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Electronic band structure in hexagonal close-packed Si polytypes

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Abstract. A full-potential band structure calculation, within the density functional theory and the local density approximation, has been performed for the hexagonal close-packed polytypes 2H, 4H and 6H of Si. Calculated lattice constants are found to be in good agreement with experimental values. Energy band gap, crystal-field splitting and spin-orbit splitting have been determined and, furthermore, the effective masses have been calculated for the lowest conduction band and the two uppermost valence bands. Throughout the paper, comparison is made with corresponding polytypes of SiC and with diamond cubic Si.

1. Introduction

The ability of semiconductor materials to crystallize in different polytypes, either by phase transition or at growth, can commercially be utilized in semiconductor device technology. For instance, polycrystalline Si films are important elements in integrated circuit devices. In these thin films, the twinning deformations cause formation of hexagonal structures [1, 2]. Furthermore, utilizing the techniques of chemical vapour deposition, whiskers with single-crystalline hexagonal structures can be grown [3]. Experimentally, the formations of hexagonal Si have been the subject of investigations [1–6], but theoretical information is still lacking about the basic properties of these polytypes.

In the present work, we have performed a relativistic band structure calculation of (diamond) hexagonal close-packed 2H-, 4H- and 6H-Si (space group D_{6h}^4); the polytype notation is according to Knippenberg [7]. The calculation was based on the density functional theory (DFT), applying the local density approximation (LDA) to describe the electron–electron interaction. Our geometric optimization of the total energy results in lattice constants which confirm available experimental values. From the calculated electronic band structures the energy band gaps, crystal-field splittings and spin-orbit splittings have been determined and the energy dispersions of the two uppermost valence bands are found to be very similar between the three polytypes. Moreover, we present the effective electron masses of the lowest conduction band and the effective hole masses of the two uppermost valence bands. The above mentioned fundamental quantities are important in investigations and analyses of the electrical and optical properties of these polytypes.

Comparisons with calculations of diamond (cubic) Si, with well known experimental values, are presented, indicating the validity of the calculations for the hexagonal polytypes. We also compare results to corresponding calculations of SiC in [8] and [9], in order

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to illustrate electronic properties of hexagonal structures. (SiC can easily be crystallized in several polytypes and represents therefore a material of great interest for studies of polytypism in semiconductors.)

2. Method

The band structure calculation was based on the LDA to the DFT [10], adopting the full-potential linearized augmented plane wave method [11]. A software program [12], based on the scalar-relativistic approximation, with the LDA exchange-correlation potential of the reparametrization by Perdew and Wang [13] of Ceperley-Alder data, was used. The DFT-LDA is well known to underestimate the energy band gap, but it is believed that most of this error is a constant shift in energy (i.e., independent of wave vector \mathbf{k}) and, thus, the curvatures of the valence and conduction bands should be less affected by this inaccurate treatment of the exchange-correlation effects.

In the self-consistent field calculation the basis set for the Hamiltonian matrix consisted in the atomic regions of spherical harmonics with azimuthal quantum number $l \leq 12$ and in the interstitial region of about 420, 850 and 1250 plane waves for the polytypes 2H, 4H and 6H, respectively. The \mathbf{k} -space matrices consisted of 32 \mathbf{k} -points per irreducible part of the Brillouin zone and the charge density was constructed using plane waves in the interstitial region and spherical harmonics with azimuthal quantum number $l \leq 6$ in the atomic regions. The total energy was calculated according to Weinert *et al* [14].

The spin-orbit interaction was not included in the self-consistent field loop, because of its minor influence on the total energy and on the charge distribution around the relatively light Si atoms. In calculation of the eigenvalues the interaction was treated within the spherical approximation, adopting the second variational method applied to the one-particle eigenfunctions from the scalar-relativistic calculation, whereas in determination of the symmetry of the eigenfunctions a fully relativistic calculation was performed. The notation of the representations used in this paper is from Koster *et al* [15].

3. Electronic band structures

The lattice constants were obtained by minimizing the total energy with respect to changes in the size of the unit cell, first by varying the parameters a and c with one and the same volume, whereupon the volume was varied keeping the ratio a/c fixed. The result, presented in table 1, shows good agreement between calculations and experiments. For example, Wentorf and Kasper [4] achieved, in high-pressure experiments, 2H-Si fragments with lattice constants $a = 3.80 \text{ \AA}$ and $c = 6.28 \text{ \AA}$ and these values together with lattice constants obtained by Eremenko and Nikitenko [5] ($a = 3.86 \text{ \AA}$ and $c = 6.31 \text{ \AA}$) agree with the present calculated values of 2H-Si: $a = 3.815 \text{ \AA}$ and $c = 6.283 \text{ \AA}$. Miyamoto and Hirata [3] have grown crystalline whiskers of 6H-Si with $a = 3.84 \text{ \AA}$ and $c = 18.59 \text{ \AA}$; values which are reproduced in our calculations: $a = 3.821 \text{ \AA}$ and $c = 18.773 \text{ \AA}$. Moreover, Hendriks *et al* [6] proposed the values $a = 3.84 \text{ \AA}$ and $2c/(ap) = 1.633$ (p is the number of bilayers: 2, 4 and 6 for 2H-, 4H- and 6H-Si, respectively) to explain their x-ray diffraction spectra of implanted and annealed silicon films. This was later confirmed by Cerva using high-resolution electron microscopy [2]. Present calculated values of the ratio are 1.647, 1.637 and 1.638. In order to ratify the validity of the calculated lattice constants, we also present in table 1 the calculated lattice constant of diamond Si which is within 0.4% of the experimental value.

Table 1. Lattice constants a and c obtained from a geometric optimization, which also provided the bulk modulus B . Since the present DFT–LDA calculation produces incorrect energy band gap E_g , a rough estimate of the band gap $E_g + \Delta_g$ has been made, where $\Delta_g = 0.73$ eV is the energy difference between the measured and calculated band gap of diamond Si. The valence band crystal-field splitting Δ_{cf} and spin–orbit splitting Δ_{so} are believed to be calculated more correctly. For comparison, calculated values of diamond (cubic) Si are also presented.

	2H-Si	4H-Si	6H-Si	Diamond Si
a, c (Å)	3.815, 6.283	3.821, 12.510	3.821, 18.773	5.451
a, c (Å) exp. ^a	3.80, 6.28	3.84, 12.54	3.84, 18.59	5.431
B (Mbar)	0.99	0.93	0.95	0.95
B (Mbar) exp. ^a				0.99
E_g (eV)	0.26	0.40	0.43	0.44
$E_g + \Delta_g$ (eV)	0.99	1.13	1.16	1.17
E_g (eV) exp. ^a				1.17
Δ_{cf} (meV)	300	144	102	
Δ_{so} (meV)	33.7	30.1	28.0	50.1
Δ_{so} (meV) exp. ^a				44.1

^a [4], [6], [3] and [16] for 2H-, 4H-, 6H-Si and diamond Si, respectively.

With optimized lattice constants, the total energy per atom was found to be similar for the polytypes. The differences in energy per atom between diamond Si and the three hexagonal polytypes were calculated to be 23, 32 and 34 meV for 2H-, 4H- and 6H-Si, respectively. This confirms a reported calculated value of 16 meV for 2H-Si [17], where the authors used an ideal axial ratio of the lattice constants: $2c/(ap) = \sqrt{8/3} \approx 1.633$. Also the bulk moduli of the cubic and hexagonal polytypes are comparable, about 0.93–0.99 Mbar (see table 1).

Having established the geometric structure for the polytypes, the electronic band structures were calculated along the symmetry directions. The Brillouin zone and the labelling of the symmetry points can be found in [9]. Resulting band structures are shown in figure 1 and one can observe that there are evident similarities in the band structures between the three polytypes, both in the valence and in the conduction bands, especially between 4H- and 6H-Si. (This is true also for SiC.) One significant difference between 2H-Si and the other two hexagonal polytypes is that the location of the lowest conduction band minimum is at the M point for 2H-Si (with M_5^+ representation), whereas both 4H- and 6H-Si have their minima along the Γ M line (both with Σ_5 representations). Thus, 2H-Si has three and 4H- and 6H-Si have six equivalent minima.

The utilized DFT–LDA method produces an incorrect band gap value of diamond Si; the error is $\Delta_g = 0.73$ eV (see table 1), and one expects that also the calculated band gaps of the hexagonal polytypes are underestimated. Nevertheless, in most semiconducting materials (like diamond Si as well as the cubic and hexagonal polytypes of SiC) the calculated location of the minima agrees with experiments and it is believed that the major part of the error in the band gap is a constant energy shift, which does not influence the location of the minimum or the curvature of the bands. Moreover, in SiC the errors in calculated band gaps are very similar between the cubic and the hexagonal polytypes; the differences between measured and calculated band gaps in SiC are 1.10, 1.22, 1.12 and 1.13 eV for the polytypes 3C, 2H, 4H and 6H [9]. (This is consistent with the fact that the SiC polytypes have comparable dielectric constants and charge densities). Therefore, a preliminary estimate of the band gaps should be to use the energy shift of diamond Si also for the hexagonal polytypes. The resulting band gap values then become $E_g + \Delta_g = 0.99, 1.13$ and 1.16 eV for 2H-, 4H- and

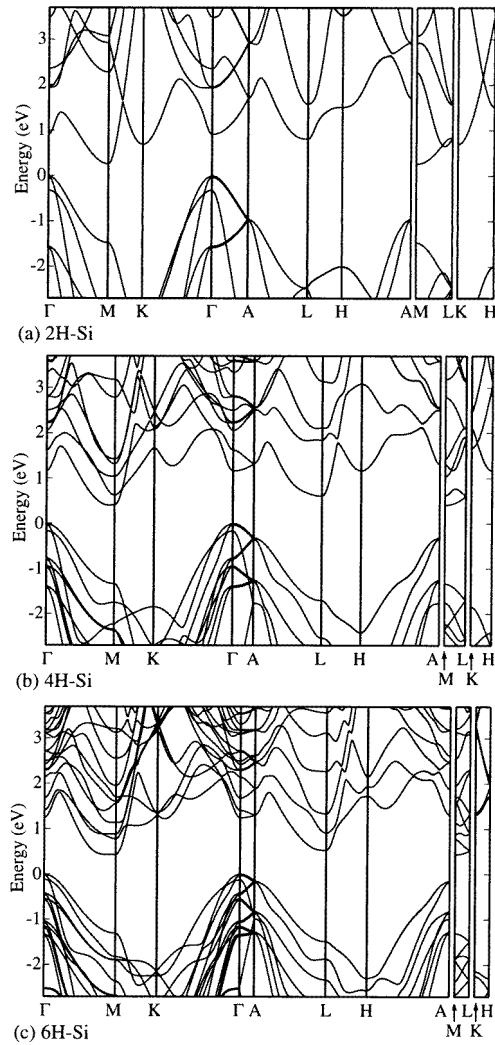


Figure 1. Energy bands for (a) 2H-Si, (b) 4H-Si and (c) 6H-Si, where the energies are referenced to the top of the valence band.

6H-Si, respectively. In contrast to the SiC polytypes, 2H-Si has the smallest and diamond Si has the largest band gap.

The crystal-field splitting Δ_{cf} , which is obtained as the energy difference between the two uppermost valence bands (Γ_5^+ representations) and the third uppermost valence band (Γ_1^+ representation) excluding the spin-orbit interaction, decreases as the number of bilayers in the unit cell is increased; the values of Δ_{cf} are 300, 144 and 102 meV for 2H-, 4H- and 6H-Si. This reduction of the crystal-field splitting as a function of the size of the unit cell is in accordance with results of the hexagonal SiC polytypes and moreover, the ratios of the splitting energies between the polytypes are very similar in Si and SiC; for Si $\Delta_{cf}^{2H-Si} / \Delta_{cf}^{4H-Si} = 2.1$ and $\Delta_{cf}^{4H-Si} / \Delta_{cf}^{6H-Si} = 1.4$ and the corresponding values for SiC are 2.2 and 1.4. There are also similarities between Si and SiC in the effects of the spin-

orbit coupling. Including spin-orbit interaction, the two uppermost valence bands are split into an uppermost band with Γ_9^+ representation and a second uppermost band with Γ_7^+ representation. The third uppermost valence band is essentially unaffected by the spin-orbit interaction, now having Γ_7^+ representation. Furthermore, in both Si and SiC crystals, the spin-orbit splitting energies Δ_{so} are similar for all three hexagonal polytypes (about 30 meV for Si and about 8.5 meV for SiC) and the ratios $\Delta_{so}^{hexagonal} / \Delta_{so}^{diamond}$ are all between 0.56 and 0.67. Hopfield [18] has derived that this ratio should be $\leq 2/3 \approx 0.67$; the equals sign holds for infinitely large crystal-field splitting and one can observe that $\Delta_{so}^{2H-Si} / \Delta_{so}^{diamond-Si} = 0.67$, noting that 2H-Si has the largest crystal-field splitting.

4. Effective masses

The employed DFT-LDA calculation has been demonstrated to accurately reproduce the curvature of the lowest conduction band minimum as well as the valence band maximum of diamond Si [8]. In 2H-Si, the lowest conduction band minimum was found to be parabolic in the three principal directions, but in both 4H- and 6H-Si, the lowest conduction band was found to have a very non-parabolic, double-well-like minimum, just as in 6H-SiC [9]. One distinct difference is that in 6H-SiC the minimum is along the ML line, whereas in 4H- and 6H-Si the minima are along the Γ M line. The double-well structures (also called camel's back structures) can be parametrized with good accuracy according to the energy dispersion of Lawaetz [19]:

$$E_{c1}(k_x) = E_{c1}(\mathbf{k}_M) + \frac{\Delta}{2} + A^2 k_x^2 - \sqrt{\frac{\Delta^2}{4} + P^2 k_x^2} \quad (1)$$

where \mathbf{k}_M is the wave vector at the M point, k_x is the wave vector in the corresponding Γ M direction and Δ , A and P are fitting parameters. (Originally, Δ described the energy difference between the two lowest bands, but here it is employed as a fitting parameter.) In the directions parallel to MK and ML, however, the minima of 4H- and 6H-Si were found to be essentially parabolic. From the second derivative of the energy dispersion with respect to the wave vector, we determined the effective electron masses. The resulting fitting parameters of the camel's back structures and the values of the effective electron masses are presented in table 2. The noticeable large mass $m_{M\Gamma} = 2.60 m_0$ in 6H-Si is a consequence of the very flat shape of its camel's back structure. The minimum of 6H-Si is located 87% out from Γ towards the M point and the energy difference between the minimum and the energy at the M point is only 4.6 meV. 4H-Si has a more pronounced camel's back structure; the minimum is located 92% from Γ towards M and the corresponding energy difference is 6.0 meV, thereby resulting in a smaller value of $m_{M\Gamma} = 0.98 m_0$.

Table 2. Camel's back structure parameters Δ , A and P (see equation (1)) and the effective electron masses for the lowest conduction band minimum. The energy difference between the minimum and the energy at the M point is 6.0 meV for 4H-Si and 4.5 meV for 6H-Si. The subscripts on the masses indicate which directions in the Brillouin zone the mass components refer to.

	Δ (eV)	A (\AA (eV) $^{1/2}$)	P (\AA eV)	$m_{M\Gamma}$ (m_0)	$m_{\parallel MK}$ (m_0)	$m_{\parallel ML}$ (m_0)
2H-Si				1.05	0.11	1.09
4H-Si	0.160	2.690	1.303	0.98	0.12	1.37
6H-Si	2.257	2.984	4.690	2.60	0.12	1.55

Parametrization of the two highest valence bands at the Γ point can be carried out utilizing the following expression, which is valid for wurtzite structures and if the crystal-field splitting is sufficiently large [9]:

$$E_{v1,v2}(\mathbf{k}) = -\frac{\Delta_{so}}{2} + \frac{\hbar^2}{2m_0} \left(ck_{\parallel}^2 + dk_{\perp}^2 \pm \sqrt{\left(\frac{m_0\Delta_{so}}{\hbar^2}\right)^2 + (d''k_{\perp}^2)^2} \right) \quad (2)$$

from which the longitudinal (\parallel) and transverse (\perp) effective hole masses for the two highest bands are obtained as $-m_0/c$ and $-m_0/d$, respectively. (The two uppermost valence bands have equal effective hole masses within this approximation.) The fitting parameters and the effective hole masses for the three polytypes are presented in table 3 and the parameters demonstrate that the polytypes have similar valence band curvatures around the Γ point.

Table 3. Valence band parameters c , d and d'' and transverse (\perp) and longitudinal (\parallel) effective hole masses for the two uppermost valence bands (see equation (2)).

	c	d	d''	m_{\perp} (m_0)	m_{\parallel} (m_0)
2H-Si	-1.83	-4.70	2.94	0.21	0.55
4H-Si	-1.72	-4.52	3.25	0.22	0.58
6H-Si	-1.78	-4.35	3.20	0.23	0.56

5. Summary

A DFT-LDA band structure calculation has been performed for 2H-, 4H- and 6H-Si, using the exchange-correlation potential of Perdew and Wang; the potential accurately describes the band curvatures in diamond cubic Si. From a geometric optimization the lattice constants were determined to be $a = 3.815$, 3.821 and 3.821 Å and $c = 6.283$, 12.510 and 18.773 Å for 2H-, 4H- and 6H-Si, respectively. These calculated values confirm available measured lattice constants.

By comparing the electronic band structure of the three polytypes, one sees evident similarities, especially in the valence band structures. There are also strong correspondences in the valence bands between hexagonal polytypes of Si and of SiC, just as different face-centred cubic semiconducting materials show similarities in their valence band structures. All three Si polytypes have indirect band gaps; in 2H-Si the minimum is located at the M point and in 4H- and 6H-Si the minima are along the Σ ($= \Gamma M$) line. The estimated values of the band gap are 0.99, 1.13 and 1.16 eV for 2H-, 4H- and 6H-Si, respectively.

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