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Published in:
Physical Review B

DOI:
10.1103/PhysRevB.54.2512

Published: 15/07/1996

Please cite the original version:
Evaluation of some basic positron-related characteristics of SiC

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(Received 26 January 1996; revised manuscript received 5 April 1996)

First-principles electronic structure and positron-state calculations for perfect and defected 3C- and 6H-SiC polytypes of SiC have been performed. Monovacancies and divacancies have been treated; the influence of lattice position and nitrogen impurities have been considered in the former case. Positron affinities and binding energies have been calculated; trends are discussed, and the results compared with recent atomic superposition method calculations. Experimental determination of the electron and positron work functions of the same 6H-SiC allows an assessment of the accuracy of the present first-principles calculations, and to suggest further improvements. [S0163-1829(96)01828-0]

I. INTRODUCTION

The current interest in silicon carbide (SiC) as a semiconductor for device technology is based on its outstanding chemical and physical properties. However, the identification of the chemical nature or atomic and electronic structures of defects in SiC, which exists in many different crystallographic structures (polytypes), is in its infancy.1,2

Positron annihilation spectroscopy (PAS) is now a well-established tool for the study of electronic and defect properties of solids.3–5 Radiation damage caused by ion implantation in 6H-SiC has recently been studied by monoelectronic positron beam techniques in combination with theoretical calculations.6 It has been shown that the main defect produced by Ge+ implantation is the divacancy. Ge+ ions were chosen for implantation because (a) Si or C ions would disturb stoichiometry, (b) the available Si ion beam is not free of N2 admixture (N would act as a dopant impurity), and (c) Ge+ ions have the same valency as Si and C and therefore do not disturb the electrical behavior of the target. The atomic superposition method used in Ref. 6 allowed the evaluation of positron lifetimes in different polytypes of bulk SiC, in carbon and silicon monovacancies, and in vacancy agglomerates consisting of up to four Si-C divacancies. The lifetimes calculated in this way correspond to neutral, unrelaxed defects; however, vacancies might be in different charge states, and this would affect the corresponding positron lifetime through modified electrostatic potentials and changes in the atomic relaxation around the vacancy.7–9 Moreover, the degree of relaxation around a defect is expected to increase with the number of vacancies in the agglomerate. A positron bound in a vacancy also interacts electrostatically with the surrounding ions, and this affects their positions; this effect has been documented in the case of GaAs.8,9

Any theoretical investigation of lattice relaxations due to open volume defects and positrons trapped therein is a very complex problem which has not, to date, been resolved. There is, however, a standard ab initio calculational method which neglects lattice relaxation around a defect; this method has been shown to form a reasonable foundation for the interpretation of data from experimental positron trapping studies.10

Recently, from first-principles electronic structure and positron-state calculations linear muffin-tin orbital atomic-sphere approximation (LMTO-ASA), positron affinities \( A_p \) and lifetimes \( \tau \) have been presented for perfect and vacancy-defected transition-metal carbides and nitrides.11 These self-consistent calculations led to a discussion of the possible trapping of positrons in precipitates formed in alloys by thermal treatment, as well as in precipitates in reactor pressure vessel steels induced by neutron irradiation.12 The application of improved LMTO-ASA calculations to different polytypes of SiC allows a more reliable treatment, compared to the atomic superposition method, of the following: (i) bulk positron lifetimes; (ii) positron lifetimes in monovacancies and divacancies and the influence of an impurity atom in the vicinity of these defects; and (iii) positron trapping in clusters of Si or Ge atoms, which might be formed by ion implantation. This last calculation was prompted by the fact that the bulk positron lifetimes given in the literature13 for Si...
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(218 ps) and Ge (230 ps) are both close to the experimental lifetime (235±3 ps) found after ion implantation.6

In connection with studies of ion implantation of 6H-SiC, it has been found that SiC may form the basis of an important moderator/remoderator for the production of slow positron beams.14 The positron work function φ, of 6H-SiC was measured to be (−3.0±0.2) eV. Measurement of the electron work function φ allows an experimental determination of the positron affinity A for SiC. φ can also be calculated from the electronic band structure of SiC, and a comparison can thus be made between experiment and theory for this fundamental materials property.

The paper is organized as follows. Sections II and III outline the experimental and theoretical methods used. The results are presented and discussed in Sec. IV, and conclusions are drawn in Sec. V.

II. EXPERIMENTAL METHODS

A. Electron affinity, band gap, and electron work function

The electronic properties of the 6H-SiC specimen were determined by use of the contact potential (CP) method, which has already been successfully applied to TiC,15 and photoacoustic spectroscopy.16 The CP between the tungsten cathode and SiC gives the electron affinity Xsc of SiC.

In determining the energy gap Eg, photoacoustic spectroscopy was employed, having an advantage over optical spectroscopy in that any error caused by light scattering is avoided. The phase-sensitive lock-in amplifier signal was monitored with a chopper frequency of 420 Hz which was relatively high. As discussed in Ref. 6 in more detail, this simplification does not affect the results appreciably.

Improvement has also been made with regard to the symmetry of the lattice. Whereas in the earlier calculations the 6H-SiC polytype was simulated by the simpler orthorhombic structure of SiC polytype for the calculation of bulk properties.22 Nevertheless, a value of εω differs slightly for 3C and 6H modifications.22

For the sake of comparison, two SiC polytypes, i.e., 3C- and 6H-SiC, were investigated. It is possible to describe the structure of both polytypes within the hexagonal representation,21 and the corresponding lattice parameters are given in Table I. For all calculations a supercell created by doubling the elemental cell in the a and b directions, i.e., in the basal plane, was used; the reason for this is that large distances between vacancies for a structure with defects are needed in order to reduce their mutual interactions. Thus there are 24 (48) atomic sites in the supercell in case of the 3C (6H) SiC polytype for the calculation of bulk properties. As the structures are open, the same number of empty spheres into the supercell is incorporated in order to describe better the interstitial charge distribution. If vacancies are included in the lattice, the number of atomic sites lowers correspondingly. In the basis s, p, and d orbitals were included, the d orbitals being downfolded.19

As in Ref. 6, the positron lifetime τ was calculated as the reciprocal value of the positron annihilation rate χ by

\[ \frac{1}{\tau} = \chi = \int |\Psi_+(r)|^2 \Gamma(n_-(r)) dr. \]  (1)

Here \(|\Psi_+(r)|^2\) is the positron density, and \(\Gamma(n)\) denotes the annihilation rate for a positron in a homogeneous electron gas.6,20 The high-frequency dielectric constant εω enters into the expression for \(\Gamma(n)\).6 Values of εω differ slightly for 3C and 6H modifications.22 Nevertheless, a value of εω=6.7 has been used for both 3C and 6H SiC polytypes in the present calculations to make results comparable with those in Ref. 6.
The differences are most significant in case of the 3C-SiC and 6H-SiC. The differences in the calculated positron lifetimes are negligibly small. Therefore, the calculations were restricted to one geometrical type of C monovacancy.

IV. RESULTS AND DISCUSSION

A. Bulk and defect positron lifetimes

Theoretical results for positron lifetimes, positron-defect binding energies, and positron affinities are presented in Table II. If we compare the values from Table II with the corresponding results from the atomic superposition method calculations, we arrive at the following conclusions.

(a) For the bulk material a slightly smaller positron lifetime is found for 3C-SiC, whereas for 6H-SiC exactly the same value has been calculated. The small difference between 3C-SiC and 6H-SiC values reflects the larger interstitial space in the 6H-SiC compared to the 3H-SiC structure.

(b) In the case of C and Si monovacancies, generally somewhat larger positron lifetimes are found for both SiC polytypes. The differences are most significant in case of the Si vacancy, which indicates a large redistribution of charges at atomic sites and in the interstitial region if a Si atom is removed. This was verified by comparing the charges at atomic sites and empty spheres for bulk and Si monovacancy cases. As in the case of bulk materials, a longer positron lifetime is found in 6H-SiC, which again reflects the larger interstitial space existing in this structure. Except for the C vacancy, generally much larger positron binding energies have been calculated for 6H-SiC.

(c) For the SiC divacancy the positron lifetime is slightly smaller (3C-SiC) or equal (6H-SiC) than in the earlier calculations, but a generally larger positron binding energy has been calculated.

(d) It is interesting to note that a Si-Si divacancy is more or less seen as two isolated monovacancies by the positron, according to the calculated positron lifetime. This effect can be understood from Fig. 1: if two nearest-neighbor Si atoms are removed there is still one C atom close to these vacancies which separates them. Therefore we have two isolated vacancies rather than one larger vacancy. In the case of the C-C divacancy the situation is similar, but the difference between the monovacancy and divacancy is more noticeable.

(e) To account for the effect of nitrogen doping, the location of a nitrogen atom in the vicinity of a Si monovacancy has been considered. This does not influence the corresponding positron lifetime in either SiC polytype, although it causes a slight increase in the positron binding energy.

(f) In general the more realistic LMTO-ASA calculations, while able to provide the positron affinity, are unable to remove the difference in positron lifetimes for the Si-C divacancy in 6H-SiC between the experimental value of $235 \pm 3$ ps and that calculated using the atomic superposition

<table>
<thead>
<tr>
<th>Positron state</th>
<th>$\tau$ (ps)</th>
<th>$E_b$ (eV)</th>
<th>$A_+$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk 3C-SiC</td>
<td>138(141)</td>
<td>-5.57</td>
<td></td>
</tr>
<tr>
<td>C vacancy</td>
<td>153(150)</td>
<td>+1.05(+0.28)</td>
<td>-4.39</td>
</tr>
<tr>
<td>Si vacancy</td>
<td>191(185)</td>
<td>+2.66(+1.69)</td>
<td>-8.22</td>
</tr>
<tr>
<td>Si+C divacancy</td>
<td>212(216)</td>
<td>+3.17(+2.39)</td>
<td>-8.18</td>
</tr>
<tr>
<td>Si+Si divacancy</td>
<td>194</td>
<td>+2.69</td>
<td>-8.93</td>
</tr>
<tr>
<td>C+C divacancy</td>
<td>160</td>
<td>+1.29</td>
<td>-4.92</td>
</tr>
<tr>
<td>Si vacancy+N</td>
<td>191</td>
<td>+2.73</td>
<td>-8.56</td>
</tr>
<tr>
<td>bulk 6H-SiC</td>
<td>141(141)</td>
<td>-5.91</td>
<td></td>
</tr>
<tr>
<td>C vacancy (1)</td>
<td>153(150)</td>
<td>+0.26(+0.28)</td>
<td>-4.30</td>
</tr>
<tr>
<td>Si vacancy (1)</td>
<td>194(183)</td>
<td>+2.46(+1.73)</td>
<td>-8.27</td>
</tr>
<tr>
<td>Si vacancy (2)</td>
<td>192</td>
<td>+2.30</td>
<td>-8.17</td>
</tr>
<tr>
<td>Si vacancy (3)</td>
<td>192</td>
<td>+2.32</td>
<td>-8.16</td>
</tr>
<tr>
<td>Si+C divacancy</td>
<td>214(214)</td>
<td>+2.95(+2.44)</td>
<td>-8.10</td>
</tr>
<tr>
<td>Si+Si divacancy</td>
<td>196</td>
<td>+2.64</td>
<td>-8.91</td>
</tr>
<tr>
<td>C+C divacancy</td>
<td>161</td>
<td>+0.58</td>
<td>-4.72</td>
</tr>
<tr>
<td>Si vacancy+N</td>
<td>194</td>
<td>+2.52</td>
<td>-8.75</td>
</tr>
</tbody>
</table>
method. The (small) difference between the measured and calculated values suggests that there may be lattice relaxation around this defect, or that perhaps an impurity atom such as nitrogen located on a lattice site near the defect. However, it should be pointed out that the improved calculations shown in Table II do not cast doubt on the interpretation of the positron annihilation studies of ion-implanted 6H-SiC given in Ref. 6.

**B. Positron trapping in Si or Ge precipitates in SiC**

A positron will be trapped by a precipitate if the difference $\Delta A_+$ between the positron affinity of the host and the precipitate is positive, and the radius of the precipitate exceeds the critical radius $r_c$ given by

$$r_c = 0.31/(\Delta A_+)^{1/2}.$$  \hspace{1cm} (2)

Here the proportionality constant is in units of nm (eV)$^{1/2}$, $\Delta A_+$ is in eV, and $r_c$ is in nm (a spherical precipitate is assumed). Although the positron lifetimes and affinities for Si and Ge are already known from the literature, they were calculated once more on equal footing with the ones for 6H-SiC. The results are given in Table III together with the critical sizes of precipitates estimated from Eq. (2).

The results collected in Table III would support the idea of positron trapping in Si and Ge clusters if formed in 6H-SiC due to ion implantation. However, the similarity of positron lifetimes in Si, Ge, and 6H-SiC after ion implantation—as mentioned in Sec. I—is not sufficient evidence of such trapping. At least one other positron method reflecting the momentum distribution of electrons participating in the annihilation process needs to be considered. Therefore, Doppler broadening of the annihilation linewidth, as reflected in the line-shape parameter $S$, was measured by slow positron implantation spectroscopy for pure Si and Ge, as well as Ge$^+$-implanted 6H-SiC, and the results are presented in Fig. 2.

For all three materials the influence of the surface properties on the mean $S$ parameter is reflected at very low incident positron energies. However, at incident positron energies above about 7 keV this influence vanishes, and the bulk properties are reflected through the corresponding $S$ values (means of the high-energy results): Si: 0.4934±0.0003; Ge: 0.4795±0.0009; 6H-SiC: 0.4929±0.0006. As measured $S$ values in Ge$^+$-implanted SiC are considerably higher than that for bulk 6H-SiC, it would appear that trapping in open-volume defects dominates trapping at precipitates, although the latter clearly needs to be studied in more detail in the future.

**TABLE III.** Positron lifetime $\tau$, and positron affinity $A_+$ for 6H-SiC, Si, and Ge. $r_c$ is the critical radius of Si and Ge clusters in 6H-SiC necessary for positron trapping, calculated using Eq. (5).

<table>
<thead>
<tr>
<th>Material</th>
<th>$\tau$ (ps)</th>
<th>$A_+$ (eV)</th>
<th>$r_c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6H-SiC</td>
<td>141</td>
<td>-5.91</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>218</td>
<td>-7.20</td>
<td>0.27</td>
</tr>
<tr>
<td>Ge</td>
<td>219</td>
<td>-7.62</td>
<td>0.24</td>
</tr>
</tbody>
</table>

**FIG. 2.** Mean $S$ parameter vs incident positron energy for Si ($\triangle$), Ge ($\bigcirc$), and 6H-SiC ($\bullet$).

**FIG. 3.** Photoacoustic phase-indicated gap absorption spectrum of 6H-SiC.
for 6H-SiC. The theoretical value for $f$ is obtained by use of Eq. (6), which allows the evaluation of the positron affinity for 3C-SiC in 1994.26

The 6H-SiC specimen used for the positron reemission measurements14 is the same as that used for the electron work-function measurements. The valence band is found to be positioned 6.51 eV below the vacuum level. This value has been used in determining the positron work function from Eq. (6). Thereby

$$
\phi_+ = (6.51 \pm 0.17) \text{ eV}. \tag{5}
$$

D. Positron affinity $A_+$

The positron affinity $A_+$ is defined by23

$$
A_+ = \mu_- + \mu_+ . \tag{6}
$$

$A_+$ is a pure bulk quantity which does not depend on the surface orientation of a crystalline sample. The values presented in Table II have been calculated using the electron chemical potential $\mu_-$ and the positron chemical potential $\mu_+$, assuming that $\mu_-$ corresponds to the top of the valence band. It is natural to use such a definition in order not to invoke any experimental numbers; moreover, the position of the electron chemical potential is not always known experimentally.

The 6H-SiC specimen used for the positron reemission measurements14 is the same as that used for the electron work-function measurements. The valence band is found to be positioned 6.51 eV below the vacuum level. This value has been used in determining the positron work function from Eq. (6). Thereby

$$
\phi_+ = -(A_+ + \phi_-) = -[-5.91 + (6.51 \pm 0.17)] \text{ eV}
= -[(0.60 \pm 0.17)] \text{ eV} \tag{7}
$$

for 6H-SiC. The theoretical value for $\phi_+$ of about $-1$ eV mentioned in Ref. 14 was estimated using an early calculation of the positron affinity for 3C-SiC in 1994.26

It is encouraging that the theory already predicts a relatively large negative positron work function, in agreement with experimentally observed positron work-function emission from 6H-SiC which suggests that this material may find use as a positron moderator in the future.13 On the other hand, the experimental estimation of both positron and electron work functions for the same material offers the unique possibility by use of Eq. (6) to evaluate the “experimental” positron affinity and compare it to the “pure” theoretical value. The present work on 6H-SiC and earlier work on W (Ref. 15) allows this comparison for two different materials (see Table IV). It is evident that in case of W an excellent agreement between theoretical and experimental positron affinity values is found, which is not the case for 6H-SiC. However, it is generally clear that the local-density approximation, widely used in electronic structure calculations, usually yields large errors for electron and positron energy levels for systems having an energy gap.27,28 To overcome this problem in the future, an improved approach to obtain reasonable gap and positron level values from first principles should be used. This would require the inclusion of self-interaction correction terms as well as modification of the electron-positron correlation potential. Such work is already in progress.

V. CONCLUSIONS

First-principles electronic structure and positron-state calculations for different SiC polytypes in perfect and defected states have been performed. The quantities studied are the positron lifetime and affinity and thereby the positron-defect binding energy has been derived. The results show that the positron lifetime is rather sensitive to the size of a defect. Compared to these rather large differences, the influence of the difference in polytype (3C-SiC and 6H-SiC) as well as of different lattice positions in the case of the Si monovacancy in 6H-SiC is negligibly small, at least with respect to the achievable accuracy in any positron measurement. However, it is remarkable that Si-Si and C-C divacancies may both be regarded as isolated monovacancies, in contrast to the C-Si divacancy. In general, much larger positron binding energies have been found compared with those calculated using the atomic superposition method for the same defect configurations.

Positron affinity calculations allow consideration of the case of positron trapping in Si and Ge clusters in 6H-SiC. In general a critical size can be estimated for such clusters, above which they would be attractive to positrons. However, slow positron beam measurements performed on Si, Ge, and 6H-SiC suggest that the formation of and positron trapping in such clusters due to Ge$^+$ implantation is unlikely.

An experimental estimation of the electron work function of 6H-SiC, combined with independent positron work-function measurements on the same 6H-SiC specimen,13 allows the evaluation of the positron affinity for this sample and its comparison with the theoretical value. Whereas excellent agreement was seen for W in earlier work,15 the less satisfactory result for 6H-SiC has prompted suggestions for improvements in the theoretical calculations which need to be confirmed by future work.

ACKNOWLEDGMENTS

The authors are grateful to Dr. W. Skorupa and Dr. V. Heera from the Institute of Ion Beam Physics and Materials Research (Research Centre Rossendorf, Inc.) for their supply of the 6H-SiC specimen and for useful discussions. Thanks are due to Professor O. K. Andersen and Dr. O. Jepsen for providing their TB-LMTO code for the calculations. J.K. acknowledges financial support of the Grant Agency of the Academy of Sciences of the Czech Republic through Project No. C111-2501.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\phi_+$ (eV)</th>
<th>$\phi_-$ (eV)</th>
<th>$A_+,\text{exp}$ (eV)</th>
<th>$A_+,\text{theor}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6H-SiC</td>
<td>-3.0</td>
<td>+6.51</td>
<td>-3.51</td>
<td>-5.91</td>
</tr>
<tr>
<td>W</td>
<td>-3.0 (Ref. 13)</td>
<td>+4.15 (Ref. 14)</td>
<td>-1.5</td>
<td>-1.31 (Ref. 23)</td>
</tr>
</tbody>
</table>

TABLE IV. Experimental positron ($\phi_+$) and electron ($\phi_-$) work functions, “experimental” positron affinity $A_+,\text{exp}$ [Eq. (6)], and theoretical $A_+,\text{theor}$ for W and 6H-SiC.
Also at Department of Low Temperature Physics, Charles University, V Holešovičkach 2, CZ-18000 Prague, Czech Republic.


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