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Geometric and electronic study of the β -SiC(100) surface

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Abstract. The Keating model is employed to determine the geometric structure of the (2×1) reconstructed β -SiC(100) surface. The symmetric dimerization for both the Si- and C-terminated (100) surfaces is obtained by minimizing the elastic energy.

The extended Hückel band calculation is performed for the electronic structures of both the ideal and the (2×1) reconstructed β -SiC(100) surfaces. The results show that the ideal surfaces are metallic, whereas the (2×1) reconstructed surfaces are semiconducting. Moreover, the band structures calculated agree quite well with the experimental results. The density of states is also calculated and discussed.

1. Introduction

Silicon carbide is considered to be a potentially useful material for electronic devices, because of its high breakdown field and chemical stability. Since the development of the chemical vapour deposition method, it is possible to grow high-quality β -SiC on a silicon substrate; this has aroused much interest in studying the characteristics of β -SiC.

In recent years, a number of experiments have been carried out on the electronic and geometric structures of β -SiC surfaces. Using medium-energy ion scattering, Hara *et al* [1] have investigated the surface structures of β -SiC(100). (1×1) , (2×1) , C (4×2) , (5×2) , (3×2) and C (2×2) reconstruction phases have been observed by heat treatment at 1065 °C. Dayan [2] and Kaplan [3] have also studied the geometric structures of β -SiC and proposed a dimer model for the $(n \times 2)$ reconstruction of the (100) surface.

Hoechst *et al* [4] have investigated the electronic structures of β -SiC(100) by angle-resolved valence band photoemission spectroscopy and a surface state located about 1.0 eV above the top of the valence band has been found. Parrill and Bermudez [5] have predicted that a surface state or a resonance state may exist at the upper edge of the valence band.

Lubinsky *et al* [6] have calculated the energy band of bulk β -SiC by a first-principles calculation. Li and Lin-Chung [7] also reported similar results using the tight-binding approximation. Lee and Joannopoulos [8] have investigated the relaxed configuration of the β -SiC(110) surface. It has been concluded that two surface bands exist in the gap for the ideal surface and move towards the valence band slightly owing to the relaxation. Craig and Smith [9] have investigated the β -SiC(100) surface by the slab-MINDO method. They have found that the symmetric dimers are formed on the C-terminated surface and

Table 1. The bond-stretching and bond-bending force constants (from [12]).

	Silicon	Diamond
α (eV Å ⁻²)	3.0271	8.0721
β (eV Å ⁻²)	0.8619	5.2903

the buckled dimers on the Si-terminated surface. Using the Monte Carlo method, Takai *et al* [10] have calculated the relaxed configuration of the β -SiC(100), β -SiC(110) and β -SiC(111) surfaces.

In the present work, the Keating model is employed to determine the geometric structure of (2×1) reconstructed β -SiC(100) surface and the extended Hückel band calculation is performed for the band structure of both the ideal and the (2×1) reconstructed β -SiC(100) surface. A conclusion is given in the last section.

2. Geometric configuration of β -SiC(100) (2×1) reconstruction

Experiments have observed various reconstruction phases of the β -SiC(100) surface [1–3]; among those the (2×1) reconstruction is of most interest. Recently Craig and Smith [9] investigated the surface structure of β -SiC(100) (2×1) by minimization of electronic energy in the framework of the MINDO approximation. In the present work, the atomic configuration of the (2×1) reconstructed β -SiC(100) surface is determined by minimization of elastic energy.

The Keating model [11, 12] has been proved to be an effective method for studying the surface reconstruction of a covalent crystal with a zincblende structure [13, 14]. The elastic energy described by the Keating model is given by

$$E = 2 \left[\sum \alpha(ij) \left(X_{ij} \cdot X_{ij} - \frac{3a^2}{16} \right)^2 + \sum \beta(ijk) \left(X_{ij} \cdot X_{kj} + \frac{a^2}{16} \right)^2 \right] / a^2 \quad (2.1)$$

where a is the lattice constant, and $X_{ij} = X_j - X_i$ is the position vector between atom i and atom j . The first sum is taken over all bonds and the second sum is taken over all nearest-neighbour bond pairs. $\alpha(ij)$ is the bond-stretching force constant depending on the bond length and $\beta(ijk)$ is the bond-bending force constant depending on both the bond length and the bond angle between the two bonds. In our calculation, the α and β are chosen to be

$$\alpha(\text{SiC}) = [\alpha(\text{SiSi}) + \alpha(\text{CC})]/2 \quad (2.2)$$

$$\beta(\text{SiCSi}) = \beta(\text{CSiC}) = [\beta(\text{SiSiSi}) + \beta(\text{CCC})]/2 \quad (2.3)$$

$$\beta(\text{SiSiC}) = [2\beta(\text{SiSiSi}) + \beta(\text{CCC})]/3 \quad (2.4)$$

$$\beta(\text{SiCC}) = [\beta(\text{SiSiSi}) + 2\beta(\text{CCC})]/3. \quad (2.5)$$

The bond-stretching and band-bending force constants for silicon and diamond are listed in table 1.

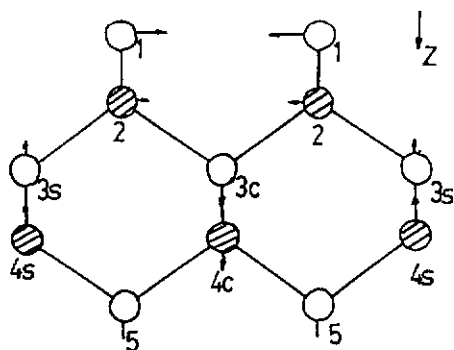


Figure 1. Geometry of a symmetric single dimer. The empty circles and the shaded circles indicate Si and C atoms for the Si-terminated surface, and C and Si atoms for the C-terminated surface, respectively. The arrows indicate the relaxed directions.

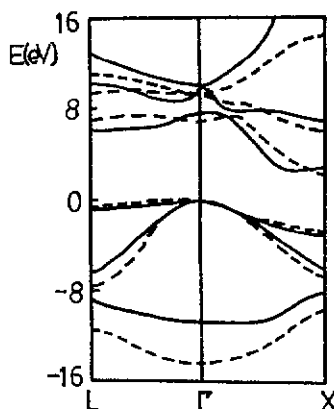


Figure 2. The band structure of bulk β -SiC. The full curves are from the present calculation, the broken curves are from the first principles calculation [6] and the full circles are from the experimental data [4].

Table 2. The coordinates of atoms in a unit cell.

Layers	X	Y	Z
1	$\sqrt{2}a/4 + X_1$	0	Z_1
	$-(\sqrt{2}a/4 + X_1)$	0	Z_1
2	$\sqrt{2}a/4 + X_2$	$\sqrt{2}a/4$	$a/4 + Z_2$
	$-(\sqrt{2}a/4 + X_2)$	$\sqrt{2}a/4$	$a/4 + Z_2$
3	0	$\sqrt{2}a/4$	$a/2 + Z_{3c}$
	$\sqrt{2}a/2$	$\sqrt{2}a/4$	$a/2 + Z_{3s}$
4	0	0	$3a/4 + Z_{4c}$
	$\sqrt{2}a/2$	0	$3a/4 + Z_{4s}$
5	$\sqrt{2}a/4$	0	a
	$-\sqrt{2}a/4$	0	a

In cases of both C-terminated and Si-terminated surfaces, the calculations indicate that the symmetric dimer model shown in figure 1 is the optimized geometry for the (2×1) reconstruction of β -SiC(100). The positions of the atoms are given in table 2.

The calculated results are shown in table 3. For the Si-terminated surface, the Si-Si dimer bond length is 2.664 Å, which is larger than a single Si-Si bond length. This indicates that the Si-Si dimer bond is not as strong as that in bulk silicon and it could be easily broken by adsorption or by heating. For the C-terminated surface, the C-C dimer bond length is 1.974 Å, which is also larger than the single C-C bond length. This result is somewhat different from that obtained by Craig and Smith [9], in which a buckle dimer is obtained for the Si-terminated surface. It is not too strange, since the electronic energy decreases owing to the reconstruction, but the elastic energy increases owing to the distortion of the lattice.

Table 3. The displacements of atoms.

Layers	Displacement (Å)			
	Si terminated		C terminated	
	ΔX	ΔZ	ΔX	ΔZ
1	-0.3466	0.0379	-0.6915	0.1269
2	-0.0266	-0.0006	-0.1539	0.0119
3c	—	0.0580	—	0.1421
3s	—	-0.0545	—	-0.1238
4c	—	0.0270	—	0.0667
4s	—	-0.0262	—	-0.0593

Table 4. The parameters K used in the calculation.

Atom	K_s	K_p	K_{sp}
Si	1.250	1.650	1.327
C	1.300	1.700	1.327

3. Electronic structure of the β -SiC(100) surface

The extended Hückel band calculation is carried out to study the electronic structure of the β -SiC(100) surface. In the Bloch representation, the secular equation is given by

$$\sum_i [H_{ij}(k) - S_{ij}(k)E_\mu(k)] C_{i\mu}(k) = 0 \quad (3.1)$$

where $H_{ij}(k)$ and $S_{ij}(k)$ can be written as

$$H_{ij}(k) = \sum_l \exp(ik \cdot R_l) H'_{ij}(R_l) \quad (3.2)$$

$$S_{ij}(k) = \sum_l \exp(ik \cdot R_l) S'_{ij}(R_l) \quad (3.3)$$

where the sums are taken over all unit cells, $S'_{ij}(R_l)$ is the overlap integral between two atomic orbitals i and j which are chosen to be Slater-type orbitals in the present calculation. Within the extended Hückel approximation, the matrix elements $H'_{ij}(R_l)$ are taken to be

$$H'_{ij}(R_l) = K_{ij}(I_i + I_j)S'_{ij}(R_l)/2 \quad (3.4)$$

where I_i is the ionization potential of the i th valence orbital, $K_{ij} = 1$ for $i = j$ and $K_{ij} = (K_i + K_j)/2$ for $i \neq j$. In our calculation, the parameters K are determined by fitting the band structures of bulk β -SiC with that obtained by first-principles calculation [6]. The values of the parameter K are listed in table 4.

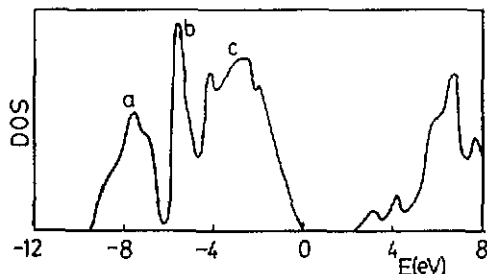


Figure 3. The total DOS of bulk β -SiC in arbitrary units.

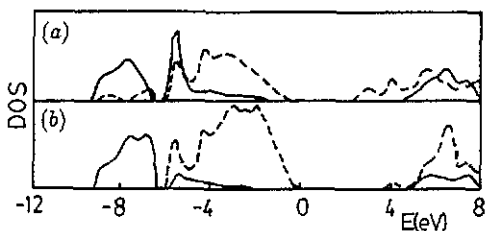


Figure 4. The local DOS of bulk β -SiC in arbitrary units for (a) a Si atom and (b) a C atom. The full curves represent the s states and the broken curves represent the p states.

3.1. Band structure of bulk SiC

The energy bands calculated for the bulk are plotted in figure 2. For comparison, the results of the first-principles calculation and experimental data are also shown. It can be seen that the present results agree fairly well with the first-principles calculation and experimental data except that the width of the valence band is somewhat narrower.

The densities of states (DOSS) are calculated by summing over the k -space and are then broadened with a Gaussian of 0.2 eV width. The total DOS and the local DOS are shown in figures 3 and 4. The total DOS is in agreement with the first-principles calculation [6] and x-ray emission spectra [15] qualitatively. The band gap is 2.2 eV. It can be seen in figure 4 that peak a in the total DOS is mainly contributed by C (2s) and Si (3s), peak b is due to the mixing of Si (3s, 3p) with C (2p), and peak c is due to the mixing of C (2p) with Si (3p). From integration of DOS, it is known that the electron charge is transferred from Si to C. In other words, the Si atom in bulk SiC is a cation and the C atom is an anion. This result is consistent with that of [9].

3.2. Ideal and reconstructed β -SiC(100) surfaces

A slab of ten layers containing alternate silicon and carbon layers is employed to describe the (100) surfaces of the β -SiC; in this slab, one surface is Si terminated and the other is C terminated. Therefore, both the Si-terminated and the C-terminated surface can be studied with one slab model. The distance between the two surfaces is 9.81 Å, and the interaction between the two surfaces can be neglected. It will be seen that a thickness of ten layers is sufficient to describe (100) surfaces.

The two-dimensional Brillouin zone is shown in figure 5. The calculated band structures of the ideal β -SiC(100) surface are presented in figure 6. The shaded region represents the two-dimensional projection of the bulk bands. The surface bands are plotted as broken curves.

It is seen that there exist two surface bands S_1 and S_2 . The surface band S_1 is contributed by the dangling bonds of the Si-terminated surface, which disperses obviously along Γ -X and X-M and fills the band gap completely. This indicates that the ideal Si-terminated surface shows metallic character. The surface band S_2 is contributed by the dangling bond of the C-terminated surface, which lies below the surface band S_1 and near the upper edge of the valence band. The S_2 band is partially filled and the Fermi

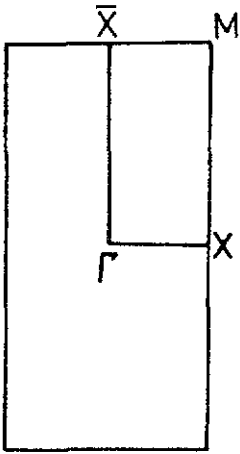


Figure 5. The Brillouin zone of the (100) (2×1) surface.

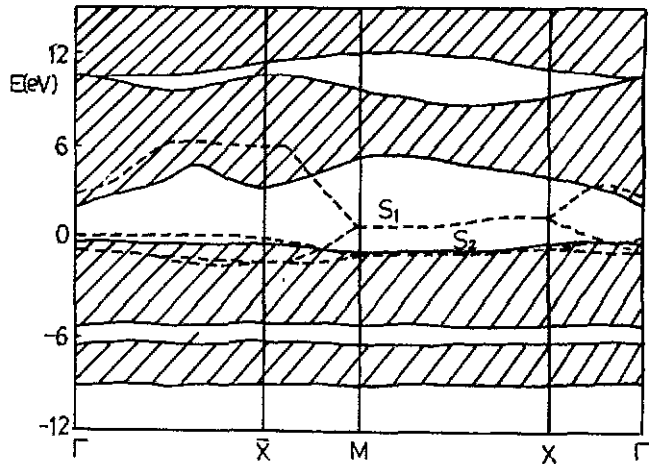


Figure 6. The band structure for the ideal (100) surface. The shaded region represents the two-dimensional projection of the bulk bands, and the broken curves represent the surface bands.

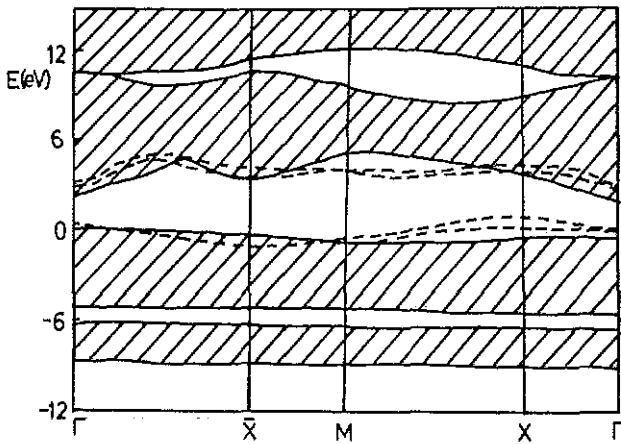


Figure 7. The band structure for the (2×1) reconstructed (100) surface. The shaded region represents the two-dimensional projection of the bulk bands, and the broken curves represent the surface bands.

level lies within it; therefore the ideal C-terminated surface still has some metallic property.

The band structure of the (100) (2×1) surface is shown in figure 7. The reconstruction splits each surface band S_1 and S_2 into two bands from point X to point M, one is near the bottom of the conduction band (corresponding to the antibonding state) and the other is near the top of the valence band (corresponding to the bonding state). The band gap reappears. These results are somewhat different from that of the Si(100) (2×1) surface [16], in which the symmetric dimer model results in a metallic surface, but in the present case, even for the Si-terminated β -SiC(100) (2×1) surface, a semiconducting surface is revealed.

The present calculation for the (2×1) reconstructed β -SiC(100) surface predicts a surface state near the top edge of the valence band for both the Si-terminated and the

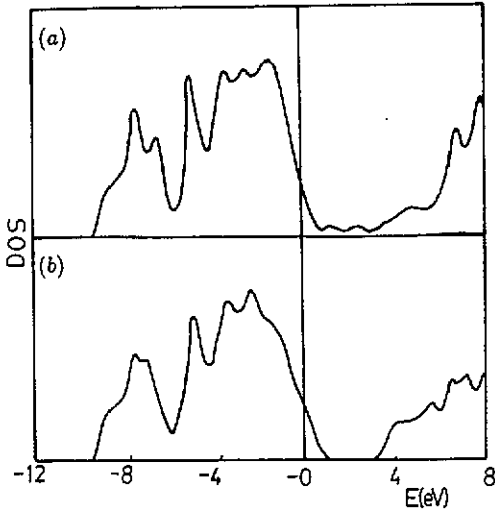


Figure 8. The total DOS in arbitrary units for (a) the ideal surface and (b) the reconstructed surface.

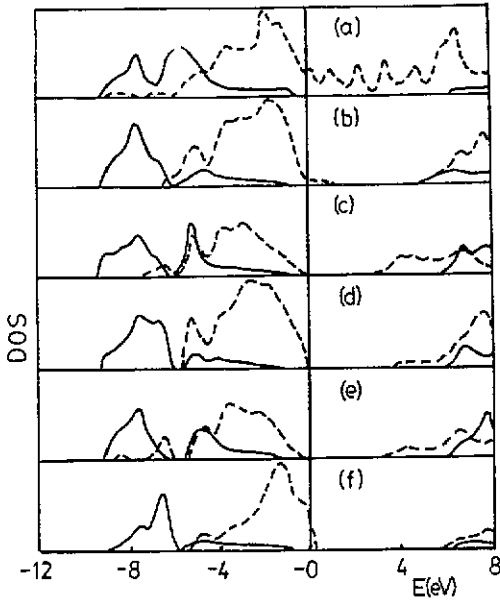


Figure 9. The local DOS of the ideal (100) surface in arbitrary units for (a) a Si atom in the surface layer, (b) a C atom in the second layer, (c) a Si atom in the middle layer, (d) a C atom in the middle layer, (e) a Si atom in the second layer and (f) a C atom in the surface layer. The full curves represent the s states and the broken curves represent the p states.

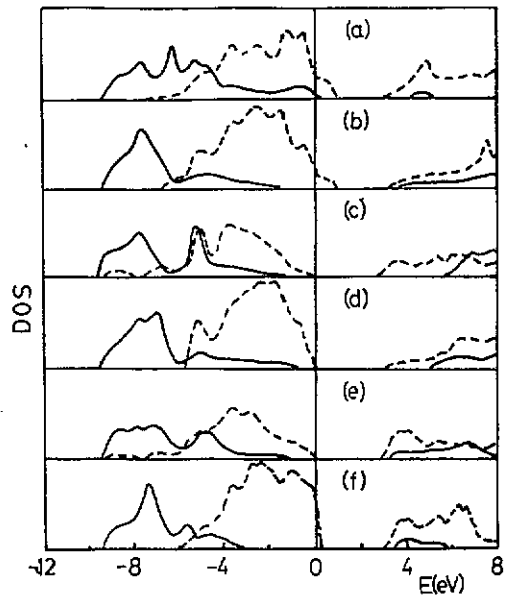


Figure 10. The local DOS of the (2x1) reconstructed (100) surface in arbitrary units. (a)-(f) have the same meanings as in figure 9.

C-terminated surfaces. This result agrees quite well with the experimental observation [4, 5].

The total DOS for both the ideal and the reconstructed surfaces are shown in figure 8 and the DOS localized at surface layers as well as middle layers are given in figures 9 and 10; the vertical lines in the figures indicate the upper edge of the valence band.

It is seen that the local DOS of Si and C atoms in the middle layers of the slab are very similar to that of the bulk (see figure 4). This means that the middle layers of the slab are not affected much by the surfaces, i.e. a slab of ten layers can be used to describe the β -SiC(100) surface quite well.

For the ideal surface the energy gap is filled by the dangling bonds, whereas the reconstruction pushes the surface states back to the valence band and leaves only a tail near the top of the valence band. For the Si-terminated surface, the width of this tail is about 0.8 eV, which agrees quite well with the experimental result quantitatively [4]. From the local DOS (figure 10), we can see that this band tail in the gap comes from the Si (3p) states with some C (2p) states. Moreover, for the reconstructed C-terminated surface, it is found that a surface state contributed by C dangling bonds is located near the top of the valence band, which agrees well with experiments [5].

4. Conclusion

The symmetric dimer model is employed to describe the (2×1) reconstruction of the β -SiC(100) surface. The ideal surface is metallic; the band gap is filled with some surface states. However, owing to the reconstruction, the surface becomes semiconducting, but a band tail remains above the valence band; it is in good agreement with the experiments [4, 5].

Acknowledgment

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