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EPR, ESE and pulsed ENDOR study of the nitrogen donor pairs on quasi-cubic lattice sites in 6H SiC

D.V. Savchenko [a,b], E.N. Kalabukhova [b,*], S.N. Lukin [b], E.N. Mokhov [c], J. Hoentsch [a], A. Pöppl [a]

[a] Fakultät für Physik und Geowissenschaften, Institut für Experimentalphysik II, Universität Leipzig, Linnéstrasse 5, Leipzig D-04103, Germany
[b] Institute of Semiconductor Physics, NASU, Pr. Nauki 45, Kiev 03028, Ukraine
[c] A.F. Ioffe Physiko-Technical Institute RAS, Politekhnicheskaya 26, St. Petersburg 194021, Russia

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ABSTRACT

D-band EPR, X-band FS ESE and pulsed ENDOR studies of the additional nitrogen (N) related centers observed in highly compensated n-type 6H-SiC wafers are presented. The D-band EPR and X-band FS ESE spectrum consists of the ^{14}N hyperfine (hf) triplet lines of the N donors incorporated at the two quasi-cubic (N_{c1}, N_{c2}) sites with the intensity ratio of $I_{Nc1}/I_{Nc2} = 0.7$ and three additional triplet lines. X-band pulsed ENDOR spectra have shown intense ^{14}N ENDOR signals of N_{c1}, N_{c2} centers and new ^{14}N lines due to the N related centers N_1, N_2, N_3 with the isotropic hf splitting: 21.04, 26.43, 29.77 MHz, respectively. It was found that the g-tensors of the N_2 and N_3 triplet lines coincide with those of N on quasi-cubic N_{c2} site. The g-tensor of the third N_1 triplet lines corresponds to the average value of the N_{c1} and N_{c2} spectrum: $g(N_1) \approx \frac{1}{2}[g(N_{c1}) + g(N_{c2})]$. It was suggested that N_1 center with $A_{iso} = 21.04$ MHz is due to the spin coupling between N on two quasi-cubic N_{c1} and N_{c2} sites while two others are tentatively attributed to the N pairs formed between N atoms on one quasi-cubic N_{c2} site.

1. Introduction

The previous X-band electron paramagnetic resonance (EPR) investigations of n-type 6H-SiC showed that besides the well known triplet lines due to nitrogen (N) at the hexagonal (N_h) and quasi-cubic carbon sites (N_{c1}, N_{c2}) two additional lines of comparatively low intensity lying exactly at half the hyperfine (hf) splitting of the N_{c2} spectrum were observed in heavily doped ($>10^{17}$ cm^{-3}) samples. These lines have been assumed to arise from N pairs and triads [1–3]. Recent high frequency EPR, field-sweep electron spin echo (FS ESE) and pulsed electron nuclear double resonance (ENDOR) studies of the n-type 4H SiC and 6H SiC wafers with low nitrogen (N) concentration ($<10^{17}$ cm^{-3}) showed besides a triplet due to N_h, additional N triplet lines labelled N_x with g-tensor corresponding to the average value of the N_c and N_h spectrum: $g(N_x) \approx \frac{1}{2}[g(N_c) + g(N_h)]$ in 4H SiC [4] and $g(N_x) \approx \frac{1}{2}[g(N_{c2}) + g(N_h)]$ in 6H SiC [5,6]. It was found that the N_x triplet lines have half of the hf splitting of the N_c center in 4H and N_{c2} in 6H SiC. Judging from experimental EPR parameters and those calculated from the first principles, the N_x triplet lines were attributed to the distant N donor $N_cSi_cN_h$ pairs on inequivalent lattice sites which are coupled to $S = 1$ centers with very small zero-field splitting [7]. This conclusion was also supported by nutation frequency experiments from which the spin state of the N related center N_x in 4H-SiC was determined as $S = 1$ [8].

In this work we used D-band EPR, X-band FS ESE and pulsed ENDOR to study the highly compensated n-type 6H-SiC wafers with $(N_D–N_A) \approx 10^{16}$ cm^{-3} to verify whether the N donor pairs occur between two quasi-cubic sites in the case when the N_h were ionized and the numbers of the paramagnetic N atoms at the two quasi-cubic positions became already very different. By analogy with N_x center model, Fig. 1 shows four among six possible configurations of the distant pairs like ($N_{ci}Si_{ci}N_{ci}$, $i = 1, 2$) which could occur between N atoms on two quasi-cubic lattice sites in 6H SiC.

2. Experimental

A series of highly compensated n-type 6H-SiC wafers grown by modified Lely method with donor concentration of about $(N_D–N_A) \approx 10^{16}$ cm^{-3} were investigated by two pulse FS ESE, ESE nutation, and pulsed ENDOR experiments on an X-band Bruker ELEXYS E580 spectrometer. For all pulse experiments selective microwave (mw) pulses with pulse lengths of $t_{\pi/2} = 0.1$ μs, $t_\pi = 0.2$ μs and a pulse delay $\tau = 1$ μs were used. The nutation experiments were done using the pulse sequence p_n–t–$\pi/2$–τ–π–τ– echo with $t = 400$ ns where the pulse length of the first pulse p_n was incremented in steps of 16 ns. Pulsed ENDOR measurements were performed using a modified Davies ENDOR pulse

* Corresponding author. Tel.: +380 44 236 0971; fax: +380 44 489 1704.
E-mail address: katia@i.kiev.ua (E.N. Kalabukhova).

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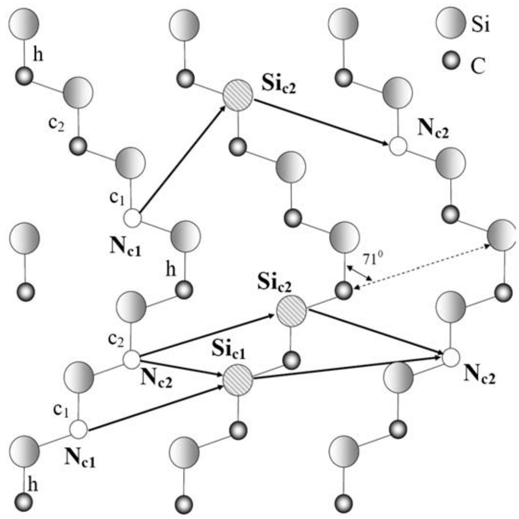

Fig. 1. Possible configurations of the distant donor pairs like ($N_{ci}Si_{ci}N_{ci}$) on quasi-cubic lattice sites in 6H-SiC shown in the $(1\,1\,\overline{2}\,0)$ plane.

sequence to enhance the sensitivity and nuclear spin relaxation [9]. In this pulse sequence an additional radio frequency (rf) pulse applied after echo detection helps the total spin system to recover to a thermal equilibrium in a much shorter time limited only by T_{1e} instead of T_{1n} as in case of the Davies ENDOR experiment. The length of the two rf pulses employed in the modified Davies ENDOR was $t_{\pi/2} = 36\,\mu s$. EPR measurements at 140 GHz were performed on a D-band EPR setup at 4.2 K.

3. Results

Fig. 2a shows the D-band EPR spectrum observed in n-type 6H-SiC wafers with donor concentration of about $(N_D–N_A) \approx 10^{16}\,cm^{-3}$ for $\boldsymbol{B}||\boldsymbol{c}$. The EPR spectrum displays intense hf triplet lines of ^{14}N on the two quasi-cubic (N_{c1}, N_{c2}) sites. Because of high compensation of the sample the single EPR line with unresolved hf splitting due to the N_h with $g_{||} = 2.0048(2)$ was not observed in EPR spectrum. The reason is that N_h has a substantially more shallow energy level ($E_i = 81.04$ meV) than N_{c1}, N_{c2} and as a result its level is not occupied in compensated samples and the EPR spectrum of the N donors on hexagonal (h) sites was not detectable [10]. The intensity ratio between N triplet lines due to the quasi-cubic sites was found to be about $I_{Nc1}/I_{Nc2} = 0.7$ indicating that the N_{c2} with the deeper energy level ($E_i = 142.4$ meV) is mostly occupied.

As seen in Fig. 2a some additional lines are observed in the D-band EPR spectrum. But even at high frequency these additional lines are overlapping with the two N_{c1}, N_{c2} triplet lines. A deconvolution of the experimental D-band EPR spectra was performed by using Easy-Spin-3.0.0 toolbox program [11]. The EPR spectrum of n-type 6H-SiC is fitted with the five triplets lines. Two of them belong to the N_{c1} and N_{c2} and three other triplets, labelled N_1, N_2, N_3, were likewise attributed to N related centers. It should be noted that due to low concentration of donors ($10^{16}\,cm^{-3}$), the D-band EPR spectrum was recorded in the saturation conditions. Therefore the agreement between experimental and simulated spectrum is not so excellent.

Fig. 2b shows an X-band FS ESE spectrum in highly compensated n-type 6H-SiC measured at 6 K for $\boldsymbol{B}||\boldsymbol{c}$. The spectrum displays a superposition of two N triplets corresponding to the N donor occupying N_{c1}, N_{c2} lattice sites. The high intensity of the central line of N_{c1}, N_{c2} triplets indicates that it coincides with

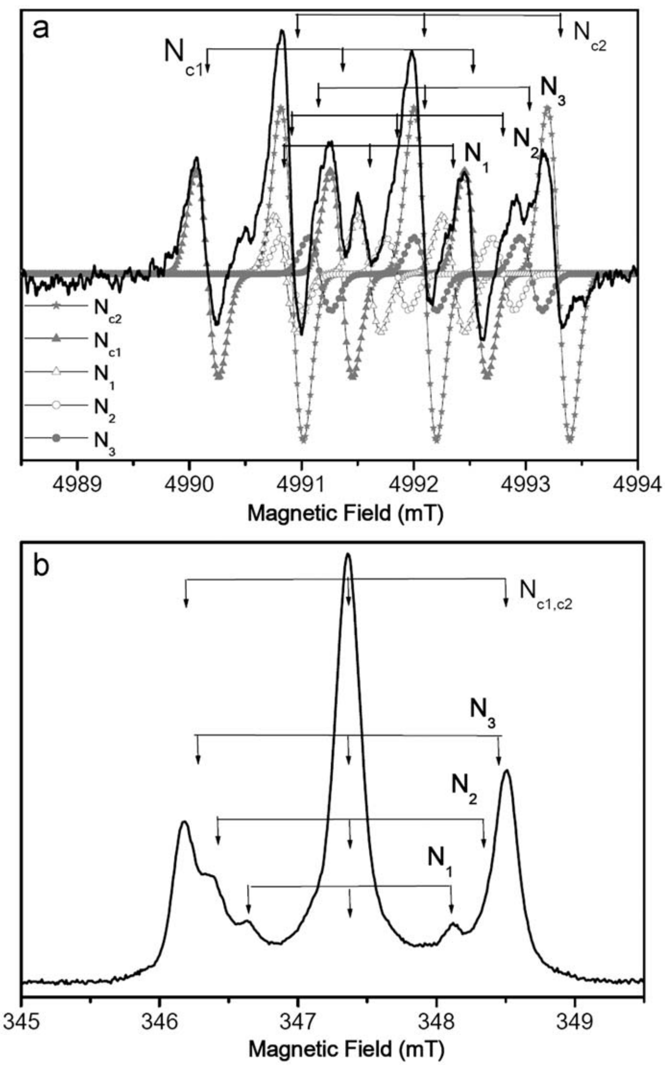

Fig. 2. D-band EPR (a) and X-band FS ESE (b) spectrum measured on highly compensated n-type 6H-SiC wafers with $(N_D–N_A) \approx 10^{16}\,cm^{-3}$ measured for $\boldsymbol{B}||\boldsymbol{c}$ at $T = 4.2$ K (a) and $\boldsymbol{B}\perp\boldsymbol{c}$ at $T = 6$ K (b). Solid lines—experimental spectra, lines with symbols—simulated spectra, for parameters see Table 1.

Table 1
The g-values and hf splitting for N donors obtained in highly compensated n-type 6H-SiC with $(N_D–N_A) \approx 10^{16}\,cm^{-3}$ from EPR, FS ESE and pulsed ENDOR data.

Center	N_{c2}	N_{c1}	N_1	N_2	N_3
$g_{\|\|}$	2.0037(2)	2.0040(2)	2.0039(2)	2.0038(2)	2.0037(2)
$g_{\perp}$	2.0030(2)	2.0026(2)	2.0030(2)	2.0030(2)	2.0030(2)
$A_{\|\|}$ (MHz)	33.32	33.6	21.04	26.43	29.77
$A_{\perp}$ (MHz)	33.32	33.6	21.04	26.43	29.77

the central line of the three N_1, N_2, N_3 triplet subspectra. The two other lines of these triplets are partially resolved between the triplet lines of N_{c1} and N_{c2}. The analysis of the angular dependences of the D-band EPR and X-band FS ESE spectra of the N donors observed in highly compensated n-type 6H-SiC yielded the spin-Hamiltonian parameters given in Table 1. The hf splitting for N_1, N_2, N_3 were found to be isotropic and smaller than those for N_{c1} and N_{c2}. But in contrast to the N_x center, having exactly half of the hf splitting of the N_{c2} in low compensated