on the local environment, and more specifically, coordination numbers. The atomic interactions are modeled with several pairwise functions of the interatomic distances, r_{ij} , as well as a function explicitly dependent on bond angle $g(\theta_{ijk})$. The functional form is [9]

$$E = \frac{1}{2} \sum_{i \neq j} f_C(r_{ij}) (f_R(r_{ij}) + b_{ij} f_A(r_{ij})), \quad (1)$$

where f_R and f_A represent the repulsive and attractive atom pair interactions, respectively,

$$f_R(r_{ij}) = A_{ij} e^{-\lambda_{ij} r_{ij}}, \quad f_A(r_{ij}) = -B_{ij} e^{-\mu_{ij} r_{ij}}, \quad (2)$$

and f_C is a cutoff function for the interactions:

$$f_C(r_{ij}) = \begin{cases} 1 & \text{for } r_{ij} < R_{ij} \\ \frac{1}{2} + \frac{1}{2} \cos\left[\pi(r_{ij} - R_{ij}) / (S_{ij} - R_{ij})\right] & \text{for } R_{ij} < r_{ij} < S_{ij} \\ 0 & \text{for } r_{ij} > S_{ij} \end{cases}. \quad (3)$$

The b_{ij} function modulating the attractive interaction has explicit bond angle dependence and includes many-body interactions

$$b_{ij} = \chi_{ij} (1 + \beta_i^n \zeta_{ij}^{n_i})^{-1/2n_i}, \quad (4)$$

$$\zeta_{ij} = \sum_{k \neq i, j} f_C(r_{ik}) g(\theta_{ijk}), \quad (5)$$

$$g(\theta_{ijk}) = 1 + c_i^2/d_i^2 - c_i^2 / \left[d_i^2 + (h_i - \cos \theta_{ijk})^2 \right]. \quad (6)$$

The parameters for the unlike pairs, Si–C, are taken to be averages of the parameters for the like pairs, Si–Si and C–C: $\lambda_{ij} = (\lambda_i + \lambda_j)/2$, $\mu_{ij} = (\mu_i + \mu_j)/2$, $A_{ij} = \sqrt{A_i A_j}$, $B_{ij} = \sqrt{B_i B_j}$, $R_{ij} = \sqrt{R_i R_j}$, $S_{ij} = \sqrt{S_i S_j}$. Values of these parameters are listed in Table 1.

The Tersoff potential has been shown to describe well bulk properties of Si, including the defect structure and elastic constants [7]. It also describes well the Si(100) surface structure, no-

Table 1
Parameters for the Tersoff potentials for Si and C; the mixed interaction parameter χ_{C-Si} is 0.9776 (from Ref. [9])

	C	Si
A (eV)	1.3936×10^3	1.8308×10^3
B (eV)	3.467×10^2	4.7118×10^2
λ (\AA^{-1})	3.4879	2.4799
μ (\AA^{-1})	2.2119	1.7322
β	1.5724×10^{-7}	1.1000×10^{-6}
n	7.2751×10^{-1}	7.8734×10^{-1}
c	3.8049×10^4	1.0039×10^5
d	4.384	1.6217×10^1
h	-5.7058×10^{-1}	-5.9825×10^{-1}
R (\AA)	1.8	2.7
S (\AA)	2.1	3.0

tably better than some other empirical potentials that have been proposed [8]. The potential has been extended to simulate multi-component covalent materials, such as SiC [9]. The energetics of point defects in bulk β -SiC predicted by the potential compare favorably with LDA calculations [10]. The calculated elastic constants also agree well with experimental values. Recently, it has been used to calculate the energetics of a carbon adatom on the (2×1) reconstructed Si(100) surface [11]. There is, however, no guarantee that the potential will adequately describe surface structures because the bonding at the surface can be significantly different from that in the bulk. Thus one goal of this study is to get an indication of the validity of the Tersoff potential for simulations of β -SiC(100) surfaces.

In this work, we have investigated β -SiC(100) surfaces with different compositions. The surface was constructed by an abrupt termination of the cubic bulk structure with either a silicon or carbon layer. A surface with excess silicon was generated by adding extra Si atoms to a Si-terminated surface. The simulation cell consisted of 12 (100) layers with the atoms in the last four layers held fixed in their equilibrium bulk positions. The size of the surface in the simulation cell was 4×4 , except for the (3×2) reconstruction for which a 6×4 cell was used. We have checked for system size effects on the energy and found that our system is large enough for this study.

In our simulations, the surface atoms are displaced according to different reconstruction models before the system is relaxed. Then all atoms in the system except for those in the four fixed layers are allowed to move to minimize the total energy calculated with the Tersoff potential. Unless otherwise specified in the text, the energy of the surface is calculated with respect to that of the ideal (1×1) surface, i.e.,

$$\Delta E = E_{\text{tot}} - E_0, \quad (7)$$

where E_{tot} is the energy of the relaxed system and E_0 is the energy of the system with the unrelaxed (1×1) surface having the same atomic composition.

3. Results

We have carried out simulations for both Si-terminated and C-terminated surfaces as well as the surface terminated with an extra silicon overlayer. In this section, we present our results and in the following section we compare our results with other theoretical calculations and experimental evidence.

3.1. The Si-terminated surface

The silicon terminated β -SiC(100) surface usually reconstructs to give a (2×1) LEED pattern [3,12,13]. This surface configuration corresponds to a dimer row structure, shown in Fig. 1a, similar to that of the Si(100) surface. Previously it was speculated that the observed $c(2 \times 2)$ LEED pattern was associated with the Si-terminated surface and a structural model with a staggered Si dimer structure [5], shown in Fig. 1b, was proposed. Table 2 gives the surface energy of the Si-terminated (1×1) , (2×1) and $c(2 \times 2)$ sur-

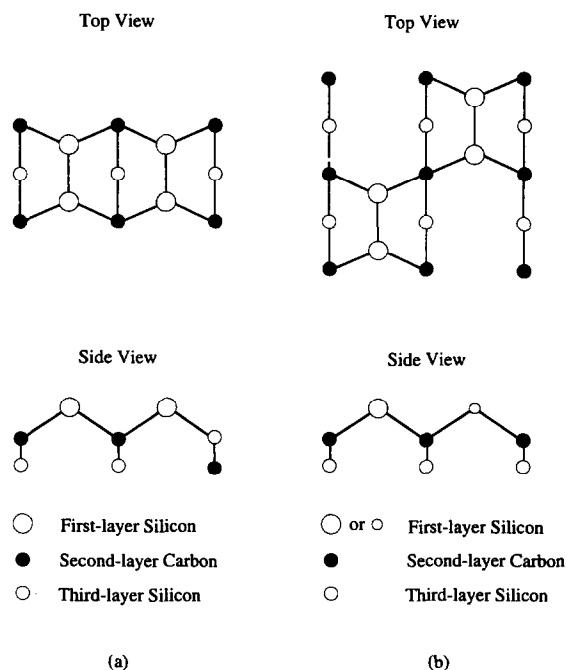


Fig. 1. Models for the Si-terminated surface: (a) (2×1) Si dimer row structure; (b) $c(2 \times 2)$ staggered Si dimer structure.

Table 2

Comparison of structural models of the Si-terminated surface; the calculated surface energy per surface atom with respect to that of the (1×1) unrelaxed surface is given as ΔE , as well as the bond length of the Si ad-dimer, $D_{\text{Si-Si}}$

Structure	ΔE (eV)	$D_{\text{Si-Si}}$ (Å)
(1×1) relaxed	-0.04	
(2×1) dimer row	-0.51	2.46
$c(2 \times 2)$ staggered	-0.46	2.54

faces calculated using the Tersoff potential. These calculations show the reconstructed surface models are clearly more stable than the unreconstructed surface. The (2×1) dimer row structure, which is consistent with experimental evidence [3,12,13], is slightly favored over the $c(2 \times 2)$ staggered dimer structure. The computed lowering of the energy by 1.02 eV per dimer (2×0.51 eV) upon relaxation for the (2×1) dimer row structure agrees very well with semi-empirical molecular-orbital calculations [14] which give a value of 1.03 eV. An earlier study using a different empirical potential [15] gave a rather poor agreement, 0.74 eV. The calculated silicon dimer distance indicates stronger Si-dimer bond on the surface in the (2×1) dimer row structure than in the $c(2 \times 2)$ staggered dimer structure.

Experimental measurements [3,13] have shown that the Si dimers on the β -SiC (2×1) surface are tilted. This is due to charge transfer between the two silicon atoms in a dimer, as evidenced in quantum chemical SLAB-MINDO calculations [16]. Similar electron transfer and tilt has been seen in calculations of the Si(100) surface. Staggered ordering of these tilted dimers can give rise to the observed $c(4 \times 2)$ LEED pattern. Empirical potentials such as the Tersoff potential, however, include only short range interactions without explicit incorporation of charge transfer and are therefore incapable of describing the surface dimer tilt.

In order to examine the stability of these structures at high temperatures, we have also performed molecular dynamics simulations at $T = 1160$ K and $T = 1740$ K. The (2×1) and $c(2 \times 2)$ phases are found to remain stable at these ele-

vated temperatures. Furthermore, starting with the unreconstructed (1×1) surface, the Si dimers are observed to form spontaneously.

3.2. The surface with excess Si

The (3×2) phase is obtained by exposing surfaces with (2×1) or $c(4 \times 2)$ LEED patterns to a Si beam at relatively low temperatures [3]. Thus additional Si atoms are being adsorbed onto the Si-terminated surface. Assuming the additional Si coverage is $2/3$ of a monolayer, Dayan proposed a missing row model for the surface structure [17], in which every third dimer row is missing, leading to a surface unit cell with (3×2) symmetry. By similar construction, the occasionally observed (5×2) phase would have $4/5$ monolayer excess silicon atoms. Careful experimental measurements [4,18], however, have revealed that the surface coverage of excess Si in the (3×2) phase is $1/3$ monolayer. Moreover, the excess Si coverage in the (5×2) phase is only about $1/5$ monolayer. Hara et al. [4] modified Dayan's model to be consistent with the measured excess Si coverage and proposed an added dimer row model which is illustrated in Fig. 2a.

While the added dimer row model produces a (3×2) LEED pattern and is consistent with the observed excess Si coverage, it is not the only possible structure. We propose here another structural model, which we call the alternate dimer row model. This model is also consistent with the available experimental data and is predicted by our calculations to be considerably more stable. The surface structure is shown in Fig. 2b. In this model ad-dimers are formed in the top layer in between the sublayer (2×1) Si dimer rows [19]. The direction of the ad-dimer is rotated by 90° from the dimers in the sublayer. In the (3×2) phase, dimers in the top layer are separated by one atom row along the dimer direction. A model for the (5×2) structure can similarly be constructed with three atom rows in the sublayer separating the dimer rows. An appealing aspect of this model is that it does not break any dimer bonds in the sublayer. Therefore this structure can be formed at rather low temperatures as is observed in experiments [3,4].

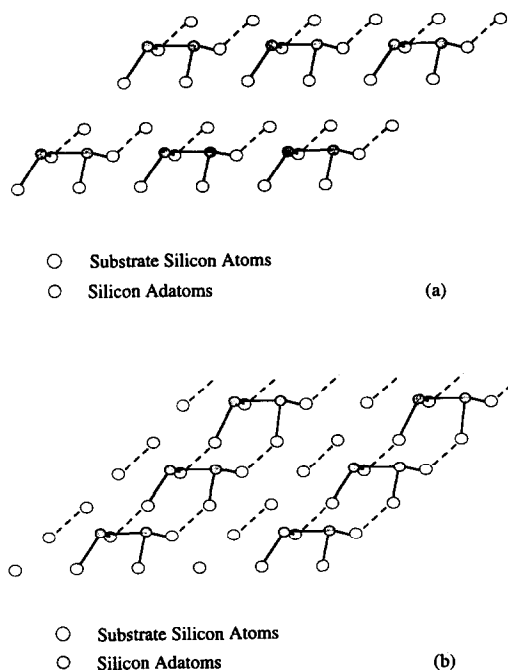


Fig. 2. Models for the (3×2) surface with extra $1/3$ monolayer of Si atoms on top of a silicon layer: (a) added dimer row model [4]; (b) alternate dimer row model proposed here. Broken lines represent dimer bonds between substrate silicon atoms.

We have calculated the relaxed energy of the added dimer row model and of our alternate dimer row model for the (3×2) reconstruction. Compared with the Si-terminated (2×1) surface of the same size, we find the relative energy per adatom in the top layer of the added dimer row structure is -4.71 eV while it is -5.13 eV for the alternate dimer row structure. The Tersoff potential, therefore, predicts that our proposed model for the (3×2) reconstructed surface is energetically favored by 0.84 eV per Si ad-dimer.

3.3. The C-terminated surface

Experiments have shown that a reconstruction with $c(2 \times 2)$ symmetry occurs on the carbon rich surface [3,4]. The surface structure is thought to involve strong C–C bonding on the surface [12]. Several models of the surface structure have been proposed. Two models which so far are consistent with most experimental observations are illus-

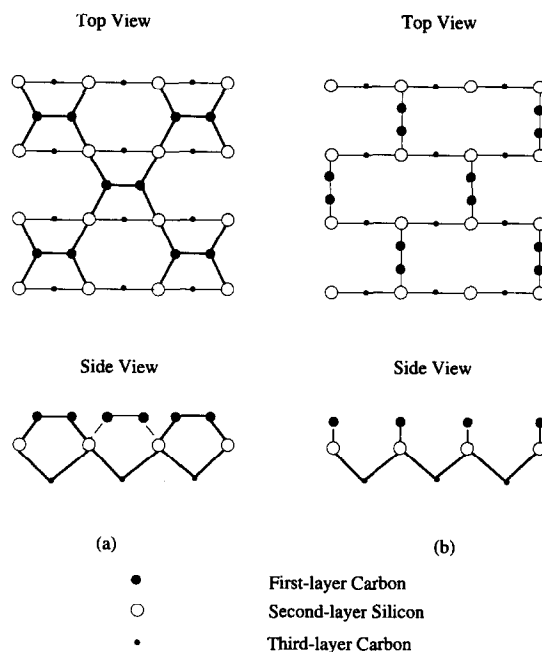


Fig. 3. Models for the C-terminated $c(2 \times 2)$ surface: (a) staggered C-dimer structure, $c(2 \times 2)$ s; (b) C-dimers on top of Si bridge sites, $c(2 \times 2)$ b.

trated in Fig. 3. One involves a staggered array of C-dimers and the other places C-dimers on top of Si bridge sites.

We have calculated the energetics of these two model $c(2 \times 2)$ structures. For comparison, we have also evaluated the energy of the (2×1) C-dimer model and the relaxed (1×1) structure. The results are listed in Table 3. Of the two $c(2 \times 2)$ models, the Tersoff potential clearly favors the staggered dimer model. The energy of the staggered dimer surface is substantially lower than the surface with C-dimers placed at Si bridge

Table 3

Comparison of structural models of the C-terminated surface; the calculated surface energy per surface atom with respect to that of the (1×1) unrelaxed surface is given as ΔE , as well as the bond length of the C ad-dimer, D_{C-C}

Structure	ΔE (eV)	D_{C-C} (Å)
(1×1) relaxed	-0.39	
(2×1) dimer row	-1.51	1.47
$c(2 \times 2)$ s staggered	-1.39	1.49
$c(2 \times 2)$ b on Si bridge	-0.27	1.45

sites (by 1.1 eV per surface atom). On the other hand, the (2×1) structure has the lowest energy, even slightly lower (by 0.12 eV per surface atom) than the $c(2 \times 2)$, which is inconsistent with the observed LEED patterns. This energy difference is small, however, compared with the uncertainty of the empirical potential, being on the order of the stabilization due to charge transfer and tilting of the dimers, which is not described by the Tersoff potential.

While the energy of the $c(2 \times 2)$ surface with C-dimers placed at Si bridge sites is predicted by the Tersoff potential to be very large, the model cannot be ruled out on the basis of these calculations. It is possible that the Tersoff potential fails to describe the bonding on this surface due to very large charge transfer between the surface C atoms and the subsurface Si atoms, as discussed below.

4. Discussion

The Tersoff potential is found to provide a reasonable description of the Si-terminated β -SiC(100) (2×1) surface. This is to be expected since the Tersoff potential has previously been shown to give a good representation of the similar Si(100) (2×1) surface, and tight-binding calculations [20] have indicated similar bonding characteristics on the two surfaces. The relative surface energy of the β -SiC(100) in our calculations is higher than that of the Si(100), indicating a weaker Si-dimer bonds on the former. This is also reflected in the different dimer bond length on the two surfaces.

With excess Si atoms, the properties of the β -SiC(100) (3×2) surface are likely to be even closer to those of a pure Si crystal surface. This is supported by the electronic density of states calculated within the tight-binding approximation [20]. The Tersoff potential can therefore be expected to describe this surface reasonably well and we expect the calculated energy preference of 0.84 eV per Si ad-dimer for the alternate dimer row model we present here to be significant. We point out, however, that the distribution of atomic charge in the tight-binding calculations

of the (3×2) surface is found to be uneven, although the overall surface bonding remains mainly covalent [20]. The Tersoff potential (as any other available empirical potential) does not take such variations in electron transfer into account and thus may not be completely reliable for a surface with significant charge redistribution.

STM images of the (3×2) surface have been reported [25], but with too low resolution to give clear information about the atomic structure. In fact, the images were interpreted as being consistent with the model of Dayan which later was shown to have incorrect Si coverage [4,18]. Alternatively, thermal He atom scattering has been used successfully to study the Si(100) surface [26] and could prove useful for studies of the SiC surface. The intensity of the diffraction peaks is a very sensitive probe of the corrugation of surface charge density and can, for example, easily resolve the Si-dimer tilt [26]. The added dimer row model and the alternate dimer row model for the (3×2) surface of SiC(100) lead to very different corrugation profiles which should be easily distinguishable in He atom scattering. The former model would give a very large corrugation in the direction perpendicular to the dimer bonds but a small corrugation in the parallel direction. The alternate dimer row model, on the other hand, would result in an intermediate corrugation in both directions.

The C-terminated surface is still not well characterized despite considerable amounts of experimental and theoretical effort. Powers et al. [21] have carried out calculations of LEED intensities for several structural models and compared with the experimentally measured intensities. Their analyses favor placing the C-dimers at Si bridge sites (the model is illustrated in Fig. 3b). This model is supported by a self-consistent total energy MNDO calculation of Badziag [22]. On the other hand, Bermudez and Kaplan have proposed a staggered C-dimer model (Fig. 3a) based on their LEED analysis [23]. Support for this structure has come from SLAB-MINDO molecular orbital calculations of Craig and Smith which predict the staggered dimer model is energetically more stable [24].

The Tersoff potential apparently does not de-

scribe the bonding at the C-terminated surface accurately enough, because it predicts the (2×1) surface model to be slightly more stable than either of the two $c(2 \times 2)$ models (see Table 3), which is inconsistent with the LEED data. This could be due to charge transfer effects which can change the bonding characteristics at the surface as compared with bulk. In particular, it is likely that the C-dimers are tilted as a result of charge transfer between the two C atoms. The energetics of such effects can easily be on the order of the energy difference between the (2×1) and staggered dimer $c(2 \times 2)$ model. It is also possible that it is important here to consider the free energy of the various models rather than just the potential energy, since the C-terminated surface is observed at high temperatures and entropy can play an important role in determining the stability of the surface structure.

While the Tersoff potential seems to rule out the model with C-dimers placed at the Si bridge sites, this result must be interpreted with caution. Recent tight-binding calculations [20] have indicated that large charge transfer occurs between the surface carbon atoms and the subsurface silicon atoms in this structure. The bonding in the top two layers thereby becomes largely ionic. This is in contrast with the Si-terminated surfaces where the bonding remains mostly covalent as in the bulk. Also, the staggered dimer $c(2 \times 2)$ and the (2×1) C-terminated surfaces have largely covalent bonds, although the charge transfer is apparently larger than for the Si-terminated surfaces. Variations in bonding characteristics associated with charge redistribution are not accounted for in current empirical potentials for covalently bonded materials. Thus, the predictions of the Tersoff potential for the energetics of the C-terminated surfaces, in particular the $c(2 \times 2)$ surface with C-dimers at the Si bridge sites, are less reliable than for the Si-terminated surfaces.

As we have discussed above, current experimental and theoretical work has not yet resolved the atomic structure of the (3×2) and $c(2 \times 2)$ surfaces of β -SiC(100). In particular, conflicting results of LEED intensity analyses and semi-empirical calculations have been reported for the atomic configurations of the C-terminated $c(2 \times 2)$

surface [21–24]. Available experimental data [3,25] are not sufficient to distinguish between different structural models proposed for the Si-rich (3×2) surface. Additional experimental measurements with atomic resolution such as high resolution STM or He atom scattering are needed to determine the atomic structure of these surfaces.

On the theoretical side, ab initio simulations involving simultaneous evaluation of the electronic wavefunction and relaxation of the atomic coordinates such as the Car–Parrinello scheme of combined molecular dynamics and density functional theory calculations [27], will be able to provide less ambiguous evidence of the energetic stability of the various structures as well as added insight into the qualitative nature of the chemical bonding and charge transfer. This type of simulation has been carried out for bulk SiC [28] but is computationally very demanding. We are presently undertaking such calculations of the β -SiC surfaces.

5. Summary

We have presented a theoretical study of the atomic structure of β -SiC(100) surfaces using the Tersoff interaction potential. The Si-terminated surface is found to reconstruct into a (2×1) silicon dimer row structure in agreement with experimental evidence. This structure is similar to the well known structure of the Si(100) surface.

We have proposed a new atomic structure model, the alternate dimer row model, for the (3×2) surface with excess silicon. This model is energetically favored in our calculations over the added dimer row model of Hara et al. [4] by 0.84 eV per surface dimer. Based on the success of the Tersoff potential on the Si-terminated β -SiC(100) surface and the Si(100) surface, we believe this preference for our alternate dimer row model is significant, although further verification by both first principles theoretical calculations and experimental measurements is necessary.

On the other hand, calculations of the C-terminated $c(2 \times 2)$ surface indicate the Tersoff potential gives a less reliable prediction of the

energetics of this surface, due to significant variations in the charge transfer and possible ionic bonding character at the surface.

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