Identification of Lattice Vacancies on the Two Sublattices of SiC

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The identification of atomic defects in solids is of pivotal interest for understanding atomistic processes and solid state properties. Here we report on the exemplary identification of vacancies on each of the two sublattices of SiC by making use of (i) electron irradiation, (ii) measurements of the positron lifetimes, (iii) coincident Doppler broadening studies of the positron-electron annihilation radiation, and (iv) a comparison of the experimental data with theoretical studies. After 0.3 MeV electron irradiation, carbon vacancies V_C are identified, where, after 0.5 MeV electron irradiation, predominantly silicon vacancies V_{Si} are observed. After 2.5 MeV irradiation, divacancies $V_{Si} - V_{Si}$ are detected. The present results are expected to be of general importance for reliable identification of defects and atomic processes in complex solids.

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Atomic lattice defects as, e.g., vacant lattice sites or vacancies, play an important role for the atomic transport and for the electrical, magnetic, or mechanical properties of solids. These vacancy defects have been studied in pure metals [1] or elemental semiconductors [2] in detail. Recent progress in vacancy studies in binary ordered solids as, e.g., intermetallic compounds [3,4], in the compound semiconductors SiC [5–11], in InP [12], in ZnS_xSe_{1-x} [13], vacancy clusters in Si [14,15] or graphite [16], vacancy impurity complexes in semiconductors [17,18], or structural vacancies in transition metal carbides [19] raised the question as to how far vacancies on the one or the other sublattice of these ordered systems can be reliably identified experimentally.

For a stringent identification of atomic defects in solids, we first have to define the fundamental features of this defect and second demonstrate these features by specific techniques. The identification of vacancies V_C or V_{Si} on the carbon or silicon sublattices of SiC is a particularly favorable case because a number of independent features can contribute:

(i) Because of different atomic masses of C or Si atoms, the vacancies V_C or V_{Si} can be selectively generated by electron irradiation. Whereas at low electron energies (0.3 MeV) exclusively C atoms are displaced, giving rise to V_C, at higher energies (0.5 MeV) Si atoms can be displaced and predominantly V_{Si} are detected (see below).

(ii) The vacancy nature of defects can be reliably detected by measuring the positron lifetime, which in this case of positron trapping at vacancies is increased [20] compared to annihilation in the defect-free bulk because of the decreased valence electron density in the vacancy.

(iii) Carbon vacancies V_C on the carbon sublattice in SiC are surrounded by Si nearest neighbors (see Fig. 1) and vacancies V_{Si} on the silicon sublattice by C atoms exclusively. Therefore, the sublattices where the vacancies are located can be analyzed by coincident Doppler broadening measurements of the positron-electron annihilation radiation [17,21] which provides a local chemical analysis of the types of atoms in the vicinity of the vacancy by measuring their core-electron momentum distributions.

(iv) The analysis of the sublattices of the vacancies in SiC by Doppler broadening experiments can be corroborated by Doppler broadening studies in the pure compounds Si and C (see below) and by theoretical studies of the Doppler broadening in V_C and V_{Si} [22].

It is shown below that all these features can be demonstrated for V_C and V_{Si} in SiC. In this sense, the present study is exemplary on the one hand for a stringent identification of defects and on the other hand for the feasibility of the detection techniques.

This is of importance and wide interest in a great many situations, in particular, when only a few of the above techniques as, e.g., Doppler broadening experiments, can be employed for defect identification.

For the present studies, 6H-SiC single crystal substrates with a 5 μm thick epitaxial 6H-SiC layer were

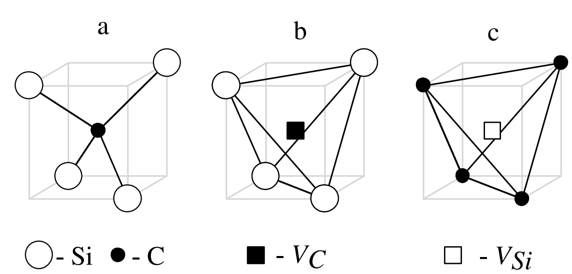

FIG. 1. Nearest-neighbor atoms of vacancies in SiC. (a) Defect-free SiC, (b) carbon vacancy, (c) silicon vacancy.

employed where the data reported here mainly stem from the substrate because of the mean positron penetration depth of about 80 μm. These n-type specimens (1.4×10^{16} cm^{-3} nitrogen doping) from Cree Inc., USA exhibit a bulk positron lifetime of 146 ps (see Table I).

The positron annihilation studies were performed by employing a ^{22}NaCl positron source (1 to 2 MBq) on a 0.8 μm Al foil stacked between two identical SiC specimen plates. The positron lifetime spectra measured by means of a fast-slow $\gamma\gamma$ spectrometer with a time resolution of 205 ps (full width at half maximum) and (2 to 4) $\times 10^6$ total coincidence counts were numerically evaluated by multicomponent fits [28].

The coincident Doppler broadening experiments were performed by coincident measurements of the energies E_1 and E_2 of the two positron-electron annihilation photons with Ge detectors of high energy resolution (FWHM = 1.2 keV). From the two-dimensional E_1, E_2 spectra with (3 to 5) $\times 10^7$ total coincident counts, Doppler broadening spectra with low background ($< 10^{-5}$) and optimum statistics were cut along the energy conservation diagonal $E_1 + E_2 = 1022$ keV with a 1 keV energy width [21,29]. These spectra extend into the range $(m_0c^2 + \Delta E) = (511 + \Delta E)$ keV with $\Delta E = 5$–10 keV (see Figs. 2 and 3) which is characteristic for core electrons and which substantially differs for different types of atoms. Here, m_0 is the electron rest mass and c the velocity of light.

The electron irradiation experiments for a selective generation of vacancies in SiC (see Fig. 1) were performed at the Stuttgart Dynamitron accelerator (see Ref. [20]) at a maximum specimen temperature of 220 K during irradiation including experiments with electron energies of 0.3 MeV and an electron dose of $\phi_1 = 2.4 \times 10^{23}$ m^{-2}, with 0.5 MeV ($\phi_2 = 7.5 \times 10^{23}$ m^{-2}), and with 2.5 MeV ($\phi_3 = 3 \times 10^{23}$ m^{-2}).

Defect-free SiC is studied first, together with measurements on the pure compounds Si and C (diamond). In defect-free SiC, a positron lifetime of 146 ps is observed as reported earlier (see Table I). The Doppler broadening spectrum of defect-free SiC is plotted in Fig. 2(a) and yields a straight line in the ratio representation of Fig. 2(b). It is located between the ratio spectrum of C (diamond) with a specific positive slope and that of Si with a negative slope in the range 5 keV $\leq \Delta E \leq$ 10 keV characteristic for core electrons. The position of the ratio spectrum of defect-free SiC in between the spectra of C and Si is due to the delocalized positron state in defect-free SiC [22] giving rise to annihilation with core electrons of both C and Si.

Vacancies can now be introduced selectively in the initially defect-free SiC on either the C sublattice or the Si sublattice by electron irradiation when the maximum collision energy E_t transferred to C or Si atoms substantially exceeds the displacement threshold energy, which is for both types of atoms determined to $E_d =$ 40 eV [30]. No vacancies are practically generated by 0.23 MeV electron irradiation where $E_t(\mathrm{C}) = 51$ eV transferred to C atoms hardly exceeds E_d, making displacement of C atoms highly unlikely and that of the heavier Si atoms impossible. In fact, the positron lifetime and the Doppler broadening spectra of initially defect-free SiC have shown no changes after our irradiation experiments by 0.23 MeV electrons (data not shown here).

By 0.3 MeV electron irradiation a substantial concentration of carbon vacancies V_C is generated due to a maximum transferred energy $E_t(\mathrm{C}) = 70$ eV, but no silicon vacancies V_Si are generated due to $E_t(\mathrm{Si}) = 30$ eV $< E_d$. In this case, a slightly increased positron lifetime of 153 ps is measured (see Table I) due to positron trapping at carbon vacancies V_C where positrons are predicted to be only slightly localized [22]. Simultaneously, the Doppler broadening ratio spectrum (see Fig. 3) shows a negative slope in the core-electron range. This behavior is characteristic for the Si nearest-neighbor atoms of carbon vacancies V_C as demonstrated in pure Si [see Fig. 2(b)] and is also confirmed theoretically [22] for V_C in SiC. By

TABLE I. Positron lifetimes for defect-free states of SiC, C (diamond), graphite (HOPG: highly oriented pyrolytic graphite), Si, and for vacancies, together with theoretical values and data from earlier papers.

Positron state	This work τ [ps]	Theory τ [ps]	Earlier experiments τ [ps]
SiC (bulk)	146 ± 1	141 [23], 131 [22]	146 [6], 144 [24], 142 [7]
V_C in SiC	153 ± 2	153 [23], 137 [22]	160 [25]
V_Si in SiC	176 ± 5	192 [23], 194 [22]	260 [25]
$V_\mathrm{C}-V_\mathrm{Si}$ in SiC		214 [23], 214 [22]	180 ± 10 [6], 209 [7]
$V_\mathrm{Si}-V_\mathrm{Si}$ in SiC	210 ± 2	196 [23]	
Diamond (bulk)	130 ± 10	90–92 [26]	107 [24]
Graphite (bulk)	216 ± 2	185 ± 6 [26]	212 [27], 210 [16]
Silicon (bulk)	219 ± 1	221 [14]	218 [2]

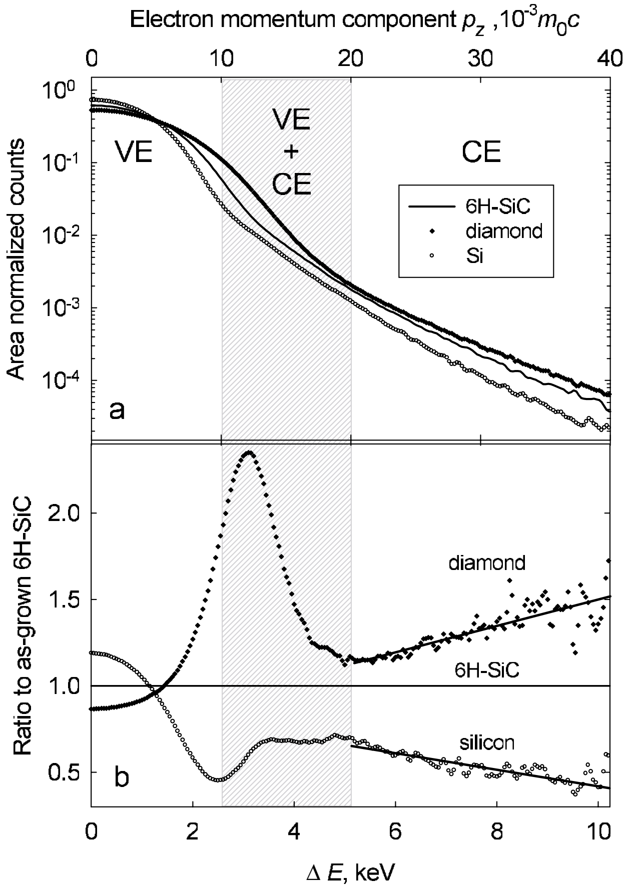

FIG. 2. (a) Doppler broadened spectra measured on defect-free 6H-SiC, C (diamond), and Si with coincident detection of the two annihilation γ photons for background suppression in order to study high-momentum core electrons. The coincidence counts in each energy channel are normalized to the integral number of coincidences. In addition to the energy abscissa scale, an electron momentum scale $p_z[10^{-3}m_0c] = 3.91 \cdot \Delta E[\text{keV}]$ is given. (b) Ratios of the Doppler broadened spectra of diamond, Si, or SiC and the Doppler spectrum of defect-free 6H-SiC. The linear approximation in the range between 20 and $40 \times 10^{-3}m_0c$ for the electron momentum distribution of diamond and Si is shown additionally with valence electron (VE) contribution and core electron (CE) contribution.

these evidences, vacancies V_C on the carbon sublattice are identified.

It may be mentioned here that after 0.3 MeV electron irradiation all positrons are annihilated from a localized state trapped in carbon vacancies V_C with an atomic concentration $C_{V_C} = \sigma_d(\text{C})\phi_1 = 3.8 \times 10^{-4}$ derived from the displacement cross section $\sigma_d(\text{C}) = 1.6 \times 10^{-27}$ m^2 (see Refs. [30–32]) and the electron dose $\phi_1 = 2.4 \times 10^{23}$ m^{-2}.

After 0.5 MeV electron irradiation the energies E_t transferred to the C or Si atoms are well above the E_d values. As the cross section $\sigma_d(\text{Si}) = 2.6 \cdot 10^{-27}$ m^2 for the displacement of Si atoms [30] is higher than for C atoms, predominantly Si vacancies are induced. Together with a higher specific positron trapping rate of Si vacancies due to a negative charge [33,34] in n-type SiC, this may be expected to give rise to positron trapping nearly exclusively at Si vacancies with a positron lifetime of 176 ps (see Table I) not far from a value predicted theoretically [23]. Again, simultaneously the Doppler broadening ratio in Fig. 3 in the core-electron regime yields specific information: its positive slope is characteristic for C atoms [see curve for diamond in Fig. 2(b)] which are the nearest neighbors of silicon vacancies V_{Si}. By these studies the vacancies V_{Si} on the Si sublattice are identified.

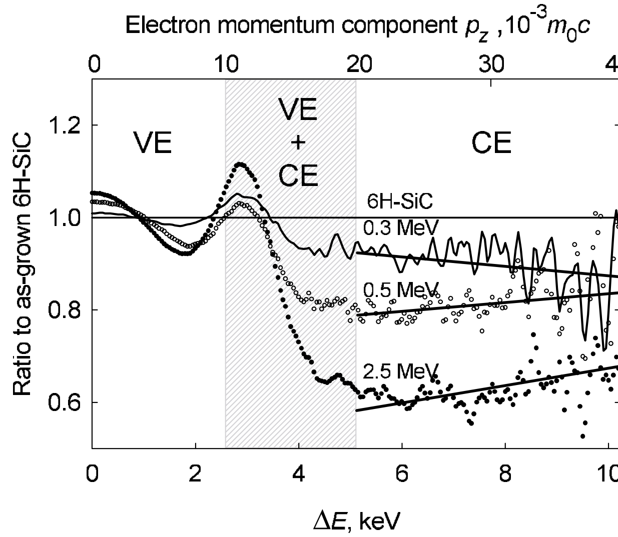

FIG. 3. Ratios of Doppler broadened spectra for SiC with vacancies after irradiation with 0.3, 0.5, and 2.5 MeV electrons and of the Doppler broadened spectrum of defect-free 6H-SiC. The linear approximation in the range between 20 and $40 \times 10^{-3}m_0c$ for the electron momentum distribution of irradiated specimens is shown additionally with valence electron (VE) contribution and core electron (CE) contribution.

After 2.5 MeV electron irradiation a vacancy-type defect with a still higher positron lifetime of 210 ps (see Table I) is detected which is ascribed to positron trapping at divacancies according to theoretical predictions. Specific information is again deduced from the core-electron regime of the Doppler broadening spectra (see Fig. 3). Here, the Doppler broadening ratio of the core electrons is further reduced as expected for a vacancy-type defect with a larger free volume. The slope of the core-electron contribution is, however, very similar to that after 0.5 MeV irradiation, showing that on the nearest-neighbor sites of the vacancies carbon atoms are located. We therefore identify this defect with a Si-Si divacancy $V_{\text{Si}} - V_{\text{Si}}$. Positron annihilation in $V_{\text{Si}} - V_C$ appears to be unlikely after 2.5 MeV irradiation because this type of vacancy is predicted to exhibit a horizontal Doppler broadening behavior [22].

In conclusion, this Letter is considered as a comprehensive case study for the stringent identification of vacancy defects in binary systems by specific contributions as selective generation of defects and identification of these defects on an atomistic level by making use of positrons as specific local probes. Theoretical corroboration is additionally available. Each of these contributions is indispensable for a trustworthy defect identification. The results reported here are thus expected to be of importance and broad interest, e.g., for a reliable electronic assignment of semiconductor defects in terms of band-gap energy levels, for an identification of defects when their origin is unclear as in as-grown compound semiconductors, for the assignment of thermal vacancies and thereby diffusion processes to a particular sublattice, for an atomic study of order-disorder processes, for a specific investigation of defects and atomic processes in complex condensed matter in general, etc.

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