# High-precision determination of atomic positions in crystals: The case of $6H$- and $4H$-SiC

A. Bauer, J. Kräußlich, L. Dressler, P. Kuschnerus, J. Wolf, and K. Goetz
*Institut für Optik und Quantenelektronik, Friedrich-Schiller-Universität Max-Wien-Platz 1, 07743 Jena, Germany*

P. Käckell, J. Furthmüller, and F. Bechstedt
*Institut für Festkörpertheorie und Theoretische Optik, Friedrich-Schiller-Universität, Max-Wien-Platz 1, 07743 Jena, Germany*

(Received 12 May 1997)

The atomic structures of the hexagonal $6H$ and $4H$ polytypes of SiC are determined by means of high-precision x-ray-diffraction measurements and first-principles calculations. The cell-internal relaxations which conform with the space-group symmetry are fully taken into account. Since the tetrahedra are distorted along the [0001] direction, an analysis of ''quasiforbidden'' reflections is possible. The measured and calculated data are compared and discussed in detail especially for $6H$-SiC. We find an almost perfect agreement for the ratio $c/a$ of the lattice constants. A comparison of the measured structure factors with those for calculated geometries is given. The atomic relaxations within the unit cell are derived. [S0163-1829(98)03405-5]

The structure of two of the most common SiC polytypes, $4H$- and $6H$-SiC, differs by the stacking of the Si-C bilayers in the [0001] direction.[1] The stacking arrangement for $6H$-SiC is shown in Fig. 1. Both polytypes belong to the hexagonal crystal system and the atomic positions obey operations of the space group $C_{6v}^4(P6_3mc)$.[2]

The stacking sequences have remarkable consequences for the atomic structure of the polytypes. In the plane perpendicular to the $c$ axis [0001] the positions are constrained to the trigonal axis. However, perpendicular to that plane they are allowed to move freely. The bonding tetrahedra are pressed or stretched. Taking into account the equivalence of the atoms in the lower and upper half of the unit cell (cf. Fig. 1), we use the relative displacements $\delta(i)$ of the Si atoms and $\varepsilon(i)$ of the C atoms [$i=1,2,\ldots,n/2$, ($n$ being the number of bilayers per unit cell)] as the structural degrees of freedom, in addition to the two lattice constants $a$ and $c$, and set $\delta(1)=0$ without loss of generality.[3]

It has been shown[3,4] that these atomic displacements related to a deformation of the ideal tetrahedra may stabilize one of the short-period hexagonal polytypes. The relaxation energies per atom are of order 1 meV and approach the differences in the cohesive energies of two polytypes. There are also indications for the importance of the local strain due to these displacements during the growth of a certain polytype by means of homo- and heteroepitaxy.[5] However, the precise experimental determination of the atomic displacements from ideal positions is much more difficult than the measurement of the lattice constants themselves. Only one trial for $6H$-SiC by means of x-ray diffraction[6] was published three decades ago. A complete theoretical prediction of the internal degrees of freedom by means of a first-principles method has been done in one case.[3] In Ref. 4 the internal structure of $4H$ and $6H$ has been only optimized until the same stress occurs, as in the cubic polytype taken at the experimental lattice constant. Usually the minimization of the total energy has been limited to the lattice constants only.[7,8]

In this paper, we report highly precise x-ray-diffraction measurements of the lattice constants and of the atomic displacements. The results are compared with values from *ab initio* calculations, where all degrees of freedom, i.e., the independent variation of the lattice constants $c$ and $a$ and three ($4H$) or five ($6H$) internal degrees of freedom are taken into account. In the case of $6H$ the measured and calculated values are discussed in detail.

The calculational method is described in detail in Ref. 3. It is based on density-functional theory (DFT) within the local-density approximation (LDA). The exchange-correlation energy is described in the form parametrized by Perdew and Zunger.[9] The wave functions are expanded in plane waves. Normconserving, fully separable pseudopoten-

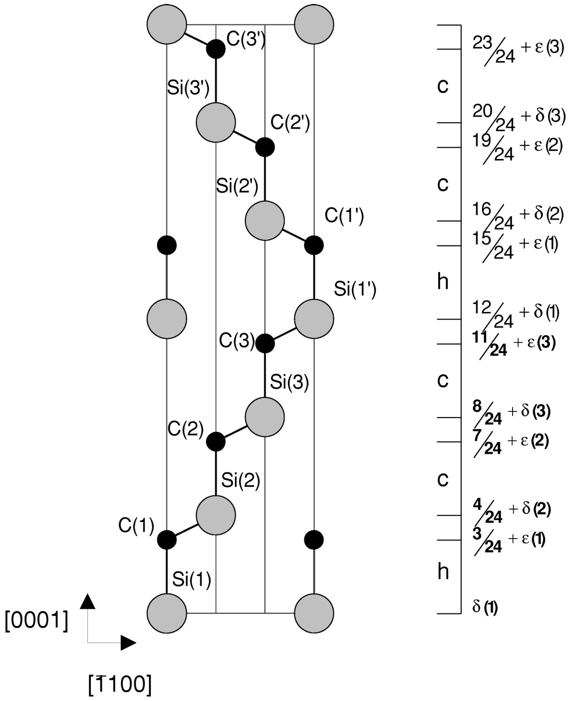

FIG. 1. The atomic structure of $6H$-SiC. The cubic ($c$) or hexagonal ($h$) character of the Si-C bilayers in the [0001] direction is identified according to the twisted ($h$) or nontwisted ($c$) bonds. The atomic coordinates in $c$ direction are given in terms of the basis vector.

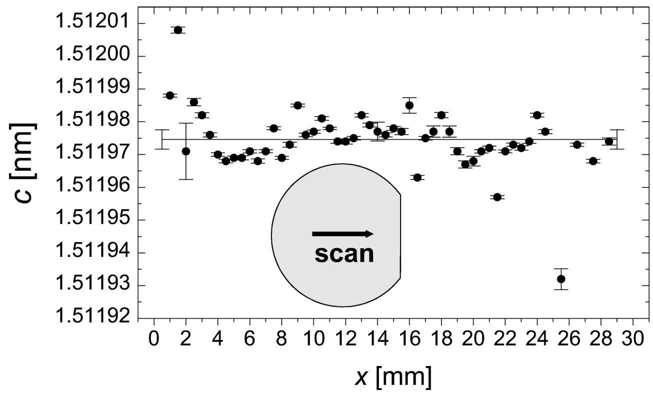

FIG. 2. The lattice parameter $c$ of $6H$-SiC linearly scanned over a wafer. The x-ray diffraction uses the symmetric 00.18 reflection and Cu $K\alpha_1$ radiation.

TABLE I. Lattice parameters of two SiC polytypes from x-ray diffraction measurements (Expt.) and calculations (Calc.) with and without inclusion of the cell-internal relaxation.

| Polytype | | $a$ (nm) | $c/n$ (nm) | $c/(na)$ |
|---|---|---|---|---|
| $6H$ | Expt. | 0.308129 | 0.251996 | 0.817812 |
| | | ±0.000004 | ±0.000001 | ±0.000012 |
| | Calc. (with) | 0.3033 | 0.2480 | 0.8177 |
| | Calc. (without) | 0.3031 | 0.2482 | 0.8183 |
| $4H$ | Expt. | 0.308051 | 0.252120 | 0.818438 |
| | | ±0.000006 | ±0.000001 | ±0.000017 |
| | Calc. (with) | 0.3032 | 0.2482 | 0.8185 |
| | Calc. (without) | 0.3027 | 0.2490 | 0.8226 |

tials of the Bachelet-Hamann-Schlüter (BHS) type[10] are implemented to describe the electron-ion interaction. The carbon potential has been modified to allow a cutoff energy of 34 Ry for the plane-wave basis. The atomic displacements are optimized using a steepest-descent method, the electronic energy is minimized with a Car-Parrinello-like approach. Explicitly, the computer code FHI93CP (Ref. 11) is used. The energy minimization with respect to the ionic degrees of freedom is finished when the Hellmann-Feynman forces are smaller than 0.005 eV/Å. This corresponds to an uncertainty of about 0.002 Å in the atomic positions for a given calculational scheme. The Brillouin-zone integration is replaced by a summation over six special Chadi-Cohen **k** points. In order to test the influence of details of the computation the condition of the norm conservation is dropped and ultrasoft Vanderbilt (V) pseudopotentials[12] are used to describe the interaction of electrons with carbon cores. In this case the plane-wave expansion is restricted by a cutoff of 19 Ry. Explicitly this procedure is implemented in the ''Vienna Ab Initio Simulation Package.''[13]

Experimental studies are carried out at SiC wafers. The lattice constants $c$ and $a$ are determined by means of the x-ray diffraction bond method[14] using Cu $K\alpha_1$ radiation. It allows an accuracy better than $10^{-6}$ for the relative changes in the lattice constants.[15] However, the commercially available SiC crystal wafers are not fully homogeneous over the sample surface (cf. Fig. 2). In most regions, with an extent of several mm, the measured fluctuations are smaller than $5\times10^{-6}$ with respect to the average value.

Experimental and theoretical lattice constants are compared in Table I. The absolute values of the calculated lattice constants are somewhat too small compared to the measured values. The reason is mainly due to the incomplete treatment of exchange correlation of the electrons within the LDA. Other parametrizations of the exchange-correlation interaction give better agreement with the measurements.[7] Nevertheless, the tendency for a better agreement after inclusion of the cell-internal parameters $\delta(i)$ and $\varepsilon(i)$ clearly shows the importance of the atomic relaxations. On the other hand, both in theory and experiment $a$ decreases, whereas $c/n$ increases with rising hexagonality. The ratio $c/(na)$ deviates from its ideal value in $3C$-SiC $c/(na)=\sqrt{2/3}$ with increasing hexagonality, indicating a stronger distortion of the bonding tetrahedra. For $c/(na)$, the agreement between experiment and theory is almost perfect when including the internal relaxations in the calculation. The deviations are smaller than about 0.01%.

The minimization of the system energy with respect to the ionic degrees of freedom ends automatically with the coordinates of the atoms in the unit cell. The relative atomic displacements $\varepsilon(i)$ and $\delta(i)$ $(i=1,\ldots,n/2)$ calculated with the two different pseudopotentials for $6H$- and $4H$-SiC are listed in Table II. To derive these quantities experimentally, the structure factors measured for various x-ray-diffraction reflections have to be analyzed in detail. The atomic coordinates can be derived by a least-squares fit assuming a certain model geometry. Since the relative deviations from the ideal positions are extremely small, the sensitivity of the method has to be improved. For that purpose the so-called ''quasiforbidden'' reflections are analyzed, analogous to Refs. 16,17. For those reflections, the structure factor $F(hkl)$, where $(hkl)$ are the Miller indices of a corresponding lattice plane, is different from zero only for nonvanishing atomic relaxations. For $6H$, the space group requires the relations $h-k=3p$, $l$ even but $l\neq 6q$ and $h-k\neq 3p$, $l=6q$, respectively, with integers $p$ and $q$.

The absolute value of the structure factors $F(hkl)$ of ''quasiforbidden'' reflections is a measure of the atomic relaxations. We study eight ''quasiforbidden'' reflections $(00.l)$ with even $l$ but $l\neq 6q$. The absolute values of the structure factors $|F(hkl)|$ are listed in Table III for $6H$-SiC and compared with other data. The structure factors are derived from the integrated measured intensities. In the case of the experimental data of Gomez de Mesquita[6] we have calculated the structure factors from his refinement model obtained by Fourier methods. The theoretical factors are de-

TABLE II. Relative atomic displacements parallel to the $c$ axis from the ideal positions calculated by means of two different kinds of pseudopotentials for $6H$-SiC (in units of $10^{-4}$).

| Polytype | Pseudopotential | $\varepsilon(1)$ | $\varepsilon(2)$ | $\varepsilon(3)$ | $\delta(1)$ | $\delta(2)$ | $\delta(3)$ |
|---|---|---|---|---|---|---|---|
| $6H$ | BHS | 3.7 | 0.6 | −0.9 | 0.0 | 0.3 | −1.2 |
| | V | 5.1 | 1.5 | −1.3 | 0.0 | 1.4 | −0.9 |
| $4H$ | BHS | 4.8 | −2.3 | | 0.0 | −2.1 | |
| | V | 6.0 | −0.8 | | 0.0 | −0.2 | |

TABLE III. Absolute values of measured and calculated structure factors.

| Reflection | X-ray diffraction | | Calculation | | |
|---|---|---|---|---|---|
| | This work | Gomez de Mesquita (Ref. 6) | This work (BHS) | This work (V) | Cheng *et al.* (Ref. 4) |
| 00.2 | 0.107 ± 0.002 | 0.0073 | 0.097 | 0.144 | 0.112 |
| 00.4 | 0.088 ± 0.006 | 0.098 | 0.076 | 0.142 | 0.090 |
| 00.8 | 0.234 ± 0.006 | 0.176 | 0.211 | 0.275 | 0.241 |
| 00.10 | 0.98 ± 0.002 | 0.166 | 0.085 | 0.078 | 0.095 |
| 00.14 | 0.117 ± 0.003 | 0.195 | 0.100 | 0.087 | 0.113 |
| 00.20 | 0.151 ± 0.002 | 0.216 | 0.140 | 0.269 | 0.170 |
| 00.22 | 0.381 ± 0.001 | 0.257 | 0.305 | 0.455 | 0.354 |
| 00.26 | 0.315 ± 0.028 | 0.244 | 0.305 | 0.456 | 0.353 |
| $R$ | | 0.04861 | 0.00205 | 0.04683 | 0.00206 |

duced by replacing the atomic coordinates by those from the *ab initio* calculations using the atomic scattering factors.[18] The experimental values may be influenced by Umweganregung (double diffraction) and extinction effects. Perturbations by Umweganregung during the measurements of the ‘‘quasiforbidden’’ reflections are avoided by measuring at azimuthal angles, where there are no umweg reflections.[19] For the ‘‘quasiforbidden’’ reflections, a correction of extinction is not necessary, since the length of extinction is much larger than the absorption depth.[20] Consequently, the kinematic approximation can be used instead of the strict dynamic approach, and influences of the real structure can be neglected. The ‘‘quasiforbidden’’ reflections are very sensitive with respect to extremely small variations in the structure. For the atomic coordinates from our *ab initio* calculation with BHS potentials, as well as the corresponding differences derived by Cheng *et al.*,[4] we observe almost the same structure factors. There are small deviations in the case of the displacements obtained with V potentials. However, estimating the degree of agreement one has to consider the smallness of the studied quantities and the different numerical approaches used together with the soft BHS and V pseudopotentials.

The comparison of the measured structure factors and those calculated for the atomic coordinates from first-principles calculations in Table III shows excellent agreement. Using the sum of the squared differences of the factors as the quality factor $R$, the relative atomic displacements from the ‘‘ideal’’ positions, derived from our total-energy minimization and the optimization of Cheng *et al.* cannot be distinguished from each other on the basis of the measured structure factors at the present time. Only in the case of the coordinates derived by means of non-normconserving Vanderbilt pseudopotentials are the discrepancies larger. However, the $R$ factor is even slightly smaller than that estimated for the comparison with the results of former measurements.[6] The relative changes approach the accuracy of the computational methods and depend on such experimental conditions as the avoidance of Umweganregung. We mention that the sensitivity to the cell-internal relaxations only holds for the ‘‘quasiforbidden’’ reflections. For the strong reflections we only find deviations smaller than 0.1% in the structure factors.

In principle, the structure factor measured for the ‘‘quasiforbidden’’ reflections allows us to extract information about the atomic coordinates. In linear approximation it holds

$$\begin{aligned} F(00l)=&\,a_1(l)[\delta(2)-\delta(3)]+a_2(l)\{[\delta(2)-\delta(1)]\\ &+[\delta(3)-\delta(1)]\}+b_1(l)[\varepsilon(2)-\varepsilon(3)]\\ &+b_2(l)\{[\varepsilon(2)-\varepsilon(1)]+[\varepsilon(3)-\varepsilon(1)]\}, \end{aligned} \tag{1}$$

where $a_i(l)$ and $b_i(l)$ are functions of $l$ and the atomic scattering factors for silicon and carbon, respectively. Unfortunately, Eq. (1) contains the relative atomic displacements $\varepsilon(j)$ and $\delta(j)$ only in four linear independent combinations. A complete determination of the atomic displacements is not possible, although the structure factors including the phases are known. For that reason we reduce the number of the considered parameters and restrict ourselves to the discussion of the relative changes

$$\frac{\Delta d_{\mathrm{Si}}(j)}{d_0}=\frac{d_{\mathrm{Si}}(j)-c/6}{c/6}=6[\delta(j+1)-\delta(j)], \tag{2}$$

TABLE IV. Changes of the thickness of Si-C bilayers and of Si-C bond lengths in the $c$ direction (in %).

| Fluctuation | X-ray diffraction | Calculation | |
|---|---|---|---|
| | | (BHS) | (V) |
| $\frac{\Delta d_{\mathrm{Si}}(1)}{d_0}$ | 0.021 | 0.018 | 0.089 |
| $\frac{\Delta d_{\mathrm{Si}}(2)}{d_0}$ | −0.102 | −0.090 | −0.138 |
| $\frac{\Delta d_{\mathrm{Si}}(3)}{d_0}$ | 0.081 | 0.072 | 0.036 |
| $\frac{\Delta L(12)}{L_0}$ | 0.27 | 0.27 | 0.37 |
| $\frac{\Delta L(13)}{L_0}$ | 0.27 | 0.27 | 0.42 |
| $\frac{\Delta L(23)}{L_0}$ | 0.00 | 0.00 | 0.05 |

$$\frac{\Delta d_C(j)}{d_0}=\frac{d_C(j)-c/6}{c/6}=6[\varepsilon(j+1)-\varepsilon(j)],$$

of the bilayer thickness measured between two Si or C atoms (cf. Fig. 1). The accurate knowledge of the lattice constant $c$ makes it possible to determine the Si-C bilayer thickness absolutely. Since, however, the absolute values for $c$ are not very well known from the *ab initio* calculations we use the relative fluctuations for a comparison. The number of independent parameters is reduced to three by the assumption $L(2)=L(3)$ in agreement with theoretical predictions.[3,4] This relation indicates that the Si-C bond lengths in the cubic layers are equal and differ only from those in the hexagonal layers (cf. Fig. 1). Including this assumption, the linear combinations of the $\delta$ and $\varepsilon$ in Eq. (1) can be determined unambigously apart from the sign. By comparison with the computed values in Table II, the structure obtained with BHS potentials has to be favored.

The results are represented in Table IV for the fluctuations in the bilayer thickness measured between two Si atomic layers and fluctuations in the Si-C bond length parallel to the $c$ axis. They are compared with calculated values. In addition we consider relative deviations of the Si-C bond lengths parallel to the $c$ axis (cf. Fig. 1),

$$\frac{\Delta L(ij)}{L_0}=\frac{L(i)-L(j)}{L_0}=8\{[\varepsilon(i)-\varepsilon(j)]-[\delta(i)-\delta(j)]\} \tag{3}$$

favors the ‘‘ideal’’ value $L_0=c/8$.

There are only very small variations in the calculated $\Delta L(23)/L_0$, indicating that the assumption of equal parallel bonds in the cubic bilayers is almost fulfilled. Excellent agreement is observed for the other fluctuations in bond length and bilayer spacing. The good agreement of the relative quantities in Tables III and IV allows us to trust the values computed with norm-conserving pseudopotentials for the absolute relative displacements in Table II. Consequently, we finish with a consistent picture of the positions of the 12 atoms in the unit cell of 6$H$-SiC.

In conclusion, we have determined the atomic coordinates in 6$H$-SiC by a combination of precise x-ray-diffraction measurements and *ab initio* total-energy calculations. The lattice constants of 6$H$- and 4$H$-SiC may be measured with an extremely high accuracy. The calculated values exhibit the typical failure of the used (DFT-LDA) theory. However, excellent agreement is found for the ratio of the hexagonal lattice constants.

When all Si and C atoms in the unit cell are assumed to be chemically equivalent, their atomic positions are given by the two lattice constants. In real crystals the atoms are slightly displaced from the ideal positions parallel to the $c$ axis. Therefore, the structure factors of the corresponding ‘‘quasiforbidden’’ reflections are nonzero and represent a direct measure of the displacements. Unfortunately, only differences of relative atomic displacements are extracted. However, such displacements have been derived from the total-energy minimization. Structure factors and bilayer or bond-length fluctuations have been compared with experimental findings. We conclude excellent predictions from the first-principles calculations. This holds especially for the significant displacements in the hexagonal bilayers, which give important contributions to the elongation of the bonding tetrahedron parallel to the $c$ axis.

This work was financially supported by the Deutsche Forschungsgemeinschaft (SFB 196, Projects No. A8 and C1).

---

[1] A.R. Verma and P. Krishna, *Polymorphism and Polytypism in Crystals* (Wiley, New York, 1966).

[2] R.W.G. Wyckhoff, *Crystal Structures* (Interscience, New York, 1964), Vol. 1.

[3] P. Käckell, B. Wenzien, and F. Bechstedt, Phys. Rev. B **50**, 17 037 (1994).

[4] C. Cheng, V. Heine, and R.J. Needs, J. Phys.: Condens. Matter **2**, 5115 (1990).

[5] G.L. Vignoles, J. Cryst. Growth **118**, 430 (1992).

[6] A.H. Gomes des Mesquita, Acta Crystallogr. **23**, 610 (1967).

[7] C.H. Park, B.-H. Cheong, K.-H. Lee, and K.J. Chang, Phys. Rev. B **49**, 4485 (1994).

[8] K. Karch, G. Wellenhofer, P. Pavone, U. Rössler, and D. Strauch, in *Proceedings of the 22nd International Conference on the Physics of Semiconductors*, edited by D. Lockwood (World Scientific, Singapore, 1995), p. 401.

[9] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[10] G.B. Bachelet, D.R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[11] R. Stumpf and M. Scheffler, Comput. Phys. Commun. **26**, 447 (1994).

[12] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[13] G. Kresse and J. Hafner, Phys. Rev. B **49**, 14 251 (1994).

[14] W.L. Bond, Acta Crystallogr. **13**, 814 (1960).

[15] J. Härtwig and S. Grosswig, Phys. Status Solidi A **115**, 369 (1989).

[16] D. Mills and B.W. Batterman, Phys. Rev. B **22**, 2887 (1980).

[17] E. Rossmanith, G. Ulrich, G. Kumpat, and R. Kurtz, HASYLAB Annual report 1993, p. 543 (unpublished).

[18] *International Tables for Crystallography* (Kluwer Academic, Boston, 1992), Vol. C.

[19] L. Dressler, K. Goetz, and J. Kräusslich, Phys. Status Solidi B **200**, 377 (1997).

[20] A.M. Afanas'ev and I.P. Perstnev, Acta Crystallogr. Sect. A Gen. Crystallogr. **25**, 520 (1969).