Ab initio LMTO calculation of surface localized and resonance states of the SiC(110) zinc-blende surface

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Abstract. The surface localized and resonance states of unrelaxed and relaxed SiC(110) zinc-blende surfaces have been investigated within the local density approximation of density functional theory (DFT), employing a first-principles full-potential self-consistent linear muffin-tin orbital (LMTO) method using a thicker (thirteen layer) slab. Intrinsic surface states appear in the fundamental energy gap for the unrelaxed surface. We have allowed non-bond-length-conserving relaxation of the surface atoms to obtain the minimum energy configuration. The shift in the surface states arising from the relaxation of atoms is small in comparison to other studied heteropolar covalent semiconductors because of the smaller value of the relaxation angle of the SiC(110) surface. New surface states have been predicted in the valence band region. The present atomic geometry is somewhat different from other theoretical results. We observe an inward displacement of the Si cation and an outward displacement of the C anion both parallel and perpendicular to the surface, different from the results of Sabisch *et al*. No experimental data are available for comparison.

1. Introduction

The enormous technological importance of SiC for various electronic devices has led to current interest in its bulk and surface properties in both experiment and theory. In fact, the physics of silicon carbide have been the subject of considerable interest because of its strong physical stability and chemical bonding. Besides, it has potential electrical, optical and thermal properties. The main thrust in SiC and their surfaces is due to their paramount significance for micro-electronic devices [1–3] in particular for high temperature, high power and high frequency applications. This material is very resistant to high temperature and radiation hazards because of its strong bonding between Si and C atoms. Knowledge of its surface structural and electronic properties is not only of technological importance but also of great scientific interest because in this material two group-IV elements of different electronegativities participate in bonding.

Thus, the extraordinary application of SiC material requires thorough knowledge of the structural and electronic properties of SiC and the studies of its surface are a matter of current interest and technological importance. In recent years structural and electronic properties of bulk SiC and its polytypes have been studied by first principles calculations [4–8] but the studies for its zinc-blende (110) surfaces are meagre.

To our knowledge, no experimental measurement have been made on the SiC(110) zinc-blende surface to date. Conversely, on the theoretical side the surface properties of various SiC polytypes and SiC(110) [9–11] have been studied by semi-empirical methods

and currently by Sabisch and his co-workers [12, 13] using *ab initio* calculations. The geometric and electronic structure of the SiC(110) surface has been calculated by Wenzien *et al* [14, 15] using the self-consistent pseudopotential method. Only recently, Sabisch *et al* [16] reported *ab initio* calculation of structural and electronic properties of the SiC(110) surface by employing smooth norm-conserving pseudopotentials in separable form.

It is well known that the application of the pseudopotential–DFT calculations has its own limitations. About three-quarters of the elements of the periodic table have quite strong pseudopotentials and the remaining one-quarter of the atoms have weak pseudopotentials to permit expansion of the pseudo-wave-functions in plane waves. Even for this one-quarter of atoms, the problem of slow convergence of the plane wave basis limits the choice of the number of atoms in the supercell. In the linear augmented plane wave method (LAPW) one again chooses a large basis. Thus, the most economical basis functions are seen to be the linear muffin-tin orbitals (LMTOs).

Usually in the application of the standard LMTO method, an atomic sphere approximation (ASA) is used to make it efficient. However, this LMTO–ASA method suffers from several disadvantages. (i) It neglects the symmetry-breaking terms by discarding the nonspherical parts of the electron density. (ii) The method discards the interstitial region by replacing the muffin-tin (MT) spheres by space-filling Wigner spheres. (iii) It uses spherical Hankel functions with vanishing kinetic energy only. The present LMTO method [17, 21] goes beyond the LMTO method employed usually in the atomic sphere approximation.

In the present communication, we have employed a parameter-free full-potential self-consistent LMTO method to obtain the atomic structure of the surface and the underlying layers and also the electronic surface band structure for this relaxed geometry. As mentioned above a similar study has been made by Sabisch *et al* [16] using the pseudopotential method. The limitations of the pseudopotential method have already been discussed above. We present the results of a comprehensive analysis of the orbital characters of surface states in the fundamental band gap, stomach gap and ionic gap of the surface Brillouin zone for a thirteen layer slab with a vacuum region equivalent to five layers between two nearby slabs.

2. Method

For detailed information about the LMTO method used, we refer to earlier articles [17–21]. The surface geometry plays an important role in studying the electronic surface band structure. For the heteropolar covalent semiconductors such as GaAs or ZnS, the anion atoms relax outward and the cation atoms relax inward with respect to the ideal surface plane and the substrate. On the other hand, in SiC, although both the atoms are tetravalent, the maximum charge has been seen to be lying quite near to the carbon atom and therefore it may be described as a heteropolar ionic semiconductor. For this surface and relaxation angle is much smaller than that of a heteropolar covalent semiconductor.

The scalar relativistic versions were performed in all the calculations. The LMTO envelope functions were formed from the spherical harmonic components having $l \leqslant 4$ with three decay energies, -0.01, -1.0 and -2.3 Ryd, inside the MT spheres occupied by real atoms and with two decays given by -0.7 and -1.0 Ryd for the interstitial region. The surface states should decay quite fast especially towards the vacuum side. Thus, high values for the decay factor have been chosen in the calculations. The local density potential of Hedin and Lundqvist [23] has been utilised. The LMTO basis functions in the valence energy region were chosen as Si (3s,3p) and C (2s,2p). The MT spheres for Si and C are chosen to be 2.1 and 1.4 (au), respectively.

Empty spheres were assumed to be present at the vacant sites and a set of appropriate s, p, d states were chosen from them. The core electrons are not frozen but are relaxed in the sense that the core electron charge density is recalculated in each iteration in the self-consistent loop. We have not considered the spin–orbital coupling but have generated the self-consistent supercell potentials by considering the scalar relativistic effects. It has been observed that spin–orbit coupling to lowest order splits only the bands and does not change the relative position of band centres. The cohesive properties are hardly affected.

3. Calculations

3.1. The bulk superlattice

The present calculation starts from the ideal geometry and the self-consistent LMTO calculations were carried out until the electron charge density was self-consistent. Figures 1(a), (b) and (c) shows the top view, projected view and relaxed surface of SiC(110) respectively.
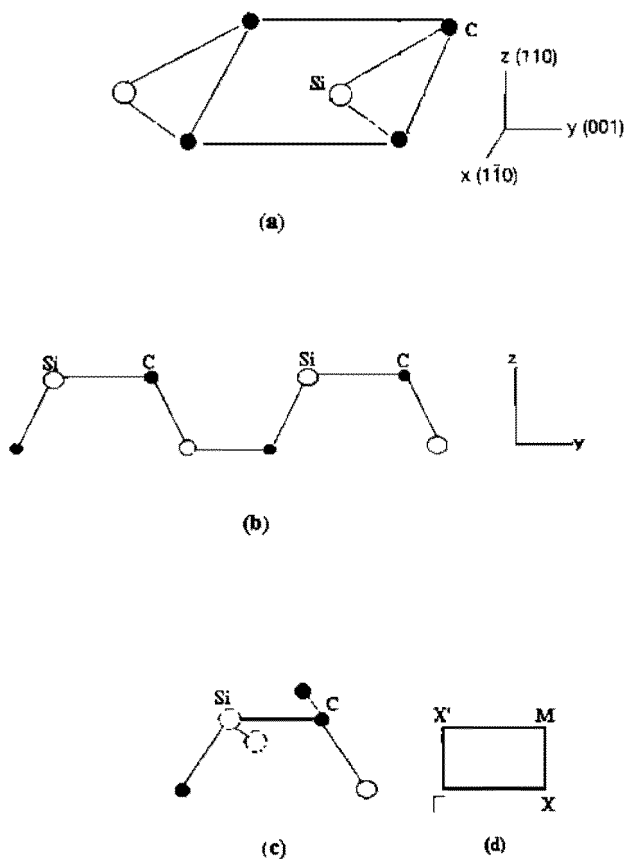

Figure 1. The surface unit cell of SiC(110): (a) a top view; (b) a projected side view; (c) relaxed surface atoms; (d) the surface Brillouin zone.

We have computed the electronic structure of a fourteen layer bulk superlattice by repeating a supercell containing 56 atoms on a lattice. Of the 56 atoms in the supercell, 28 are real and 28 are empty spheres to fill the vacant interstitial space. The Gaussian broadening is chosen to be 0.015 Ryd. For the bulk slab, the minimum energy appears at a lattice parameter of 4.34 Å which is in good agreement with the experimental value of 4.36 Å.

3.2. The SiC(110) surface

We use a thirteen layer slab containing surfaces at both ends. We select a vacuum region equivalent to five layers. A similar vacuum region for the electronic structure has been used by a number of other worker [24–26]. We have also made a separate calculation for a nine layer slab. However, we observe an appreciable effect of the interaction of the two surfaces of a nine layer slab especially in the fundamental gap region where the occupied and the unoccupied states split. This splitting originates from the long range nature of the surface states. The necessity of choosing a slab containing a larger number of layers should be noted as almost all the calculations for the semiconductor surfaces performed earlier have chosen a slab containing only nine layers [16, 22]. The surface being a planar defect will induce surface states, resonance and/or localized ones which would be characterized by the decay of the wave functions as we move away from the surface defect on either side. The transitional invariance of the surface is preserved in the two directions parallel to the surface (i.e. x- and y-directions) while in the z-direction we have formed a superlattice consisting of the SiC slab and vacuum region, alternatively. x is taken parallel to the direction of the chains $\langle 1\bar{1}0 \rangle$, y is parallel to $\langle 001 \rangle$ and z is perpendicular to the surface plane as shown in figure 1(a).

At first, the calculations were performed for the unrelaxed SiC(110) surface but allowing relaxation between the surface layer and the underlying layer but without making any change in the interspacing of the remaining bulk layers. The minimum energy configuration is obtained for a 3% dilation of the underlayer next to the surface layer.

For the atomic relaxation from their zinc-blende sites we have allowed non-bond-length-conserving relaxation of the surface atoms until the total energy is minimized. The present calculated atomic displacements for the top two layers are shown in table 1. The Si cation moves towards the substrate whereas the C anion shifts above the surface. The present calculated Si displacement is in agreement with that of Sabisch *et al*. However, we observe displacement of the C anion both parallel to the surface and outward normal to the surface, which has not been observed by the latter authors. In the absence of any experimental results we have compared the present calculated surface bond rotation angle and surface bond length change with the other theoretical calculations in table 2.

Table 1. Calculated atomic displacements (Å) for the top two layers of atoms at the cubic SiC(110) surface.

Layer	Atom	Δz	Δy
1	Si	0.155	0.285
1	C	−0.307	−0.108
2	Si	−0.067	0.030
2	C	−0.098	−0.126

$R_{Si-C} = 1.88$ Å.

Table 2. A comparison of the present calculated surface bond rotation angle (ω) and surface bond length change (%) of the cubic SiC(110) surface with other available theoretical calculations.

	Present work	Sabisch *et al* [16]	Wenzien *et al* [15]	Lee and Joannopoulos [9]	Mehandru and Anderson [11]
ω (°)	14.75	16.9	15.4	7.4	6.0
$\Delta R_{surface}$ (Si–C)	−7.02	−6.0	—	—	—

We found a relaxation characterized mainly by a surface bond length change (ΔR_{Si-C}) of −7.02% and a surface bond rotation angle of 14.75°. Obviously, this is in contrast to III–V(110) compound semiconductor surfaces such as GaAs and InP where the surface bond rotation angles have been found to be of the order of $30 \pm 5°$. Our results for surface bond rotation angle and surface bond length change are close to those obtained by Sabisch *et al* [16]. The change in surface bond rotation angle is also close to the result of Wenzien *et al* [15] but is rather higher than the value of Lee and Joannopoulos [9] and Mehandru and Anderson [11].

4. Results and discussion

4.1. Surface band structure

We have chosen a mesh of 18 selected k-points in the irreducible wedge of the surface Brillouin zone to achieve self-consistency. The surface Brillouin zone is shown in figure 1(d). The symmetric points of the surface Brillouin zone are $\Gamma(0, 0, 0)$, $X(0.5, -0.5, 0.0)$, $M(0.5, -0.5, 0.5)$ and $X'(0, 0, 0.5)$ and they lie in the k-plane parallel to the surface (110). The surface states are determined by identifying those states for which the square of the modulus of the eigenvector calculated on the MT spheres decreases as one moves away from the layer underneath to the surface layer. These states are mainly localized either on the surface layer or on the underneath layer. Here the states are taken as surface states when the magnitude of the eigenvector at the surface atom is greater than or equal to 0.35 and its value decreases by more than 30% at each layer.

We have employed the Mullikan decomposition technique to determine the magnitudes of the wave functions at the different lattice sites occupied by the real atoms. A similar procedure has been adopted by Fiorentini *et al* [27].

4.1.1. The unrelaxed surface. The dispersion curves for the unrelaxed SiC(11) surface are shown in figure 2. For an unrelaxed surface we find in all two intrinsic surface states in the fundamental energy gap. The cation derived (Si) dangling bond surface state appears just below the conduction band minimum (CBM). Similarly, the anion derived (C) dangling bond surface state appears in the whole energy gap region. In fact at the X-point it enters the valence band. The upper intrinsic state shows downward dispersion along Γ–X, Γ–X′ and Γ–M directions.

In the stomach gap region, cation derived surface states appear in the M–X and M–X′ directions which are slowly and fast decaying localized surface states respectively. A number of resonance states are seen to appear in the −1.0 to −8.0 eV energy region.

In the ionic or heteropolar gap region, localized an resonance surface states appear around the symmetry points X and M respectively. Resonance states appear throughout the Brillouin zone in the lowest valence band in the energy region from −11.0 to −13.0 eV. However, the present calculated surface states are lower than those of Sabisch *et al*.

SiC (110) Unrelaxed surface

DISPERSION CURVE WITH SURFACE STATES

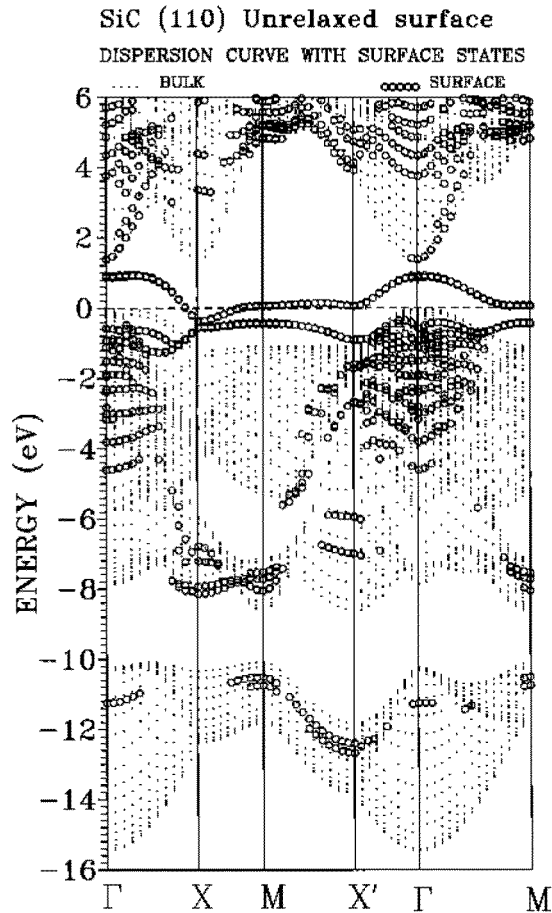.... BULK   ooooo SURFACE

Figure 2. Dispersion curves with projected bulk band structure along with surface localized and/or resonance states for the SiC(110) unrelaxed surface.

4.1.2. The relaxed surface. In figure 3, we have shown the dispersion curves for the relaxed SiC(110) surface. The effect of atomic relaxation is different in different energy regions. In the band gap region there is an overall shift of surface state towards the high energy side. The C derived surface state now reveals comparatively small dispersion except in the Γ–X direction. On the other hand, the Si derived surface state filling the entire energy gap shows much larger dispersion. In fact the band width is doubled as compared to that seen in the unrelaxed case. Such an effect has also been observed by Sabisch *et al.*

The states in the upper part of the stomach gap have also shifted up. In the ionic gap surface states appear around the M symmetry point which extend in the M–X direction and up to some region in the M–X′ direction as localized ones and as resonance states thereafter. Overall for the relaxed geometry the surface states in the valence band region are faster decaying than seen in the unrelaxed geometry.

The energy locations of the conduction band states are not reliable because of the well known LDA effects. The interpretation of the energy location of these states is somewhat
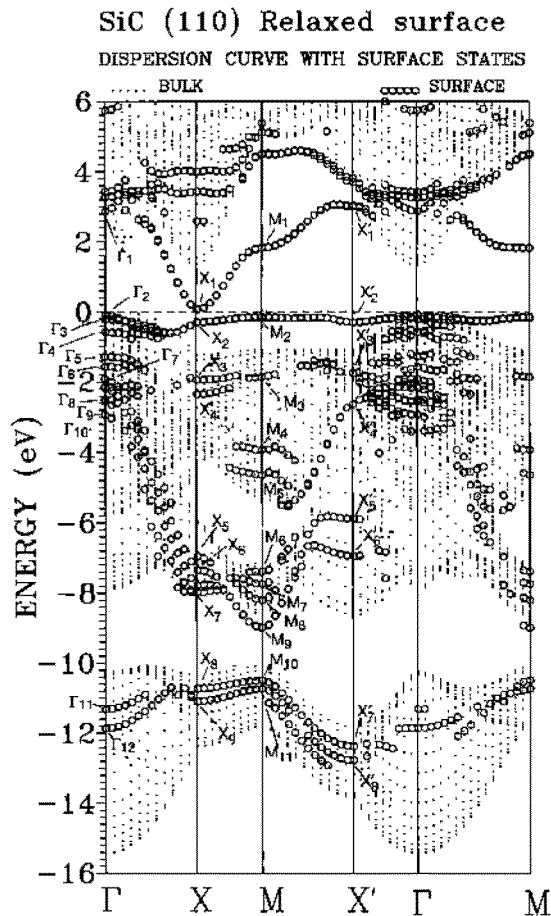
Figure 3. The same as in figure 2, but for the SiC(110) relaxed surface.

complicated because of the limitation of the LDA theory where the on-site correlation effects have been ignored and the calculated energies of the states above the valence band region are lower. A deficiency of the local density theory is that the calculated value of the fundamental energy gap is smaller than the experimental one. This arises from the fact that the excitation energies of these systems are not given by eigenvalues of the Kohn–Sham equations [28, 29]. The quasi-particle energies and wide band gap can be obtained by employing the so-called GW approximation for the calculation of the electron self-energies Σ. This self-energy is seen to be a non-local energy dependent effective potential. This is beyond the scope of the present work.

Our calculated surface states at Γ, X, M and X′ symmetry points of the surface Brillouin zone for a relaxed SiC(110) surface are shown in table 3 and are compared with the available results of other calculations. In general our values are lower than those of Sabisch *et al*. It may be noted that in the present calculation the exchange–correlation potential of Hedin and Lundqvist [23] has been utilized whereas Sabisch *et al* employed the Ceperley–Alder [30] form of the exchange and correlation potential.

Table 3. A comparison of the calculated surface states with the other available calculation at Γ, X, M and X′ symmetry points in the surface Brillouin zone of the SiC(110) relaxed surface. All energies are in electron volts.

Surface states	Present calculation	Other calculation	Surface states	Present calculation	Other calculation [16]
Γ_1	2.86		X_1	0.06	1.0
Γ_2	−0.08	0.2	X_2	−0.30	0.5
Γ_3	−0.22		X_3	−1.93	
Γ_4	−0.57		X_4	−2.34	
Γ_5	−1.28		X_5	−6.96	−6.0
Γ_6	−1.56		X_6	−7.35	
Γ_7	−1.9		X_7	−7.78	
Γ_8	−2.16		X_8	−10.7	−10.0
Γ_9	−2.5		X_9	−11.1	
Γ_{10}	−2.9				
Γ_{11}	−11.3	−10.40			
Γ_{12}	−11.8				
M_1	1.82	2.0	X'_1	3.00	3.0
M_2	−0.2	0.4	X'_2	−0.3	−0.2
M_3	−1.8		X'_3	−1.7	
M_4	−3.9		X'_4	−2.6	
M_5	−4.6		X'_5	−5.9	−3.15
M_6	−7.4	−7.0	X'_6	−7.0	
M_7	−7.7		X'_7	−12.4	−11.80
M_8	−8.2		X'_8	−12.8	
M_9	−8.9				
M_{10}	−10.5	−10.0			
M_{11}	−10.7				

4.2. Orbital characters

In order to describe the orbital characters of the localized surface states for the relaxed SiC(110) surface at high symmetry points of the surface Brillouin zone, we choose the following notation for assigning the p orbitals: $p_{\sigma xy}$ and $p_{\sigma z}$ are the p orbitals lying in the surface and the other layers along $\langle 1\bar{1}0 \rangle$ and $\langle 001 \rangle$ directions respectively, whereas $p_\perp$ is along the $\langle 110 \rangle$ direction normal to the surface.

The occupied dangling bond states lying at the valence band maximum (VBM) are mainly comprised of the sp^3 hybrid orbitals of the anion. However the relative contributions of s, p_σ and $p_\perp$ vary with the wave vector. At Γ and X′ symmetry points, these states originate from the hybridized $p_{\sigma xy}$ orbitals of both the anion and cation. On the hand, at the X and M symmetry points, the dominant contributors in order of magnitudes are the $p_\perp$, s and $p_{\sigma z}$-like orbitals of the anion mixed with some $p_{\sigma xy}$-like orbitals of the cation.

The orbital characters of the unoccupied dangling bond states lying in the vicinity of the conduction band minimum (CBM) are the hybridized sp^3 orbitals of the cation mixed with some orbitals of the anion. Again, the relative contributions of the various types of orbital are different in the *k*-space. At Γ and X′ symmetry points the states are comprised of the dangling sp^3 hybrid orbitals of both cation and anion, whereas at X and M symmetry points the dominant contributors in order of magnitude are $p_\perp$, $p_{\sigma z}$ and s-like orbitals of the cation mixed with some $p_{\sigma xy}$ orbitals of the anion.

In the central region of the bulk valence band (stomach gap), the well localized surface state is composed of the s-like orbital of the cation mixed with some $p_{\sigma xy}$ orbitals of the anion. Near the bottom of the valence band in the ionic gap, the surface state is essentially dominated by the s-type orbital of the anion with some mixing of $p_{\sigma xy}$ orbitals of the cation at the Γ and X′ symmetry points. On the other hand, at X and M symmetry points the state is dominated by the s-character of the anion with some mixing of s and $p_{\sigma z}$-like orbitals of the cation.

5. Conclusions

The structural and the electronic properties for unrelaxed as well as relaxed SiC(110) zinc-blende surfaces have been investigated by employing a first-principles full-potential self-consistent linear muffin-tin orbital (LMTO) method by using a thirteen layer slab. We have calculated the atomic displacements, surface bond rotation angle and surface bond length change by minimizing the energy of the slab and predicted the surface localized states as well as the resonance states in the various energy regions. Both the Si cation and C anion move parallel as well as perpendicular to the surface but in the opposite directions, the Si cation moving inwards and the C anion moving outwards. The detailed analysis of the orbital character of the surface states reveals that the relative contributions of the orbitals vary with the wave vector. No experimental data are available for comparison.

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