

Spin-coupling in Heavily Nitrogen-doped 4H-SiC

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Abstract. EPR and ESE in nitrogen doped 4H- and 6H-SiC show besides the well known triplet lines of ^{14}N on quasi-cubic ($\text{N}_{\text{c,k}}$) and hexagonal ($\text{N}_{\text{c,h}}$) sites additional lines (N_{x}) of comparatively low intensity providing half the hf splitting of $\text{N}_{\text{c,k}}$. Frequently re-interpreted as spin-forbidden lines, arising from $\text{N}_{\text{c,k}}$ pairs and triads or resulting from hopping conductivity, only recently the theoretical calculation of the corresponding g-tensors lead to a tentative model of distant N_{C} donor pairs on inequivalent lattice sites which are coupled to $S = 1$ assuming a fine-structure splitting too small to be observed in the EPR and ESE experiments. In this work, we present ESE nutation measurements confirming $S = 1$ for the N_{x} center. Analysing the nutation frequencies in comparison with that of the $\text{N}_{\text{c,k}}$ ($S = 1/2$) spectrum as well as the line width of ESE and EPR spectra we obtain a rough estimate between $5 \cdot 10^4 \text{ cm}^{-1}$ and $50 \cdot 10^4 \text{ cm}^{-1}$ for the fine-structure splitting demonstrating efficient spin-coupling between nitrogen donors in 4H-SiC.

Introduction

Nitrogen is the common donor in all SiC polytypes and dominates the electrical properties of *n*-type SiC which is used as substrates for the fabrication of high-power electronic devices. Nitrogen can easily be introduced into SiC during growth using a controlled N_2 gas flow, but in contrast to other semiconductors like silicon or diamond, the situation is more complicated. Especially in the hexagonal polytypes like 4H-SiC, the possibility for the nitrogen dopant to occupy different inequivalent sites of the carbon sublattice leads to different ionization energies of 52.1 meV and 95.8 meV for nitrogen at the hexagonal ($\text{N}_{\text{c,h}}$) and quasi-cubic carbon sites ($\text{N}_{\text{c,k}}$), respectively. Moreover, EPR and electron spin echo (ESE) measurements in nitrogen doped ($\sim 10^{17} \text{ cm}^{-3}$) 4H-SiC and 6H-SiC samples show besides these well known triplet lines additional lines of comparatively low intensity providing exactly half the hf splitting of the $\text{N}_{\text{c,k}}$ spectrum (see figure 1). Originally, these lines have been assumed to arise from $\text{N}_{\text{c,k}}$ pairs and triads [1, 2], or re-interpreted as spin-forbidden lines [3]. Later on, the higher resolution of Q band ESE shows that the additional lines ‘in-between’ (labeled N_{x}) do not follow the angular dependence of $\text{N}_{\text{c,k}}$, but provides roughly an average of the g-tensors of $\text{N}_{\text{c,h}}$ and $\text{N}_{\text{c,k}}$ instead. However, hopping conductivity [4] between the two donor types has to be excluded from energetical reasons (largely different ionization energies). Only recently, based on the symmetry of the corresponding g-tensors in 4H-SiC calculated from first principles an alternative model was proposed, that was able to get rid of the contradiction in experimental data [5]: Distant N_{C} donor pairs on inequivalent lattice sites which are coupled to $S = 1$ centers but with very small zero-field splittings, are calculated to give rise to an essentially $S=1/2$ like N_{x} spectrum. Similar high-frequency measurements in 6H-SiC show that this model remains feasible also in the case of 6H-SiC [6]. The fact that the N_{x} center occurs less readily in 6H sub-

strates than in 4H-SiC supports the model consisting of one nitrogen atom on each symmetry site because the number of hexagonal sites in 6H-SiC is only half the number of quasi-cubic sites. However, in order to verify the proposed spin-coupling to an $S = 1$ center, explicit experimental resolution of the corresponding fine-structure or the electron spin is still required.

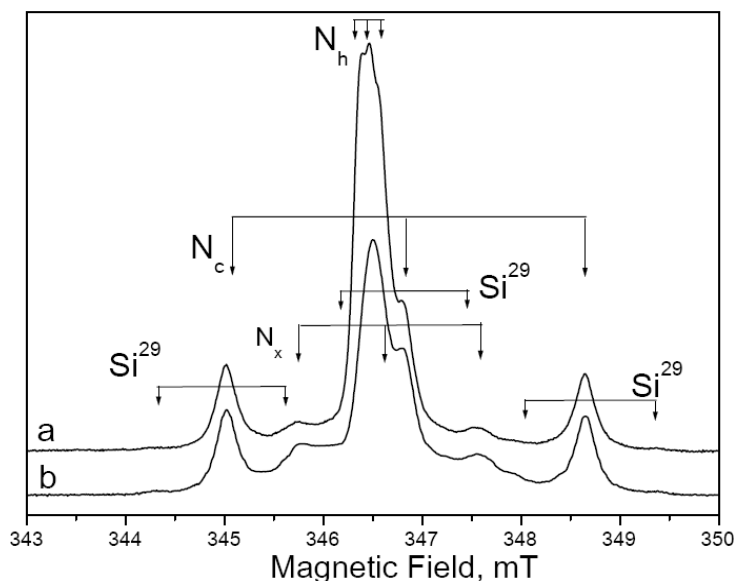


Fig. 1: X-band field-sweep ESE spectra detected in 4H-SiC samples grown by the SSM method with different compensation degree. ($N_D - N_A \approx 10^{17} \text{ cm}^{-3}$, $B_0 \parallel c$, $T = 6 \text{ K}$).

a low compensation,
b high compensation.

Experimental and Discussion

In this work we performed pulsed electron nuclear double resonance (ENDOR) measurements (see figure 2) for the N_c , N_h and N_x ESE lines shown in figure 1. To enhance the sensitivity and nuclear spin relaxation pulsed ENDOR measurements were performed using modified Davies pulse sequence [10]. With B_0 at the central N_c triplet line ENDOR lines at 2.41 MHz and between 24 and 27 MHz with small quadrupole splitting were observed in the X-band ENDOR spectra. The lines at 2.41 MHz were attributed to nitrogen on the hexagonal lattice site (N_h) [9]. The ENDOR lines observed between 24 and 27 MHz are due to N_c . All other lines belong to ^{29}Si and ^{13}C hf interactions.

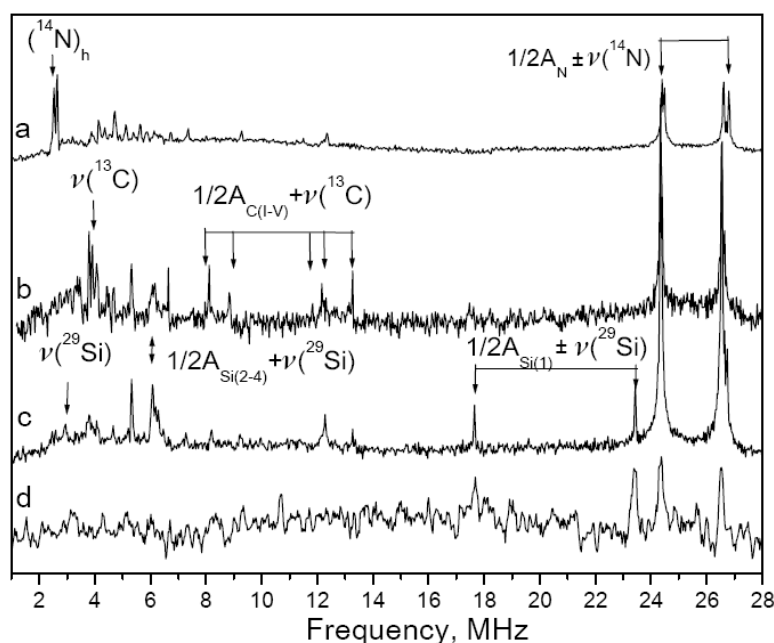


Fig. 2: X-band pulse-ENDOR spectrum measured in modified Davies pulse sequence in 4H-SiC. ($N_D - N_A \approx 10^{17} \text{ cm}^{-3}$, $(B_0 \parallel c, T = 6 \text{ K})$. For the line positions (B_0) see figure 1.

a B_0 is set to the N_h line, which coincides with the central N_c triplet line,
b B_0 is set to the low-field line of the N_c triplet,
c B_0 is set to the low-field line of the N_x triplet,
d B_0 is set to the low-field line of Si^{29} .

The measurements confirmed $S = 1/2$ for the isolated donors $N_{c,k}$ and $N_{c,h}$, while the situation was ambivalent for the N_x center: pulsed ENDOR measurements performed on the N_x EPR lines show the same ^{14}N hyperfine lines known from ^{14}N on the quasi-cubic site (figure 2). This

confirmed that within experimental error (2 kHz) the hf interaction constant is exactly half of that of $N_{c,k}$. For N_x and assuming $S = 1$, we expect at least 3 ENDOR transitions at $\nu(m_s = 1) = 26.6$ MHz, $\nu(m_s = -1) = 24.6$ MHz, and $\nu(m_s = 0) = 1$ MHz. According to experience, ENDOR transitions for $\nu < 1$ MHz are hard to detect, which was also the case for the expected $m_s = 0$ line of N_x . Unfortunately, those expected for $m_s = \pm 1$ interfere with the $m_s = \pm 1/2$ lines of $N_{c,k}$. As a consequence, the ENDOR measurements were not able to verify the $S = 1$ spin-coupling, but on the other hand, $S = 1$ also cannot be excluded. In other words, in the case of the N_x -center in 4H-SiC, ENDOR is not helpful to determine the total spin S .

Here, the ESE nutation measurements are shown to be superior to the ENDOR measurements. We performed ESE nutation measurements for the N_c , N_h and N_x lines. Figure 3 shows the nutation spectra recorded on ESE signals of the nitrogen spectra revealing two different nutation signals at 2.203 MHz and 1.708 MHz, respectively. Whereas the nutation spectra for isolated nitrogen donors $N_{c,k}$ and $N_{c,h}$ around $\omega_{nut}(N_c) = 1.708$ MHz are almost the same, the nutation frequency found in the N_x lines is clearly enhanced, confirming unambiguously $S > 1/2$ for the electron spin of the N_x -center.

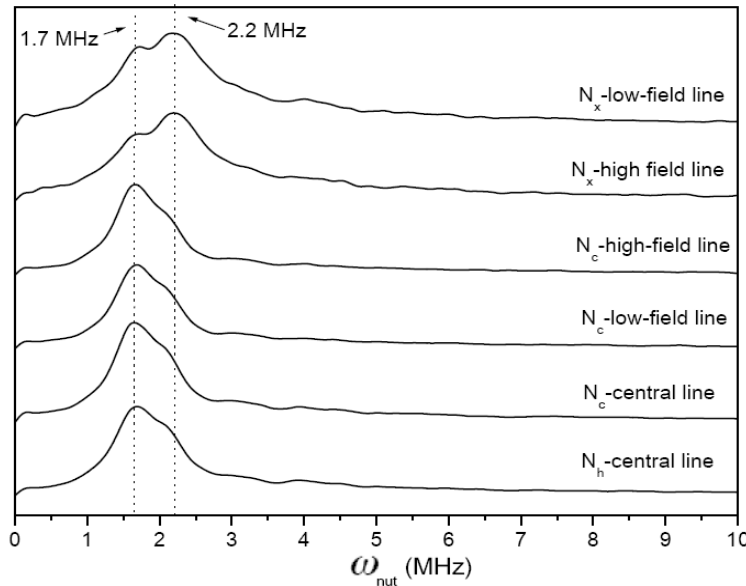


Fig. 3: ESE nutation spectra observed in 4H SiC at different field-sweep ESE line positions as indicated for N_x , N_c , N_h in figure 1.

Going into more detail, the ratio of the nutation frequencies is found to be $\omega_{nut}(N_x)/\omega_{nut}(N_c) = 1.29$. Assuming vanishing zero-field splitting the nutation frequency would be independent from the electron spin of the center [7]. In the limit of a fine-splitting large in comparison with the nutation frequency, the nutation frequency for a given total spin S is given by [7]

$$\omega_{nut}(m_s, m_s + 1) = \omega_1 [S(S+1) - m_s(m_s + 1)]^{1/2} \quad (1)$$

with $\omega_1 = \frac{g\beta_e B_1}{\hbar}$ whereby β_e is the Bohr magneton of the electrons. Moreover, using equation (1) the ratio expected for two centers having $S = 1$ and $S = 1/2$, re-spectively, is given by

$$\frac{\omega_{nut}(S=1)}{\omega_{nut}(S=1/2)} = \frac{\omega_1 \cdot 2^{1/2}}{\omega_1} = 2^{1/2} \quad (2)$$

In other words the ratio 1.29 experimentally observed for the N_x -center lies in between the limits 1.0 and 1.414, for a vanishing fine-structure splitting D (1.0) and a fine-structure $D \gg H_1 = \frac{g\beta_e B_1}{\hbar} S = \omega_1 \cdot S$ large in comparison with the nutation frequency, respectively. As a

result, the fine structure has to be expected in the same order of magnitude than $H_1 = 5 \cdot 10^{-4} \text{ cm}^{-1}$ providing a lower limit for the zero-field splitting, whereby an upper limit can be determined to $50 \cdot 10^{-4} \text{ cm}^{-1}$ by analyzing the linewidth of the ESE and EPR spectra at various microwave frequencies up to 140 GHz. Indeed, the observed fine structure is small compared to those usually observed in e.g. spin triplet systems [8].

Conclusion

In summary, the value $S = 1$ for N_x is confirmed unambiguously by the ESE nutation measurements, although the zero-field splitting is too small to be observed in the experiments. By a detailed analysis of the linewidth of the ESE and EPR spectra and of the ratio of the nutation frequencies for the $S = 1/2$ donor spectra and the N_x -center we obtain a rough estimate between $5 \cdot 10^{-4}$ and $50 \cdot 10^{-4} \text{ cm}^{-1}$ for the fine structure splitting demonstrating efficient spin-coupling between nitrogen donors in 4H-SiC.

Acknowledgements

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