

# Calculated differential reflectance of the (110) surface of cubic silicon carbide

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(Received 31 October 1994; accepted for publication 12 April 1995)

Surface band structure and differential reflectance spectra of the (110)(1×1) surface of cubic silicon carbide crystals are investigated within a self-consistent tight binding theory. The surface electronic band structure is characterized by the pronounced surface states in the gap and show metallic character. Optical transitions between the surface states cause an enormous reflectivity within the range of 1.0 to 1.5 eV and reveal strong polarization anisotropy. Influence of the atomic geometry of the (110)(1×1) surface on the differential reflectance of 3C SiC is studied. © 1995 American Institute of Physics.

At present there has been a significant interest in the study of silicon carbide (SiC), which is a promising material for high-temperature, high-frequency, and high-power electronic devices. For the applications of SiC for microelectronic and optoelectronic devices, where physical processes on the surface are very important, the knowledge of the surface electronic band structure and the specific optical properties caused by electronic transitions between the surface states is necessary.

The optical functions of cubic (3C) SiC crystals have recently been measured in visible and ultraviolet regions by the use of reflectance spectroscopy<sup>1</sup> and spectroellipsometry.<sup>2</sup> Equilibrium geometry and electronic band structure of the (110)(1×1) surface of SiC have been studied by the use of an *ab initio* theory<sup>3</sup> and a semiempirical tight binding method.<sup>4,5</sup> In Ref. 3, a metallic character of the surface band structure has been reported. However the tight binding studies<sup>4,5</sup> showed the (110)(1×1) surface of 3C SiC to be semiconducting. Equilibrium atomic geometries found in these studies were quite different. Differential reflectance (DR) spectroscopy, which is sensitive to the atomic geometry of the surfaces,<sup>6,7</sup> has been demonstrated to be a powerful tool for optical investigations of the solid surfaces (see Ref. 8 and references therein).

In this work surface electronic band structure and DR spectra of the (110)(1×1) surface of 3C SiC are calculated within a self-consistent tight binding scheme.<sup>9</sup> The influence of the atomic geometry of the (110)(1×1) surface on the DR of 3C SiC is investigated.

The surface electronic band structure is calculated within the super-cell (slab) method.<sup>10</sup> The electronic states of the slab and their energies  $E_n$  at different  $k_{||}$  points of the two-dimensional Brillouin zone (2D BZ) are obtained by solving the 2D-Schrödinger equation. The Hamiltonian ( $\hat{H}$ ) matrix elements are calculated using a  $sp^3s^*$  tight binding basis. To incorporate the effects of the nonlocality of the potential, the Coulomb electron-ion intra-atomic and inter-atomic interactions are taken into account.<sup>9</sup> The electronic occupancies are determined self-consistently. The model used has been described in more detail in Refs. 7 and 11. Only interactions between the first nearest neighbors are included in the calculation of the  $\hat{H}$ -matrix elements. Tight binding parameters of

the inter-atomic interactions are chosen to reproduce experimental data for both the bulk band structure and optical functions of bulk 3C SiC. It has been shown that the choice of tight binding parameters determined in the standard manner from adjusting the calculated characteristic energies and gaps to the well known values of 3C SiC, (see e.g., Ref. 12) is not unique. A comparison of the calculated optical functions to the experimental data helps in obtaining a more realistic description of the dispersion of the electronic bands. The tight binding parameters used in this work for the calculation of the  $\hat{H}$ -matrix elements are given in Table I and Table II. The highest valence bands and the lowest conduction bands of 3C SiC are fitted most carefully to the well known data from the literature<sup>1-3,13</sup> to calculate a realistic optical reflectivity in the visible and nearest ultraviolet spectral regions. The characteristic energies of the bulk band structure of 3C SiC calculated in this work are given in Table III in comparison with the data of the literature.

Optical functions are calculated by the parameterization of the intra-atomic matrix elements of the momentum operator.<sup>6</sup> The optical functions of 3C SiC are calculated within the random-phase approximation neglecting of local-field and many-body effects. The surface contribution to the diagonal components of the dielectric tensor  $\epsilon_{\alpha\alpha}$  for the polarization  $\alpha=x,y,z$  has been calculated according to the expression<sup>14</sup>:

$$\text{Im}(\Delta\epsilon_{\alpha\alpha}) = \frac{8\pi^2 e^2}{\hbar^2 m^2 V_u \omega^2} \sum_{\mathbf{k}_{||}, i, j} |\langle \mathbf{k}_{||}, i | p_{\alpha} | \mathbf{k}_{||}, j \rangle|^2 \times \delta[E_j(\mathbf{k}_{||}) - E_i(\mathbf{k}_{||}) - \hbar\omega],$$

where  $p_{\alpha} = -i\hbar\nabla_{\alpha}$ ,  $V_u$  is the volume of the unit cell, and  $i, j$  denote the dangling bond states only.

TABLE I. Values (in eV) of the on-site tight binding parameters of Si and C atoms.

Parameter	Si	C
$E_s$	1.69	-3.10
$E_p$	5.84	6.31
$E_{s^*}$	10.07	9.05

TABLE II. Tight binding parameters (in eV) for calculation of matrix elements of the interactions between Si and C orbitals.

Parameters	Energy
$(ss\sigma)$	-1.45
$(ss^*\sigma)$	0.0
$(s_a p_c \sigma)$	0.92
$(s_a^* p_c \sigma)$	2.60
$(p_a s_c \sigma)$	0.80
$(p_a s_c^* \sigma)$	0.42
$(pp\sigma)$	2.41
$(pp\pi)$	-0.44

The matrix elements of the momentum operator between eigenfunctions of the electrons needed to evaluate optical properties in the tight binding scheme used are calculated according to the relation:  $\mathbf{p} = i(m/\hbar)[\hat{H}, \mathbf{r}]$ . The commutator is determined in the  $sp^3s^*$ -basis by taking into account nearest-neighbors interactions only. This has been done previously on Si<sup>6,15</sup> and diamond.<sup>7</sup> Only two intra-atomic matrix elements of  $\mathbf{r}$  with values  $\langle s|x|p_x \rangle = 0.13 \text{ \AA}$ , and  $\langle s^*|x|p_x \rangle = 0.15 \text{ \AA}$  are used. This allows quite a good description of the bulk optical properties of 3C SiC. The real part of  $\epsilon$  is calculated from  $\epsilon_2$  using the Kramers-Kronig relations. In Fig. 1 the theoretical reflectivity spectrum of 3C SiC calculated by the method described is shown in comparison with experimental reflectance measured in Ref. 1. In Table III the energies of some characteristic gaps in 3C SiC are given in comparison with the data of the literature.

The equilibrium atomic geometries of the (110)(1×1) surface of 3C SiC have been reported in Refs. 3–5. Tight binding studies<sup>4,5</sup> and Monte Carlo simulations using semi-empirical potentials<sup>16</sup> gave an inward displacements of Si and C atoms by the relaxation. This is in contrast to the *ab initio* study<sup>3</sup> where displacements of the Si and C atoms into different directions have been reported.

The atomic geometries found in Refs. 3 and 4 are similar. The most essential difference of these results is the buckling of the surface bonds. The value of the buckling ( $\sim 0.24 \text{ \AA}$ ) obtained by the *ab initio* calculations<sup>3</sup> exceeds remarkably the data reported previously, e.g.,  $\sim 0.09 \text{ \AA}$  found in Ref. 4. Proven in this work is that the surface gap depends strongly on the buckling of the surface Si–C bonds. To demonstrate further the sensitivity of the differential reflectance to the buckling of the surface bonds the  $\Delta R/R$  spectra are

TABLE III. Characteristic energies (in eV) of 3C SiC calculated in this work and those available in the literature.

Energy	This work	Theory (Ref. 1)	Exp.
$\Gamma_{15v} - \Gamma_{1c}$	7.58	7.40	...
$\Gamma_{15v} - \Gamma_{15c}$	8.81	8.27	...
$X_{5v} - X_{1c}$	6.07	5.80	6.0 <sup>a</sup>
$X_{5v} - X_{3c}$	8.14	8.52	8.3 <sup>a</sup>
$X_{3c} - X_{1c}$	2.27	2.90	3.10 <sup>a</sup>
$\Gamma_{15v} - X_{1c}$	2.38	2.38	2.38 <sup>b</sup>

<sup>a</sup>Reference 13.

<sup>b</sup>Reference 1.

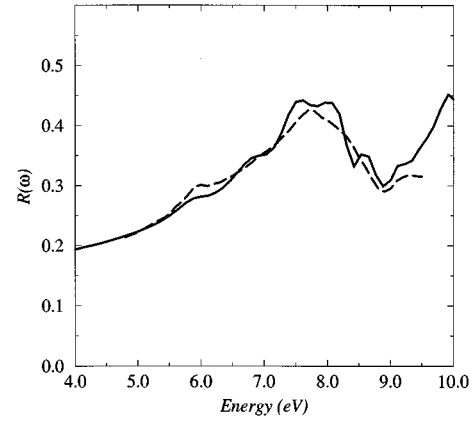


FIG. 1. Reflectivity  $R(\omega)$  of 3C SiC calculated in this work (solid line) and measured in Ref. 1 (dashed line). Spectrum of real part of dielectric function ( $\epsilon$ ), needed for evaluation of  $R(\omega)$  is determined from imaginary part of  $\epsilon$  by the Kramers-Kronig relations.

calculated for the surface geometries, reported in Refs. 3 and 4.

In Fig. 2 the surface electronic band structure has been shown for the atomic geometry given in Ref. 3. The upper unoccupied band is mainly related to the Si-dangling bonds and the lower occupied band arises mainly from C-dangling orbitals. The results presented in Fig. 2 are in reasonable agreement with the data of the *ab initio* calculations.<sup>3</sup> However there are some important discrepancies between the results of *ab initio* theory<sup>3</sup> and the present data. It is instructive to analyze these differences in more detail.

The main discrepancies of the present results with Ref. 3 arise in the region close to the  $\Gamma$ -point in the BZ. In Ref. 3 the bonding surface states were located in the valence band, but in this work they are found in the gap. In the model used here the electronic exchange and correlation effects in 3C SiC are not completely described. This can explain the discrepancies in the dispersion of the bonding surface states near the  $\Gamma$ -point calculated in the present work from the data of the *ab initio* study.<sup>3</sup>

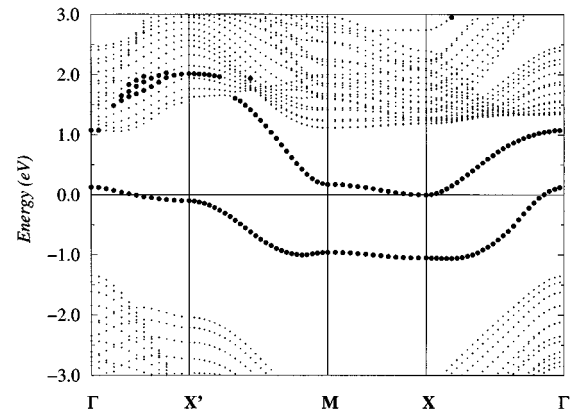


FIG. 2. Electron energy structure of the surface states on relaxed (110)(1×1) surface of 3C SiC (bold circles). Bulk band structure has been projected on 2D Brillouin zone of the (110) surface. The zero of the energy scale indicates position of the Fermi energy.

Another important difference is that according to Ref. 3 in the  $X-M$  region in the BZ the surface bonding and antibonding bands are found to overlap, which indicates the vanishing of the interatomic interaction between dangling bonds for  $\mathbf{k}_{\parallel}$  vectors along  $X-M$  direction.<sup>3</sup> This does not agree with the results of the present calculations where the interatomic interactions between the dangling bonds of the surface atoms do not vanish (see Fig. 2). In Ref. 3 the density functional theory (DFT) with the local density approximation (LDA) has been used. Strictly speaking the one-particle LDA-eigenvalues have no formal justification as quasiparticle energies.<sup>17</sup> Further investigations of the SiC-surface band structure show<sup>18</sup> that the quasiparticle correction to the LDA leads to the increase of the gap between the occupied and empty surface states and some changes in the dispersion of the surface bands.

On the other hand the semiempirical scheme of tight binding theory may include corrections to the one-particle band structure on the many-body and local-field effects by the fitting to the experimental data.<sup>12</sup> However the restriction of the number of interatomic interactions to be included into the Hamiltonian to nearest neighbors only leads to the errors in the calculations of the eigenvalues. For a more realistic description of the conduction band in SiC, in the present calculation the excited  $s^*$  state has been added into the basis of the Hamiltonian. This scheme has been shown previously to provide reliable predictions of the surface band structure and DR of Si<sup>6,15</sup> and some A<sup>3</sup>B<sup>5</sup> compounds (see e.g., Ref. 8 and references therein) which agree well with the experimental data. The forbidden gap between empty and occupied surface states corresponds to the value of the interaction between the dangling bonds. The present tight-binding results are in better agreement with the *ab initio* calculation of Ref. 18, which include quasiparticle corrections than with the earlier DFT-LDA calculations of Ref. 3 which did not.

In Ref. 4 the (110)(1×1) surface of 3C SiC, in contrast to Ref. 3, has been found to be semiconducting. In this work the surface has been found to be metallic for both geometries in Refs. 3 and 4. The metallic character of the surface band structure obtained here is in conflict with the results reported previously by the use of the similar semiempirical tight binding method,<sup>5</sup> where a gap as large as ~2.0 eV was found. In Ref. 5 the surface Si and C atoms are found to be displaced inward by the relaxation, but the atoms of Si remains somewhat higher than C. In contrast to this, the *ab initio* theory predicts that Si and C atoms displaced in opposite directions give rise to reversed buckling. Thus a further investigation of this point is needed.

Anisotropy of the surface reflectance of the normally incident light polarized along the  $\alpha$  direction has been calculated according to Ref. 14:  $(\Delta R/R) = (4\omega/c) \text{Im}\{[\Delta\epsilon_{\alpha\alpha}(\omega)]/[\epsilon_b(\omega) - 1]\}$ , where  $\Delta R = R_y - R_x$ , is the difference between the optical reflectance obtained for the light polarized along  $y = \langle 1\bar{1}0 \rangle$  and  $x = \langle 110 \rangle$  directions, and  $R_0$  is given by the Fresnel formula,<sup>15</sup>  $\epsilon_b$  is the bulk dielectric function.

The calculated spectra of  $\Delta R/R$  for the atomic geometries found in Refs. 3 and 4 are presented in Fig. 3. One can see a strong peak of the  $\Delta R/R$  caused by the optical transi-

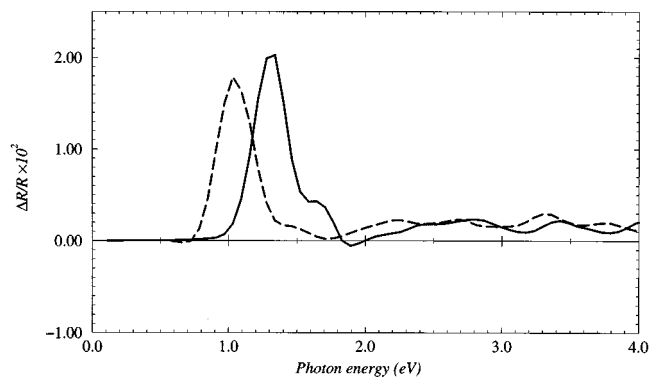


FIG. 3. Calculated differential reflectance,  $\Delta R/R = (R_{(110)} - R_{(1\bar{1}0)})/R_0$ , of the relaxed (110)(1×1) surface of 3C SiC for atomic geometries reported in Refs. 3 (solid line) and 4 (dashed line).

tions between almost parallel bonding and antibonding dangling bonds related surface bands in the  $X-M$  region in BZ. As expected the spectral position of the  $\Delta R/R$  peak depends strongly on the buckling of the surface bonds (see Fig. 3).

In conclusion, the surface band structure of the (110)(1×1) surface of 3C SiC is characterized by the existence of the bonding and antibonding dangling bond states in the gap and shows a metallic character. Differential reflectance spectra reveal a strongly polarized peak in the region around 1.0–1.5 eV. The spectral position of this peak is strongly dependent on the buckling of the surface bonds, and may thus provide information on the latter.

The author is thankful to F. Bechstedt for helpful discussions.

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