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1993 J. Phys.: Condens. Matter 5 883

(http://iopscience.iop.org/0953-8984/5/7/015)

J. Phys.: Condens. Matter 5 (1993) 883–890. Printed in the UK

Strain effects on the band structures of β-SiC

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Received 16 July 1992, in final form 23 September 1992

Abstract. The linear muffin-tin orbital method is used with the atomic-sphere approximation to study the electronic properties of β-SiC. The equilibrium lattice constant, bulk modulus and band structures calculated are in good agreement with the experimental results. The strain effect on the band structures is discussed; the results show that, when the lattice constant parallel to the surface is expanded by 8% or more, the indirect fundamental gap might become direct.

1. Introduction

Because of its large band gap, temperature stability and chemical inertness, silicon carbide (SiC) is considered to be a promising material applicable to electronic and optical devices under certain special conditions, such as a high temperature and strong irradiation environment. Its high thermal conductivity and breakdown field also indicate that high-density integration of devices made from SiC could be achieved.

In the early days, difficulties involved in growing high-quality large-area single crystals made the application of SiC unrealistic. SiC has recaptured much attention since techniques have been developed for the formation of β-SiC (cubic) [1–5] and α-SiC (hexagonal) [6] on silicon substrates, and applications in electronic devices have become possible [7, 8]. β-SiC is of particular interest, because of its easy epitaxial deposition and its reproducible characteristics [9, 10].

Recently, a number of theoretical and experimental studies have been made on the properties of bulk β-SiC. Churcher *et al* [11] have studied the ground-state properties of cubic SiC using the norm-conserving pseudopotential method and obtained the equilibrium lattice constant, bulk modulus and phonon frequencies which are in agreement with experiments. Using the *ab initio* total-energy pseudopotential method, Chang and Cohen [12] investigated the phase transition of SiC and suggested that the cubic phase of SiC transforms into the more ionic rocksalt structure as the applied pressure increases above 600 kbar. Cheong *et al* [13] have also investigated the pressure dependence of band gaps and optical-phonon frequencies in β-SiC. Recent experiments have shown that the fundamental gap of β-SiC varies linearly with pressure up to 10 kbar, but a strong sublinear behaviour is exhibited for pressures from 10 to 15 kbar [14].

Generally, β-SiC is grown on the silicon (100) surface [5]. Owing to the 20% lattice mismatch between β-SiC and silicon, strain effects are important. Moreover, during the growth of a diamond film on the silicon substrate, transition layers of β-SiC

0953-8984/93/070883+08$07.50

exist in the interface between the diamond film and the silicon. The lattice mismatch between β-SiC and diamond is also about 20%. This also shows the importance of studies on the strain effects. Up to now, only the deformation potential of β-SiC induced by strain has been calculated by Lambrecht *et al* [15] and Brey *et al* [16]; no experimental investigations of the strain effects on the electronic structures of β-SiC have been done. In the present paper, the linear muffin-tin orbitals (LMTO) method [17, 18] is used to study ground-state properties and the strain effect on the band structures.

This paper is organized as follows. Section 2 outlines the method of calculation. The results and discussion are presented in section 3 and a summary is given in the last section.

2. Method of calculation

In our calculation, the LMTO method [17, 18] is used with the atomic-sphere approximation (ASA). As usually done for the open structure [19], two empty spheres in a cell are introduced at tetrahedral interstitial sites in order to provide an adequate description of the charge density and potential in interstitial regions. The radii of the empty sphere are chosen to be equal to those of the real atomic spheres. The basis set includes s, p and d orbitals for all real and empty spheres. Bachelet and Christensen [20] have explicitly shown for GaAs that the ASA with interstitial empty spheres provides results which are in very good agreement with first-principles pseudopotential calculations involving no spherical shape approximation for the potential. Since β-SiC has the same zincblende structure as GaAs, similar accuracies could be expected. The exchange–correlation potential is approximated by the von Barth–Hedin [21] parametrization, which has proved to be adequate for semiconductors. Although the errors induced by the ASA are unimportant for many applications, it is necessary to include the combined correction term in the cases where energy bands of high accuracy are needed [18].

The density of states (DOS) is calculated by means of the tetrahedron technique [22]. In this approach, the irreducible wedge of the Brillouin zone is divided into several tetrahedra. The DOS and the integral of the DOS are calculated by the sum over these tetrahedra. In the practice calculation, we first use 20 k-points and then use 89 k-points to obtain the self-consistent energy bands.

If the lattice constant parallel to a surface is compressed or expanded, the lattice constant perpendicular to the surface will be expanded or compressed correspondingly. While considering the strain effects on the band structure, the variation in geometry is described by the Keating [23] model. The bond-stretching and bond-bending parameters in the Keating model are determined by fitting the phonon dispersion relation of bulk β-SiC [24].

3. Results and discussion

In the present paper, we mainly concentrate on the strain effects on the band gaps, and the ground-state properties and band structures of the perfect crystal are also studied.

3.1. Ground-state properties and band structures

The calculated equilibrium lattice constant a_0, the bulk modulus and its pressure derivative are listed in table 1 together with other theoretical and experimental values. The calculated equilibrium lattice constant a_0 is 4.34 Å, which is smaller than the experimental lattice constant of 4.360 Å [25] by only about 0.5%. The existing experimental values of the bulk modulus B_0 given by various workers are 2.24 Mbar [26], 2.25 Mbar [27] and 2.30 Mbar [28], although a value of 0.97 Mbar has also been reported [25]. Our calculated bulk modulus B_0 is 2.30 Mbar, which is in good agreement with the experimental values. The pressure derivative of the bulk modulus is predicted to be 6.1, which is close to that obtained in [29] but is twice that obtained in [11, 12].

Table 1. Calculated lattice constants, bulk moduli and pressure derivatives of the bulk modulus.

	Value in the following studies				
	Present work	[11]	[29]	[12]	Experiment
a_0 (Å)	4.340	4.326	4.365	4.361	4.360 [25]
B_0 (Mbar)	2.30	2.49	2.00	2.12	2.24–2.30 [26–28]
B_0'	6.1	3.2	7.2	3.7	

The energy band for β-SiC calculated with the LMTO method is presented in figure 1. The zero point of energy is chosen to be at the valence band maximum. It is found that the fundamental band gap of β-SiC is indirect from Γ_{15v} to X_{1c}. The gap width calculated is 1.50 eV, which is narrower than the experimental value (2.2 eV at room temperature) [25] by 32%. As is well known, band gaps and more generally optical interband transition energies are underestimated in the local-density-functional theory; the discrepancy between our calculated and experimental gap width is also due to this. Using the correction of Bechstedt and Del Sole [30] to the band gap, we find that the fundamental band gap is 2.47 eV. This value is close to the experimental result [25].

By comparing the band structure with those of diamond and silicon, it is found that the splitting of levels is due to the loss of the inversion symmetry with respect to the centre of the interatomic bond in the unit cell. As a consequence, the valence band of β-SiC is divided into two parts by lifting the degeneracy along the lines XW and WK. The results are in agreement with that given by a previous first-principles calculation using a linear combination of atomic orbitals [31] except for the width of the indirect band gap Γ_{15v}–X_{1c}.

The electronic structure with k-vectors along the line ΓX in the bulk Brillouin zone has been obtained by the angularly resolved normal emission valence band spectra [32]. The experimental data are indicated by full circles in figure 1. Our calculated results agree quantitatively with the experimental data along the line ΓX. No experimental data are available for other k-vectors.

The total DOS of the bulk β-SiC is plotted in figure 2. The DOS consists essentially of four peaks A, B, C_1 and C_2 at about 12.5 eV, 7.0 eV, 3.3 eV and 2.0 eV, respectively, below the valence band maximum. The x-ray emission spectra [31] have shown these four peaks at about 12.8 eV, 8.5 eV, 5.0 eV and 3.0 eV, respectively, below the valence band maximum. The first peak A consists of mainly the Si 3s and the C 2s orbitals,

the second peak B of the Si 3s, Si 3p and C 2p orbitals, and the third and fourth peaks C_1 and C_2 of the Si 3p and C 2p orbitals. Our results are in agreement with those observed by x-ray emission [33] and other calculations [31, 34].

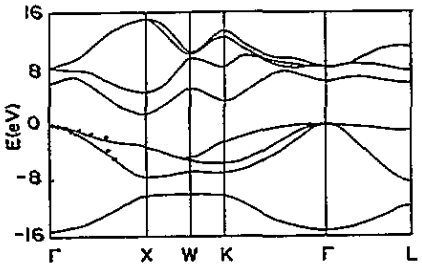

Figure 1. Band structures of bulk β-SiC: ●, from experiments [27].

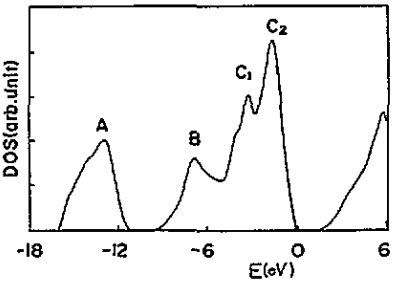

Figure 2. Total DOS for bulk β-SiC.

3.2. Strain effects on the band structure

During the growth of β-SiC on the silicon substrate or the growth of a diamond film on a β-SiC/Si substrate, as lattice mismatches exist between both β-SiC/Si and β-SiC/diamond, the strain effect is important. Compressions and expansions of the lattice constant parallel to the (100) surface up to 10% have been considered in the present work. An expansion of 10% corresponds to the β-SiC/Si system and a compression of 10% corresponds to the β-SiC/C system. The variation in the lattice constant along the [001] direction perpendicular to the surface is determined by the Keating [23] model. The parallel and perpendicular lattice constant obtained are listed in table 2.

Table 2. Parallel lattice constant $a_{\parallel}$ and perpendicular lattice constant $a_{\perp}$ obtained from the Keating model.

$a_{\parallel}$ (Å)	2.775	2.836	2.929	3.021	3.083	3.145	3.237	3.330	3.391
$a_{\perp}$ (Å)	4.977	4.864	4.686	4.495	4.360	4.217	3.988	3.738	3.558
$\sqrt{2}a_{\parallel}/a_0$	0.90	0.92	0.95	0.98	1.00	1.02	1.05	1.08	1.10

Owing to the strain along the (100) surface, the sublattice structures of both Si and C change from a face-centred cubic (FCC) structure to a body-centred tetragonal (BCT) structure. The FCC structure is described by the space group T_d, and the BCT structure is described by the space group D_{4h}. Since the symmetry in the BCT structure is lower than that in the FCC structure, the states will split when the structure changes from FCC into BCT.

For the BCT lattice, the triplet Γ_{15v} (p-like state) will split into a doublet Γ_5^+ ($p_{x,y}$-like state) and a singlet Γ_1^- (p_z-like state) at the special point Γ. At the special points X and L, the doubly degenerate band X_{5v} and L_{3v} will split into two singlets. The splitting energies, i.e. the difference between the energy levels of the doublet

and the singlet at the Γ point and the differences between the energy levels of the two singlets at the X and L points, are listed in table 3. For the Γ point, variations in the doublet and the singlet are plotted in figure 3, from which it can be seen that, when $a_{\parallel}$ expands, the energy of the doublet is higher than that of the singlet and, when $a_{\parallel}$ is compressed, the opposite behaviour exists, as is expected.

Table 3. Splitting energies of the Γ, X and L points due to strain along the (100) surface.

$\sqrt{2}a_{\parallel}/a_0$	0.90	0.92	0.95	0.98	1.00	1.02	1.05	1.08	1.10
ΔE_Γ (eV)	0.641	0.566	0.274	0.192	0.000	0.233	0.673	1.470	1.871
ΔE_L (eV)	1.570	1.276	0.816	0.332	0.000	0.442	1.329	2.572	3.684
ΔE_X (eV)	0.387	0.277	0.230	0.062	0.000	0.126	0.240	0.412	0.458

In [35], the energy splitting is expressed by the linear term $b_i|\epsilon_{xx} - \epsilon_{zz}|$, and $b_i/2$ is defined as the deformation potential. In the present calculation, splitting is expressed approximately by the following equation:

$$\Delta E_i = b_i|\epsilon_{xx} - \epsilon_{zz}| + c_i(\epsilon_{xx} - \epsilon_{zz})^2 \tag{1}$$

where ΔE_i indicates the splitting at the i (≡ Γ, L and X) point, and ϵ_{xx} and ϵ_{zz} are the components of the uniaxial strain tensor. If ϵ_{xx}, $\epsilon_{zz} \ll 1$, the squared term can be neglected and equation (1) is the same as that given in [34]. In the present work,

$$\epsilon_{xx} = \left(\sqrt{2}a_{\parallel} - a_0\right)/a_0 \tag{2}$$

$$\epsilon_{zz} = (a_{\perp} - a_0)/a_0. \tag{3}$$

We calculate the energy bands for the parallel lattice constant varying from −10% to 10%, and use the least-squares fitting to determine the coefficients b_i and c_i. The results show that, for the lattice constant expanding parallel to the (100) surface, the splitting ΔE_i can be given approximately by

$$\Delta E_\Gamma = 3.62|\epsilon_{xx} - \epsilon_{zz}| + 12.29(\epsilon_{xx} - \epsilon_{zz})^2 \tag{4}$$

$$\Delta E_L = 7.34|\epsilon_{xx} - \epsilon_{zz}| + 18.71(\epsilon_{xx} - \epsilon_{zz})^2 \tag{5}$$

$$\Delta E_X = 2.32|\epsilon_{xx} - \epsilon_{zz}| - 2.63(\epsilon_{xx} - \epsilon_{zz})^2 \tag{6}$$

while, for the lattice constant compressing parallel to the (100) surface, the splitting ΔE_i is

$$\Delta E_\Gamma = 3.23|\epsilon_{xx} - \epsilon_{zz}| - 4.09(\epsilon_{xx} - \epsilon_{zz})^2 \tag{7}$$

$$\Delta E_L = 6.51|\epsilon_{xx} - \epsilon_{zz}| + 0.02(\epsilon_{xx} - \epsilon_{zz})^2 \tag{8}$$

$$\Delta E_X = 1.22|\epsilon_{xx} - \epsilon_{zz}| + 1.61(\epsilon_{xx} - \epsilon_{zz})^2. \tag{9}$$

If the average value of the linear coefficients for the expansion and the compression is taken, one can obtain the deformation potential $d_{3i} = (\sqrt{3}/2)b_i$ defined in [15]. For the Γ and X points, the deformation potentials calculated in the present work are

2.97 eV and 1.54 eV, respectively, which are different from those given by Lambrecht *et al* [15]: 3.81 eV and 1.19 eV for Γ and X respectively. For the L point, we obtain 6.00 eV; no result available could be compared. For the conduction band, the deformation potentials in the present calculation are 6.61 eV and 14.40 eV for Γ and X points, respectively, which are close to those in [15] (7.72 eV and 12.29 eV, respectively). For the L point, the value is 4.38 eV. As mentioned in [15], the calculation of the deformation potential is not easy; we had hoped that some experimental results could be compared with the theoretical values. The discrepancy between our calculation and that in [15] might be due to the use of a different potential.

Variations in the fundamental band gap Γ_{15v}–X_{1c} and the other band gaps Γ_{15v}–Γ_{1c} and Γ_{15v}–L_{1c} with the expansion ($\sqrt{2}a_{\parallel}/a_0 > 1$) are shown in figure 4. When the lattice constant $a_{\parallel}$ is expanded and $a_{\perp}$ is compressed, the fundamental band gap Γ_{15v}–X_{1c} increases and the other band gaps Γ_{15v}–Γ_{1c} and Γ_{15v}–L_{1c} decrease. When $a_{\parallel}$ expands by 8% or more, the ratio of $a_{\perp}$ (3.738 Å) to $a_{\parallel}$ (3.330 Å) is equal to or smaller than 1.1 (under no strain, it is $\sqrt{2}$), i.e. the sublattices of Si and C become approximately body-centred cubic. Under this strain, the gap Γ_{15v}–Γ_{1c} is smaller than the gap Γ_{15v}–X_{1c}. Therefore, it might be possible that SiC crystals change from an indirect-gap semiconductor to a direct-gap semiconductor, when pressure is applied in the direction perpendicular to the (100) surface. This might make β-SiC a promising material for opto-electronic applications. It is hoped that some experimental data might be available in the near future for comparison with the results calculated above.

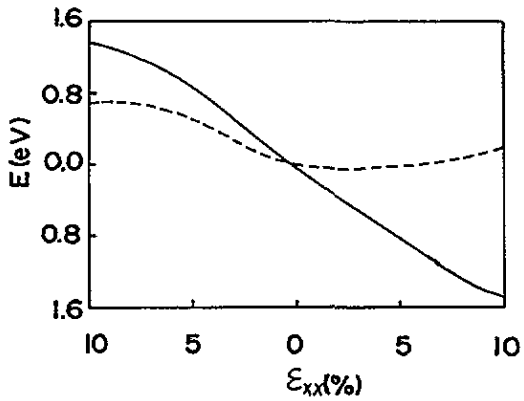

Figure 3. Variations in the singlet Γ_1^- (——) and doublet Γ_5^+ (– – –) with strain.

4. Summary

In summary, in the present paper, the fundamental electronic properties of β-SiC have been studied. The equilibrium lattice constant, bulk modulus and energy band structures obtained from the calculation are in reasonable agreement with the experimental results. The strain effects on band gaps of β-SiC parallel to the (100) surface are considered and it is found that the fundamental gap might become direct

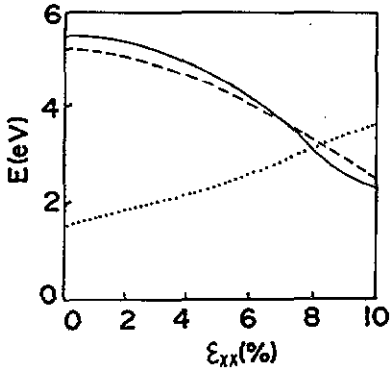

Figure 4. Strain effects on the band gaps: ——, Γ_{15v}–Γ_{1c} gap; – – –, Γ_{15v}–L_{1c} gap; ·····, Γ_{15v}–X_{1c} gap.

if $a_{\parallel}$ expands by 8% or more. The energy splitting and deformation potential induced by (100) strain are also discussed. Compared with the full-potential LMTO calculation, the values of deformation potential obtained by the present work are larger for the X point and smaller for the Γ point.

Acknowledgment

We are grateful to Yang Weidong for providing his Keating parameters of bulk β-SiC prior to publication.

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