Hyperfine interaction of the nitrogen donor in 4H-SiC

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Shallow N donors in n-type 4H-SiC were studied by electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR). For the N donor at the cubic site (N₃) in 4H-SiC, the hyperfine (hf) constants of the interaction with the nearest-neighbor (NN) ²⁹Si atom along the c axis were determined as Aₙ=41.07 MHz and Aₜ=41.31 MHz. In ENDOR experiments, this hf structure was confirmed. The hf interaction with the other three NN Si atoms in the basal plane was observed and the principal values of the hf tensor were determined as Aₚ=5.94 MHz, Aᵣ=5.06 MHz, and Aᵥ=14.25 MHz. Our EPR and ENDOR observations unambiguously confirm that the N donor occupies the C site in the 4H-SiC lattice and also reveal a considerable amount of the spin density of Nₙ (~23.9%) which was not obtained in previous studies.

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Nitrogen is the most common residual impurity which introduces shallow donor levels in SiC and causes n-type conductivity. In 4H- and 6H-SiC, the ionization energy of N on the hexagonal lattice site (N₃) is much shallower than that of the center on the cubic site (N₃) and the central hyperfine (hf) interaction of Nₙ is also much smaller.¹⁻³ Previous electron paramagnetic resonance (EPR) studies⁴ showed that the ¹⁴N hf splitting of Nₙ is about 1.8 mT for 4H-SiC (~1.2 mT for 6H-SiC), whereas the corresponding values for Nₙ determined by electron nuclear double resonance (ENDOR) is only about 0.1 mT (Aₙ=3.06 MHz and Aₜ=2.82 MHz) for 4H-SiC and slightly less for the 6H polytype. With the central ¹⁴N hf being about 15 times larger for Nₙ in 6H-SiC (~20 times larger in 4H-SiC), it is expected that the hf interactions with ²⁹Si nearest-neighbor (NN) atoms of Nₙ also should be larger compared to that of Nₙ. Surprisingly, the hf interactions with neighboring atoms of N at different inequivalent lattice sites h, kₜ and k₂ in 6H-SiC were found to be similar.⁴ The highest ²⁹Si hf constants obtained for Nₙ in both 4H- and 6H-SiC are unexpectedly small (only a few MHz), which are only about 10% of the central ¹⁴N hf constants.⁴ In 6H-SiC, the measured hf interactions with ¹²C neighbors are even considerably larger than that of ²⁹Si atoms and the spin density was found to be mainly located on C sublattice (less than 2.5% and 11% on Si and C atoms, respectively), whereas the corresponding values in 4H-SiC are 20.4% and 6.6% (Ref. 4). The inconsistency in the hf data in 4H- and 6H-SiC and the small values for ²⁹Si hf constants seem to indicate that the hf interactions with NN atoms may not have been observed in Ref. 4, which resulted in incorrect assignments of the hf lines. Recent EPR studies⁵ reported the observation of two weak satellites of Nₙ in 4H-SiC with a splitting of ~51 MHz. These satellites were attributed to the hf interaction with one ¹²C nucleus in the NN shell of Nₙ and therefore N was suggested to occupy the Si site in 4H-SiC (Ref. 5). However, the hf structure observed in Ref. 5 is not so clear and a careful verification is required.

In this work, we used EPR and ENDOR to study the hf interaction of N in 4H-SiC. Since ENDOR spectra at the frequency region below a few MHz have already been carefully studied in Ref. 4, we focus on the higher-frequency part and look for large hf interactions, which may not have been detected in previous studies.

The samples used for our ENDOR studies are on-axis commercial n-type 4H-SiC substrates with a concentration of the N donor of ~1×10¹⁷ cm⁻³. For EPR measurements, low-doped n-type (~1×10¹⁵ cm⁻³) 4H-SiC substrates grown by high-temperature chemical vapor deposition (HTCVD) were used. The pulsed-ENDOR measurements were performed on a Bruker ELEXSYS E580 X-band spectrometer using the Mims pulse sequence.⁶

Figure 1 shows the EPR spectrum of the N donor observed in low-doped 4H-SiC grown by HTCVD at 77 K for the magnetic field B along the c axis. At this temperature, the spectrum of Nₙ was not observable due to its short spin-lattice relaxation time and only the Nₙ spectrum with a large ¹⁴N hf splitting (1.8 mT) was detected. As can be seen in Fig. 1(a), each main line is accompanied by two weak hf lines with a splitting of 1.46 mT (or 40.9 MHz). The intensity ratio of these hf lines and the central line is about 4.5%—5%, which corresponds to the natural abundance of one ²⁹Si (4.7%, I=1/2). The angular dependence studies show that these hf lines have C₃ᵥ symmetry with a nearly isotropic splitting. These satellites are therefore assigned to the hf structure of the NN ²⁹Si atom along the c axis [labeled Si(1)]. An analysis of the EPR line shape indicates that the shoulder of the main line may contain the unresolved hf structure due.
to the interaction with the three nearest Si atoms in the basal plane [labeled Si(2–4)]. At B||c, the three Si(2–4) atoms are equivalent and give rise to the same hf lines, whose splitting was estimated to be ~0.525 mT (~14.7 MHz). A simulated spectrum using the hf splittings of 1.46 mT for Si(1), 0.525 mT for Si(2–4), and 1.8 mT for $^{14}$N is shown in Fig. 1(b) for comparison. As can be seen in the figure, the simulation represents very well the observed EPR spectrum, supporting our assignment of the Si hf interactions.

Figure 2 shows an electron spin-echo (ESE) spectrum in 4H-SiC measured at 10 K for B parallel to the c axis. By optimizing the conditions for detecting centers with short spin-lattice relaxation time we could observe an intense N$_h$ signal while suppressing the N$_k$ signal to just above the noise level. It is therefore possible to observe the $^{14}$N hf structure of N$_h$ which consists of three lines with a splitting of 0.212 mT between the two outer lines (see Fig. 2 and the inset). In continuous-wave EPR studies (see Refs. 1–3), the N$_k$ and N$_s$ spectra were always detected at the same time. At low microwave (mw) frequencies (X band), this results in a broad, unresolved middle line due to overlapping. At high mw frequencies (~37 or ~142 GHz (Refs. 4 and 5)), the N$_h$ and N$_s$ spectra are well separated, but the broader linewidth makes the small splitting $^{14}$N hf structure of N at the h site unresolvable. The $^{14}$N hf constant of N$_h$ is determined to be 0.106 mT or 2.97 MHz, which is very close to the value determined by ENDOR (Ref. 4). No resolved $^{29}$Si or $^{13}$C hf structures were detected by EPR for N$_h$. The line shape of the N$_s$ spectrum is different from that of N$_h$, showing no shoulder. From the shape and width of the EPR lines, we can estimate that the highest $^{29}$Si hf splitting for N$_h$ in 4H-SiC should be smaller than 0.3 mT or less than 8.5 MHz.

In order to confirm our EPR observation of the large hf interactions with $^{29}$Si for N$_h$ in 4H-SiC we performed pulsed-ENDOR experiments. Figures 3(a) and 3(b) show the ENDOR spectra of N$_h$ in 4H-SiC measured at 40 K with B||c and B⊥c, respectively. The high-frequency part (above 16 MHz) was measured with B set at the position of the $^{29}$Si hf line of the high-field $^{14}$N line. The two highest-frequency ENDOR lines are from $^{14}$N and correspond to the transitions $A_{N}/2 \pm \nu'$ ($^{14}$N) and $A_{N}/2 + \nu'$ ($^{14}$N) [the contributions of the quadrupole tensor of $^{14}$N, ±3$P_{N}/2$, to the ENDOR transitions vanish since $P_{N} \approx 0$ (Ref. 4)]. Here $A_{N}$ is the hf constant of $^{14}$N at the k site and $\nu'$ ($^{14}$N) is the nuclear Zeeman frequency of $^{14}$N. Similarly, two lines at 17.645 MHz and 23.429 MHz in Fig. 3(a) are identified as $^{29}$Si hf lines corresponding to the transitions $A_{Si}/2 \pm \nu'$($^{29}$Si) and $A_{Si}/2 + \nu'$($^{29}$Si). The splitting at B⊥c is slightly larger. The deduced $A_{Si}$ value is 41.07 MHz, which is close to the hf value of 40.9 MHz determined by EPR for the nearest Si(1) atom and therefore confirms the
identification by EPR. The lower-frequency parts of the ENDOR spectra (below 16 MHz) in Figs. 3(a) and 3(b) were measured with B set at the shoulder of the high-field line of the N\textsubscript{2} spectrum, which is about 0.26 mT from the peak. This is the position of the Si(2–4) hf line as estimated from the EPR spectrum. With the magnetic field at this position, the pulses are expected to be able to excite the NN Si(2–4) and other \(^{29}\)Si and \(^{13}\)C nuclei in the outer neighbor shells. As can be seen in Figs. 3(a) and 3(b), several other ENDOR lines with frequencies above the previously reported values\(^3,4\) were also detected, which can be identified as due to \(^{29}\)Si [labeled Si(2–4)] or \(^{13}\)C (labeled by roman numbers). The angular dependences of ENDOR lines with B rotating in the (11\(\bar{2}\)0) plane are shown in Fig. 4. The Si(1) and \(^{13}\)C(I-V) hf lines follow \(C_{3v}\) symmetry. The \(^{13}\)C(II) hf line is broad and partly overlapping with the \(^{13}\)C(III) line. It is possible that the symmetry of this line is lower but the splittings may be not resolvable in our X-band ENDOR experiments. As shown in Fig. 4, the symmetry of the Si(2–4) hf lines is \(C_{1h}\). The angular dependences of the \(^{29}\)Si and \(^{13}\)C hf lines can be described by the spin Hamiltonian

\[
H = \mu_B \mathbf{B} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A}_N \cdot \mathbf{I}_N - \gamma_N \mathbf{B} \cdot \mathbf{I}_N + \sum_i (\mathbf{S} \cdot \mathbf{A}_i - \gamma_B) \cdot \mathbf{I}_i. \tag{1}
\]

Here \(S=1/2\), \(A_N\) is the hf tensor of \(^{14}\)N, \(I_N\) is the hf tensor of \(^{29}\)Si and \(^{13}\)C nuclei, \(\gamma_N\) is the magnetogyric ratio for \(^{14}\)N and \(\gamma\) is the magnetogyric ratio for \(^{29}\)Si and \(^{13}\)C nuclei. The values of \(g\) and \(A\) for N at the \(k\) site were taken from Ref. 4. The quadrupole tensor \(P_N\) for \(^{14}\)N was not included in the spin Hamiltonian since the principal values \(P_N \sim 0\) (Ref. 4). The hf tensors are described in the principal coordinates with the \(z\) and \(x\) axes lying in the (11\(\bar{2}\)0) plane and the \(y\) axis perpendicular to this plane. \(\beta\) is the angle between the principal \(z\) axis of the hf tensor and the \(c\) axis. The obtained hf values are given in Table I.

Combining the EPR and ENDOR data, we assign both hf lines with a splitting of 1.46 mT (40.9 MHz) observed by EPR (see Fig. 1) and the Si(1) ENDOR lines (Fig. 3) to the interaction with the nearest \(^{29}\)Si atom along the \(c\) axis, Si(1). The Si(2–4) hf lines are attributed to the interaction with three nearest \(N\) atoms in plane. The intensity of the Si(2–4) line at \(B||c\), which is about 3 times that of the Si(1) hf line, also supports the identification. The angle \(\beta \sim 77^\circ\) for the principal \(z\) axis of the Si(2–4) hf tensor indicates the direction of three N-Si bonds. The principal hf values for Si(2–4) atoms are very close to the values estimated from EPR. We attributed the \(^{13}\)C(I-V) hf lines to the interaction with \(^{13}\)C atoms in the next-nearest-neighbor (NNN) and outer shells.

Since the principal hf values for Si(2–4) are nearly axial symmetric, we can estimate the isotropic \(a=\frac{1}{3}(A_{xx}+A_{yy}+A_{zz})\) and anisotropic \(b=\frac{2}{3}(A_{xx}-\frac{3}{2}(A_{yy}+A_{zz}))\) parts of the hf tensor and hence the corresponding \(s\) and \(p\) spin densities. \(\beta\) is the angle between the principal \(z\) axis of the hf tensor \(A\) and the \(c\) axis. The error is about \(\pm 0.02\) MHz. All the hf tensors have \(C_{3v}\) symmetry, except the hf tensor of Si(2–4) nuclei is \(C_{1}\). The hf constants corresponding to the lower-frequency lines are not given since they have been observed and carefully analyzed in Ref. 4.

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<th>(z)</th>
<th>(A_{xx}) (MHz)</th>
<th>(A_{yy}) (MHz)</th>
<th>(A_{zz}) (MHz)</th>
<th>(\beta) (deg)</th>
<th>(a) (MHz)</th>
<th>(b) (MHz)</th>
<th>(s) (%)</th>
<th>(p) (%)</th>
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<td>51.11</td>
<td>51.12</td>
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densities. In Ref. 4, the observed largest $a$ and $b$ values for 4H-SiC are only 6.54 MHz and 1.26 MHz, respectively, for $^{29}\text{Si}$ and $^{13}\text{C}$, respectively, for $^{29}\text{Si}$ and $^{13}\text{C}$ in the nearest and NNN shells of $N_k$ in 4H-SiC were not detected in Ref. 4. In those experiments, due to the line broadening in $^{13}\text{C}$-enriched samples, the hf lines from Si(1) and Si(2–4) atoms were not resolved from the main EPR line and the ENDOR spectra were measured with the magnetic field set on the N peak, which is rather far away from the positions of the Si(2–4) and Si(1) hf lines ($\sim 0.26$ mT and $\sim 0.73$ mT, respectively). These correspond to large frequency separations of $\sim 7.3$ MHz and $\sim 20.5$ MHz. It is likely that the mw pulses could not excite the corresponding nuclei, resulting in no contribution from larger-splitting hf lines to the spin-echo signal. Consequently, only small-splitting hf lines close to the N peak could be excited and observed in the ENDOR spectra. The failure in detection of large $^{29}\text{Si}$ and $^{13}\text{C}$ hf interactions explains why the total spin density estimated for $N_k$ was reported to be only $\sim 30\%$ ($\sim 2.8\%$ on N, 20.4% and 6.6% on the Si and C sublattices, respectively). Our newly observed $^{29}\text{Si}$ hf values give the $s$ and $p$ spin densities on the four nearest Si neighbors of about 8.19% +0.97% = 9.2%. If we use the same average number of six atoms in each shell as in Ref. 4 for the outer shells, the spin density corresponding to the C(I-V) hf lines is estimated to be (2.28% +0.163%) $\times 6 = 14.7%$. Thus, the spin densities on the four nearest Si neighbors and on C atoms in outer shells, which have not been obtained in previous studies, are about 9.2% +14.7% =23.9%. Including the spin densities observed in Ref. 4 for Si (20.4%) and C (6.6%) sublattices, the observed total spin density on $N_k$ ($\sim 2.8\%$) and the surrounding Si and C nuclei then becomes $\sim 53.7\%$.

The spin densities on the Si and C sublattices found for N at $h$, $k_1$, and $k_2$ sites in 6H-SiC in Ref. 4 are very small [for the $h$ site, 2.4% (Si) and 10.92% (C); for the $k_1$ site, 1.2% (Si) and 6% (C); for the $k_2$ site, 1.8% (Si) and 10.4% (C)] compared to the corresponding values observed in our experiments for $N_k$ in 4H-SiC. The difference in the spin localization for N donors in the hexagonal and cubic sites in 6H-SiC, especially between the $h$ site (13.3%) and the $k_1$ site (7.2%), does not seem to reflect the electronic structure of the centers. It is likely that in ENDOR experiments of 6H-SiC (Ref. 4) the hf interactions with the nearest-neighbor nuclei may not have been detected. In the $^{13}\text{C}$-enriched (to $\sim 35\%$) samples, the observation of $^{13}\text{C}$ ENDOR should be easier and this may explain why the spin density found on the C sublattice is larger.

In summary, we have observed new hf structures due to the interactions with the nearest $^{29}\text{Si}$ neighbors and $^{13}\text{C}$ atoms in outer shells of the N donor at the $k$ site in 4H-SiC. Our observation confirms that the N donor occupies the C site in 4H-SiC lattice and not the Si site. The newly observed hf interactions with the nearest $^{29}\text{Si}$ neighbors and $^{13}\text{C}$ atoms in outer shells account for $\sim 23.9\%$ of the spin densities for the $N_k$ donor. The higher spin density found for $N_k$ ($\sim 53.7\%$ with $\sim 2.8\%$ on N, $\sim 29.6\%$ and $\sim 21.3\%$ on the Si and C sublattices, respectively) is consistent with the deeper ionization energy for the N donor at the $k$ site.

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