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The spin relaxation of nitrogen donors in 6H SiC crystals as studied by the electron spin echo method

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We present the detailed study of the spin kinetics of the nitrogen (N) donor electrons in 6H SiC wafers grown by the Lely method and by the sublimation "sandwich method" (SSM) with a donor concentration of about $10^{17} \, cm^{-3}$ at $T = 10$–$40 \, K$. The donor electrons of the N donors substituting quasi-cubic "k1" and "k2" sites ($N_{k1,k2}$) in both types of the samples revealed the similar temperature dependence of the spin-lattice relaxation rate (T_1^{-1}), which was described by the direct one-phonon and two-phonon processes induced by the acoustic phonons proportional to T and to T^9, respectively. The character of the temperature dependence of the T_1^{-1} for the donor electrons of N substituting hexagonal ("h") site (N_h) in both types of 6H SiC samples indicates that the donor electrons relax through the fast-relaxing centers by means of the cross-relaxation process. The observed enhancement of the phase memory relaxation rate (T_m^{-1}) with the temperature increase for the N_h donors in both types of the samples, as well as for the $N_{k1,k2}$ donors in Lely grown 6H SiC, was explained by the growth of the free electron concentration with the temperature increase and their exchange scattering at the N donor centers. The observed significant shortening of the phase memory relaxation time T_m for the $N_{k1,k2}$ donors in the SSM grown sample with the temperature lowering is caused by hopping motion of the electrons between the occupied and unoccupied states of the N donors at N_h and $N_{k1,k2}$ sites. The impact of the N donor pairs, triads, distant donor pairs formed in n-type 6H SiC wafers on the spin relaxation times was discussed. © 2016 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4945438]

I. INTRODUCTION

Nowadays, the relaxation processes in the spin systems are of great interest because of the spintronics development and the prospects for building the quantum computers on the basis of the shallow donors in semiconductors like the phosphorus donors in silicon (Si:P) or GaAs quantum dots. The reason is that the electrons bound to shallow donors have rather long spin-lattice relaxation (SLR) (T_1) and phase memory (T_m) times to maintain fidelity of gate operations for a nuclear spin quantum computer. Particularly, the T_m time, which is more relevant for the quantum information processing, is required to be no shorter than a few microseconds.[1] At the low donor concentrations ($<10^{16} \, P/cm^3$), the T_1 time in Si:P varies from microseconds at $20 \, K$ to thousands of seconds at $2 \, K$[2,3] and is independent of the phosphorus concentration. The phase memory time in the isotopically purified ^{28}Si:P was estimated to be $T_m \sim 60 \, ms$ at $7 \, K$.[1] At the same time, the experiments on the isolated donors in n-type silicon carbide (SiC) have shown that the shallow nitrogen (N) donors in 6H polytype of SiC have a sufficiently long T_m time at temperatures higher than in Si:P.[4] It was found that

the T_m time exceeds $100 \, \mu s$ at $50 \, K$ (125, 333, and $588 \, \mu s$ at $50 \, K$, $40 \, K$, and $20 \, K$, respectively) for the shallow N donors substituting quasi-cubic ("k1," "k2") sites ($N_{k1,k2}$) in 6H SiC with a donor concentration ($N_D - N_A) \approx 1 \times 10^{17} \, cm^{-3}$ (N_D and N_A are donor and acceptor concentrations, respectively),[4] according to the pulsed electron paramagnetic resonance (EPR) studies. It was expected that the T_m time should be increased if the donor concentration is lowered.

While the values of the spin relaxation times were found in 6H SiC for $N_{k1,k2}$ donors, there are no data about the T_1 and T_m times for the N donors substituting hexagonal "h" position (N_h) and the mechanism of relaxation times in SiC remains still poorly understood in the wide temperature range. The data available in the literature concern mostly the concentration dependence of the spin-lattice relaxation (SLR) rate (T_1^{-1}) for the N donors without accounting for the difference in the behavior of the SLR for N_h and $N_{k1,k2}$ centers in 6H SiC.[5]

It is known that the EPR spectra of N donors in SiC are inhomogeneously broadened due to the superhyperfine interaction with ^{29}Si and ^{13}C nuclei,[6,7] and homogenous line broadening contributions due to spin relaxation processes are difficult to extract from the continuous wave (CW) EPR line widths. In contrast to CW EPR measurements, the electron spin echo (ESE) experiments provide the opportunity to

measure independently both spin relaxation times T_1 and T_m. Therefore, the measurements of relaxation times using ESE spectroscopy allow to identify the value of the relaxation time T_m which does not depend on magnetic field inhomogeneity nor on hyperfine (hf) coupling and hence has an advantage over the EPR linewidth method.[8] Moreover, at $T < 20$ K, the N donors in SiC have long T_1 times and the two-pulse sequence that gives an ESE is repeated faster than about once every five times the T_1 relaxation time, so that the spin system will not return to equilibrium between pulse sequences. In this case, the z-magnetization is decreased, less magnetization is available to project into the xy plane, and the ESE amplitude is decreased.[8] As a result, the T_1 time can be determined from the dependence of the ESE amplitude on pulse repetition rate and if the spectral diffusion makes a constant contribution over the range of repetition times used, the measured T_1 approximates the actual T_1.[8] Thus, at $T < 20$ K, the described technique has an advantage over the inversion-recovery pulsed EPR methods that are affected by spectral diffusion effects taking place and saturation recovery experiments which are less subjected to spectral diffusion but are experimentally more demanding in general.[9]

In the present work, we report a new comprehensive study of the temperature behavior of the T_1 and T_m times for $N_{k1,k2}$ and N_h donors in 6H SiC crystals grown by different methods in the temperature range of 4.2–40 K, employing the ESE phenomenon to get the detailed information about the mechanism of the relaxation processes.

II. MATERIALS AND METHODS

The n-type 6H SiC wafers with $(N_D - N_A) \approx (1–5) \times 10^{17}$ cm^{-3} were grown by the Lely method and the sublimation "sandwich method" (SSM).[10,11] The growth of the n-type 6H SiC wafers by the modified Lely method was carried out around 2200–2400 °C of the growth temperature and 30–50 mbar of Ar pressure with the growth rate of 1.2 mm/h on [0001] Si face using polycrystalline SiC as source materials. The growth of the n-type 6H SiC wafers by SSM was carried out at 1900 °C with the growth rate of 0.2 mm/h on the [0001]C face in a tantalum container under Si excess partial pressure using SiC micropowder with Si/C ~ 1.05 as a source of vapor composition. The size of the samples was about $7 \times 4 \times 0.3$ mm.

The CW and pulsed EPR measurements were performed on X-band (9.4–9.7 GHz) Bruker ELEXYS E580 spectrometer in the temperature range from 130 K to 10 K. The CW EPR experiments were carried out using the ER 4122 SHQE SuperX High-Q cavity, while for the pulsed EPR measurements the EN 4118X-MD4 cavity was used. The field sweep detected electron spin echo (FS ESE) spectra were measured using two-pulse Hahn echo sequence: $\pi/2 - \tau - \pi - \tau -$ echo with the pulse lengths: $\pi/2 = 96$ ns, $\tau = 600$ ns, and $\pi = 192$ ns. The T_1 time of paramagnetic centers (PCs) was estimated from ESE signal intensity changing under the variation of the shot repetition time,[9] while the T_m time was determined from the two-pulse ESE decay.

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. The temperature behavior of the CW EPR and FS ESE spectra in 6H SiC crystals

Fig. 1 shows the X-band CW EPR spectra of N donors observed in Lely grown 6H SiC and in 6H SiC grown by SSM in the temperature range from 60 K to 130 K. At 60 K, the EPR spectrum consists of two overlapping triplet lines from N_{k1} ($g_{||} = 2.0040(3)$, $g_\perp = 2.0026(3)$, $A_{||} = A_\perp = 1.20$ mT) and N_{k2} ($g_{||} = 2.0037(3)$, $g_\perp = 2.0030(3)$, $A_{||} = A_\perp = 1.19$ mT) donors.[6] The central line of $N_{k1,k2}$ triplets coincides with the EPR spectrum of N_h ($g_{||} = 2.0048(3)$, $g_\perp = 2.0028(3)$) representing the line with a small unresolved hyperfine (hf) splitting ($A_{||} = 0.1$ mT, $A_\perp = 0.08$ mT).[7] Along with the EPR spectrum from the isolated N centers, the lines of comparatively low intensity are observed in-between of $N_{k1,k2}$ triplet lines. In accordance with Ref. 6, the N_x lines ($g_{||} = 2.0043(3)$, $g_\perp = 2.0029(3)$, $A_{||} = A_\perp = 0.6$ mT) were attributed to the triplet center with $S = 1$ responsible for the distant donor pairs between the N atoms residing at quasi-cubic and hexagonal sites ($N_{k1,k2}Si_kN_h$). It is clearly seen from Fig. 1 that the contribution of the distant donor pairs in the EPR spectrum of the N donors in SSM grown 6H SiC is small. The detailed analysis of the temperature behavior of CW EPR spectra in both samples was undertaken in Ref. 12. Particularly, from the simulation of the ESR spectra measured in the 6H SiC samples at 60 K, the relative intensity ratio $I(N_{k2})$: $I(N_{k1})$: $I(N_h)$: $I(N_x)$ was found to be 1.0: 1.3: 1.9: 0.2 for the Lely grown and 1.0: 0.9: 3.0: 0.1 for the SSM grown 6H SiC samples. Thus, the intensity of the EPR line from N_h donors with respect to that of $N_{k1,k2}$ triplet lines is higher in SSM grown 6H SiC than in the
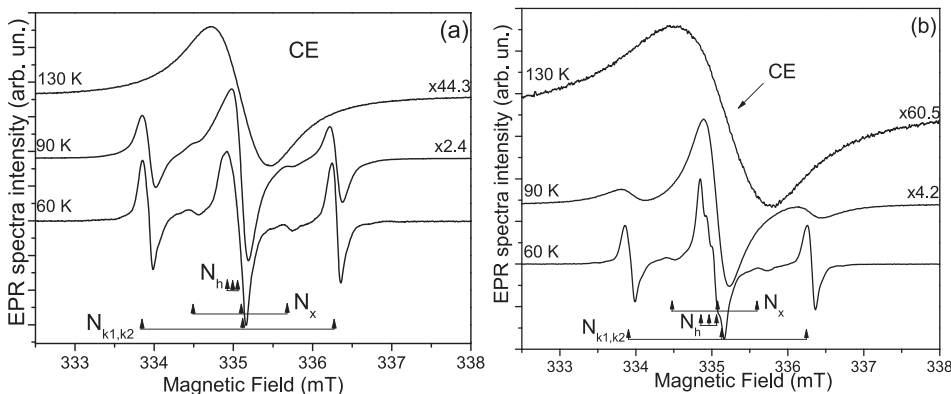

FIG. 1. The temperature behavior of the X-band EPR spectra measured in Lely (a) and SSM grown (b) 6H SiC samples measured from 60 K to 130 K, **B**||**c**. On the right side of each spectrum, the multiplication unit of the EPR spectra intensity is pointed with respect to the intensity of the EPR spectra measured at 60 K that was taken equal to 1.
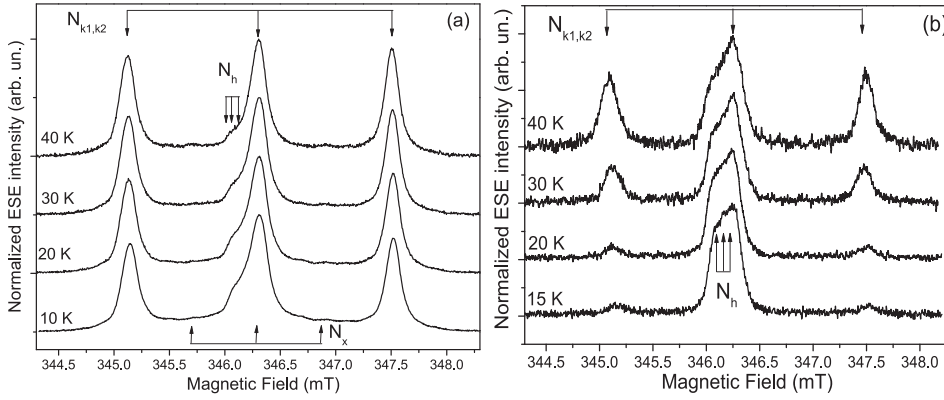
FIG. 2. The temperature behavior of the FS ESE spectra measured in Lely grown (a) and grown by SSM (b) 6H SiC, **B**||**c**. The shot repetition time for the Lely grown sample was set to 12.24 ms, for SSM grown sample it was 10.2 ms at $T = 40$–20 K and 40.8 ms at $T = 15$ K.

Lely grown 6H SiC sample indicating that N_h donors are mostly in isolated state in 6H SiC grown by SSM. And the intensity of N_x triplet is lower in SSM grown sample than in the Lely grown 6H SiC.

With the increase in temperature up to 70 K, the single line of Lorentzian shape with $g_{||} = 2.0043(3)$, $g_\perp = 2.0030(3)$ appears in the EPR spectrum. The emergence of the single EPR line is accompanied by the disappearance of the N_h EPR line at 80 K and $N_{k1,k2}$ triplet lines at 100–110 K. In accordance with Ref. 12, the observed single Lorentzian line with the temperature-dependent linewidth and intensity was attributed to the conduction electrons (CE).

A further decrease of the temperature to 40 K gives rise to the saturation of EPR spectra in both types of the samples due to the increase of the spin relaxation times of the N paramagnetic centers and, as a result, the measurements of the T_1 and T_m times of N centers become possible using the ESE phenomenon at $T < 40$ K. It should be noted that saturation effect can be reduced by the registration of the EPR spectrum at high frequency due to the shortening of the spin-lattice relaxation time T_1 at high magnetic fields.[13]

Fig. 2 shows the two-pulse FS ESE spectra of N donors in the 6H SiC samples grown by the Lely method and by SSM in the range of 40–10 K. Comparing the temperature behavior of the intensity ratio between the N_h and $N_{k1,k2}$ FS ESE signals in both samples, one can see that it has a different character. The intensity ratio between N_h and $N_{k1,k2}$ FS ESE signals remains unchanged in the Lely grown 6H SiC sample in the whole temperature interval, while in 6H SiC grown by SSM, it varies significantly between 40 and 10 K. This indicates that in contrary to the Lely grown 6H SiC

sample, the spin relaxation times for N_h and $N_{k1,k2}$ donors in 6H SiC grown by SSM have a different temperature behavior.

B. The temperature dependence of spin relaxation times of N donor electrons in 6H SiC sample grown by the Lely method and by SSM

1. The temperature dependence of spin-lattice relaxation time

Fig. 3 shows the temperature dependence of the SLR rate in the temperature interval from 10 K to 40 K for donor electrons of $N_{k1,k2}$ and N_h in the 6H SiC samples grown by the Lely method and by SSM. As shown in Fig. 3(a), the SLR rate for $N_{k1,k2}$ donors increases continuously with the temperature increase in both 6H SiC samples and can be described by the classical spin-phonon interaction (under the condition $T \ll \theta_D$, where θ_D is the Debye temperature for crystal) as a relaxation process via the acoustic phonons

$$T_1^{-1}(T) = w_1 T + w_2 (T/\Theta_D)^9, \tag{1}$$

where T is the temperature (in K) and $w_{1,2}$ are the relaxation rates in the one-phonon direct process and in two-phonon process for spins in Kramers doublet states, respectively.

The solid lines in Fig. 3(a) show the calculated T_1^{-1} values using Eq. (1) that are well fitted with the experimental data using the parameters given in Table I. Analyzing the data in Table I, one can see that the SLR rate for $N_{k1,k2}$ donors has close values in both types of the samples.
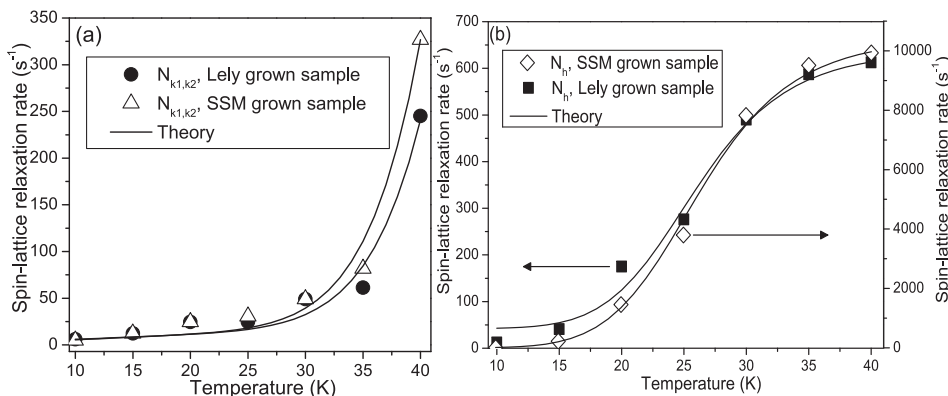

FIG. 3. The temperature dependence of SLR rate for the $N_{k1,k2}$ (a) and N_h (b) donors in 6H SiC samples grown by the Lely method and by SSM measured in the 40–10 K temperature range. Dots are experimental data and solid lines are the fitting using Eq. (1) (a) and Eq. (3) (b).

In contrast to the temperature behavior of the SLR rate for $N_{k1,k2}$ donors, the temperature dependence of the SLR rate for N_h centers at higher temperatures has smooth character and becomes flat at $T \geq 40$ K (see Fig. 3(b)). Such temperature behavior of the SLR rate occurs when the PC relaxes via the fast relaxing (FR) spin system through the cross-relaxation process. For the N_h donors, which have shallow energy levels and a larger radius of the wave function in comparison with $N_{k1,k2}$ donors, the CE may play the role of the FR spin system. In this case, in accordance with Ref. 15, the SLR involves two following steps: in the first step, the donor spin system transfers their energy to the FR spin system through the spin-spin exchange interaction and then, in the second step, the FR spin system relaxes fast via spin-lattice interaction. The relaxation rate is controlled by the slower step of the relaxation process and the whole process can be described by the following function:[15]

$$T_1^{-1}(T) = \frac{n_{FR} U W_{FR}}{(1 + N_d/n_{FR}) n_{FR} U + W_{FR}}, \qquad (2)$$

where n_{FR}, N_d are the concentrations of the FR spin system and shallow donors, respectively, $(N_d/n_{FR} \gg 1)$, U represents cross-relaxation rate between two spin systems and does not depend on the temperature, and $W_{FR}(T) = W_{FR,0} \times T^n$ is the rate of the SLR of the FR spin system, where $W_{FR,0}$ is the rate of SLR of FR system at $T = 1$ K.[15]

At low temperatures, the free electrons relax via a spin-orbit mechanism, and the SLR is described by the function: $W_{FR,0} \times (T)^5$. At high temperatures (when $W_{FR} \gg N_d U$), the T_1^{-1} becomes equal to $n_{FR} U$ and since the CE concentration is a temperature dependent value $n(T) \sim \exp(-E/kT)$, Eq. (2) becomes a continuously increasing function with the temperature. For this reason, the free electron spin system cannot be considered as a FR system for the N_h donor.

The second candidate that can be considered as the FR centers are exchange pairs or triads formed between PCs.[16] The distant donor pairs N_x cannot be considered as FR centers because their spin relaxation times are comparable with that for the N donors. The experimental curves plotted in Fig. 3(b) for the N_h donors are well described in Eq. (2) with the following function:

$$T_1^{-1}(T) = c_0 T + \frac{c_1 T^7}{c_2 + T^7}, \qquad (3)$$

where c_0 is the intrinsic SLR of the donor electrons at $T = 1$ K, $c_1 = n_{FR} \times U$ is the cross-relaxation rate, $c_2 = N_d \times U/W_{FR,0}$, and $W_{FR,0}$ can be calculated as $W_{FR,0} = (N_d/n_{FR}) \times (c_1/c_2)$.

The fitting parameters of Eq. (3) with experimental data are given in Table II. The $W_{FR,0}$ values were obtained with $n_{FR} \approx 2 \times 10^{11}$ cm^{-3}. The n_{FR} value was estimated as the concentration of the exchange pairs of the two N donor centers, when $N_d = 10^{17}$ cm^{-3}. Thus, the N_h donor electrons relax through the FR exchange pairs or clusters of the donor centers by means of the cross-relaxation process.

2. The temperature dependence of spin-spin relaxation time

It was found that the time decay of the ESE signal amplitude for the N donor centers in 6H SiC is described by a superposition of two exponential functions

$$I(t) = A_1 \exp(-t/T_{m,f}) + A_2 \exp(-t/T_{m,s}), \qquad (4)$$

where t is time, A_1, A_2 are constant values, and $T_{m,f}$ and $T_{m,s}$ are fast and slow components of ESE decay, respectively.

The main contribution to the ESE decay comes from the slow exponent $T_{m,s}$, while the exponent with the order of magnitude faster time $T_{m,f}$ gives the negligible small contribution to the total exponential decay of the ESE signal for the N_h donors in both types of the samples, as well as for the $N_{k1,k2}$ donors in the Lely grown 6H SiC. In contrast, the main contribution in the time decay of the ESE signal for the $N_{k1,k2}$ donors in 6H SiC grown by SSM is single exponential with a short decay constant $T_{m,f}$. As it is seen from Fig. 4, the temperature dependence of $T_{m,s}^{-1}$ and $T_{m,f}^{-1}$ rates extracted from the ESE time decay curves using Eq. (4) for the $N_{k1,k2}$ donors 6H SiC grown by the Lely method has an opposite character: the $T_{m,s}^{-1}$ grows while $T_{m,f}^{-1}$ decreases with the temperature increase.

Recording the curves of the ESE time decay at different temperature points, one can obtain the temperature dependence of the phase memory relaxation rate (T_m^{-1}) for the N donors in both samples as shown in Fig. 5. As can be seen from Fig. 5(a), the enhancement of the T_m^{-1} with the temperature increase was observed for the shallow N_h donors in both samples as well as for the $N_{k1,k2}$ donors in the Lely grown 6H SiC crystal. At the same time, in 6H SiC grown by SSM, the T_m^{-1} for the $N_{k1,k2}$ exhibits a dramatic increase with the temperature lowering (see Fig. 5(b)).

In principle, the T_m^{-1} value should be temperature-independent because it is determined by the local fields of spin-spin interactions of the PC. Therefore, the observed temperature dependence of the T_m^{-1} indicates that there is a significant spin-coupling between N donors and other spin system, which has a temperature-dependent behavior. Among such spin systems, the free electrons, having a

TABLE I. Relaxation rates of the one-phonon (w_1) and two-phonon (w_2) processes in 6H SiC samples grown by the Lely method and by SSM obtained from the fitting of Eq. (1) with experimental data for $N_{k1,k2}$ donors shown in Fig. 3.

Samples	w_1 (s^{-1})	w_2 (s^{-1})	θ_D (K)
Lely grown 6H SiC	0.5	8.9×10^{15}	1300
6H SiC grown by SSM[a]	0.55	6×10^{15}	1200

[a] θ_D for 6H SiC is 1200 K.[14]

TABLE II. The fitting parameters of Eq. (3) with experimental data for N_h donors.

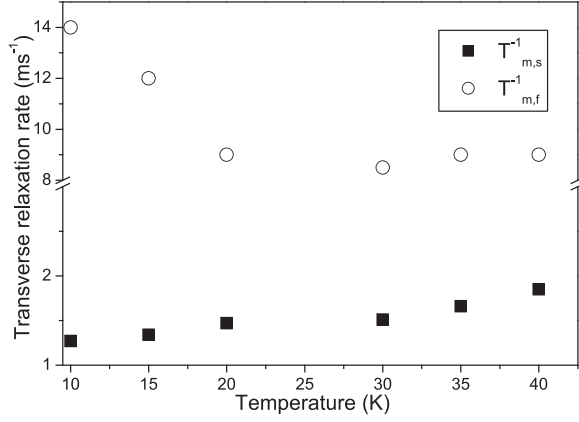| Samples	c_0 (s^{-1})	c_1 (s$^{-1} \times$ K^{-7})	c_2 (K^7), 10^9	$W_{FR,0}$ (s$^{-1} \cdot$ K^{-7})
Lely grown 6H SiC	12	6×10^2	8	4×10^{-2}
6H SiC grown by SSM	<2	1.05×10^4	10.7	6×10^{-1}

FIG. 4. The temperature dependence of $T_{m,s}^{-1}$ and $T_{m,f}^{-1}$ rates extracted from the ESE time decay curves for $N_{k1,k2}$ in Lely grown 6H SiC sample using Eq. (4).

temperature-dependent concentration value n, are the most suitable candidates. In this case, the T_m^{-1} is determined by the exchange interaction between N donors and free electrons, governing by the spin flip-flop rate, and will depend on the concentration of the free electrons n.

In the case of the weak compensation ($N_D \gg N_A$), the free electron concentration n as a function of the temperature is known as

$$n(T) = ((N_D - N_A)N_c)^{1/2} \exp{(-\Delta E_D/2kT)}, \qquad (5)$$

where $N_c = 2.8 \times 10^{15} \times T^{3/2}$ is a number of electron states in the conduction band for 6H SiC and $\Delta E_D = E_c - E_D$ is the distance between the conduction band bottom and the donor energy level. The free electron concentration in the conduction band (n) estimated from Eq. (5) varies from $1.4 \times 10^{11} \, \mathrm{cm}^{-3}$ to $2 \times 10^{13} \, \mathrm{cm}^{-3}$ with the temperature increase from 10 K to 40 K.

The spin-spin relaxation rate T_m^{-1} due to exchange scattering can be written as following:[15]

$$T_m^{-1}(T) = T_{m,0}^{-1} + U \times n(T). \qquad (6a)$$

Substituting Eq. (5) for $n(T)$ into Eq. (6a), one can get an expression for the temperature dependence of T_m^{-1}, which describes well the experimental data for the N_h and $N_{k1,k2}$ donors in the Lely grown 6H SiC and for the N_h donors in 6H SiC grown by SSM samples shown in Fig. 5(a):

$$T_m^{-1}(T) = T_{m,0}^{-1} + \frac{w_2}{1 + \left(1 + 8 \times (N_D/N_{c,0}) \times (300)^{3/2} \times \exp(\Delta E_D/kT)/T^{3/2}\right)^{1/2}}, \qquad (6b)$$

where $T_{m,0}^{-1}$ is the intrinsic phase memory relaxation rate of the (isolated) N donor spin, $N_{c,0} = 2.5 \times 10^{19} \times (m^*/m)^{3/2}$, and $w_2 = 2(N_D - N_A) \times U$ is the spin-spin relaxation rate caused by exchange interaction between donor and free electron spins. The results of fitting of Eq. (6b) with experimental T_m^{-1} values for the N_h and $N_{k1,k2}$ donors in the Lely grown 6H SiC and for the N_h donors in 6H SiC grown by SSM are shown in Fig. 5(a). The corresponding fitting parameters are represented in Table III.

Thus, the obtained data show that the exchange scattering plays an important role in the spin-spin relaxation process for the N donor spins. The ΔE_D values in Table III represent the distance between the bottom of the conduction band and the energy level of the shallowest donor N_h, which mostly contributes to the free electrons into the conduction band. The reduction of the activation energy values compared to that accepted for the N_h donors (80 meV)[17] can be explained by the formation of an impurity band when the concentration of N donors becomes high enough. In this case, the impurity band approaches the conduction band and the ionization energy of N decreases because the upper edge of the impurity band for N donors begins to play the main role in the thermal ionization process of the donor electrons.

As shown in Fig. 5(b), in 6H SiC grown by SSM the T_m^{-1} for the $N_{k1,k2}$ donors (in contrast to N_h) exhibits a dramatic enhancement with the temperature decrease and the
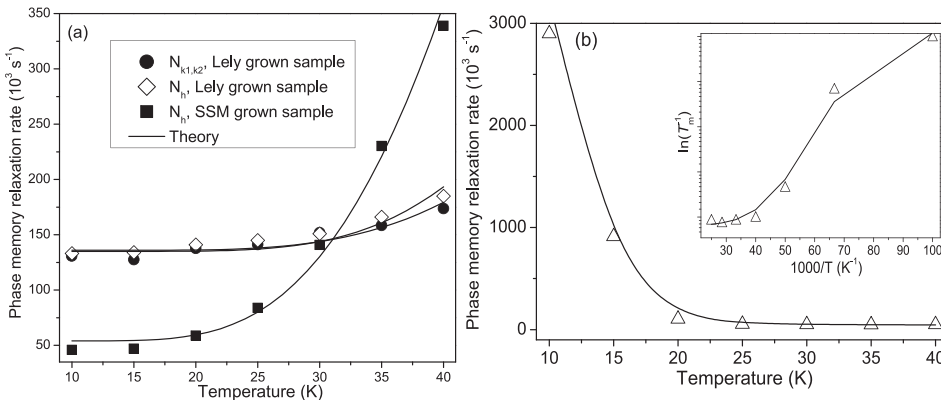

FIG. 5. The temperature dependence of T_m^{-1} for the $N_{k1,k2}$ and N_h donors in Lely grown 6H SiC, for the N_h donors in 6H SiC grown by SSM (a) and for the $N_{k1,k2}$ donors (b) in SSM grown 6H SiC. The inset of Fig. 5(b) shows the temperature dependence of T_m^{-1} in the logarithmic scale.

TABLE III. $T_{m,0}^{-1}$, w_2, and ΔE_D parameters for N_h and $N_{k1,k2}$ donors in Lely grown 6H SiC and N_h donors in 6H SiC grown by SSM obtained from the fitting of the experimental data with Eq. (6).

Samples	Donor	$T_{m,0}^{-1}$ (10^5 s^{-1})	w_2 (10^8 s^{-1})	ΔE_D (meV)	N_D, (10^{17} cm^{-3})
Lely grown 6H SiC	N_h	1.40	1.5	55.7	1.32
	$N_{k1,k2}$	1.35	1.4	55.7	1.32
6H SiC grown by SSM	N_h	0.5	0.45	32	2.4

main contribution to the time decay of the ESE signal amplitude for $N_{k1,k2}$ comes from the exponent with the $T_{m,f}$ time. The increase of the T_m^{-1} for $N_{k1,k2}$ donors can be explained by the influence of the hopping conduction process that occurred in 6H SiC grown by SSM. A small contribution of the $T_{m,f}^{-1}$ in T_m^{-1} for the $N_{k1,k2}$ and N_h donors in the Lely grown 6H SiC was likewise explained by the small effect of the hopping conduction process in this sample.

It should be noted that the known phenomenon of the "motional" narrowing of EPR linewidth (the latter is a reciprocal spin-spin relaxation time)[18] is caused by the hopping motion of electrons with the variable length of jumps[19] within the system of N donors and exchange interaction between the N donors and CE.[12,20]

For the $N_{k1,k2}$ donors in 6H SiC grown by SSM, the electron hopping motion induces the fluctuation of the local magnetic field at the donor site due to the exchange coupling between N donors and free electrons. Following Mott and Twose,[19] the fluctuation frequency is equal to the probability of the electron hopping between different sites

$$\tau_h^{-1}(T) = v_{ph} \exp((-T_0/T)^\lambda), \qquad (7)$$

with $\lambda = 1/4$, $1/3$, or $1/2$; and ν_{ph} is maximum of the acoustic phonon frequency (18.9 THz in 6H SiC).[19]

On the other hand, the randomly fluctuating magnetic field causes the spin diffusion due to the spin-spin interaction between N donors and free electrons, which leads to the random excitation of the spin system. In this case, according to the theory of the time evolution of spin density matrix, the kinetic equations for the transversal magnetization contain T_m^{-1} (the inverse time for relaxation of transversal component of magnetization), which is expressed through the Fourier transforms $j(\omega - \omega_0)$, $j(\omega)$ of the correlation functions c_h of the local magnetic field fluctuations[18]

$$M_\pm \times i(\omega - \omega_0) = -i\omega_1(M_z - M_0)$$
$$+ (j(\omega - \omega_0) + j(\omega)) \times M_\pm, \qquad (8)$$

where the real part of the right side of Eq. (8) plays the role of the inverse relaxation time $T_m^{-1} = j(\omega - \omega_0) + j(\omega)$, ω and ω_0 are the MW field and resonance magnetic field frequencies, respectively, ω_1 is the amplitude of the MW field, and M_z is the equilibrium value of z-component of the magnetization.

The correlation function of the local field fluctuations can be represented by the exponentially decaying function with the correlation time $\tau_h \ll T_m$ (Ref. 18)

$$c_h(t) = \gamma^2 \langle h_L \times (t + \tau) h_L \times (t) \rangle = \langle \gamma^2 h_L^2 \rangle \times \exp(-t/\tau_h), \qquad (9)$$

where $\gamma = (g\mu_B/\hbar)$ and $\langle h_L^2 \rangle$ is an average square of the exchange local field, when the exchange interaction between free electron spin system and donor spins is written as $\hat{H}_{ex} = \mathbf{h} \cdot \mathbf{M}$.

From Eq. (9), it follows that:

$$j(\omega - \omega_0) = \frac{\langle \gamma^2 h_L^2 \rangle \tau_h}{1 + (\omega - \omega_0)^2 \tau_h^2}, \qquad (10)$$

where τ_h is a correlation time of the electron hopping motion.

As a result, the experimental curve shown in Fig. 5(b) can be described by the expression

$$T_m^{-1}(T) = T_{m,0}^{-1} + \frac{w_h \exp((T_0/T)^\lambda)}{1 + (\omega - \omega_0)^2 w_h^2 \exp(2(T_0/T)^\lambda)}, \qquad (11)$$

with following parameters $T_{m,0}^{-1} = 4.5 \times 10^4$ s^{-1}, $w_h = 0.1$ s^{-1}, $T_0 = 3700$ K, and $\lambda = 1/2$. Comparing the obtained values with those given in Table III, it is seen that the intrinsic lifetime of the $N_{k1,k2}$ donor electron spins in the 6H SiC grown by SSM is longer (22 μs) than that (7.4 μs) in the Lely grown 6H SiC.

IV. CONCLUSIONS

The mechanisms of spin-lattice and spin-spin relaxation times for the N donor electrons substituting quasi-cubic ("k1," "k2") and hexagonal ("h") positions in n-type 6H SiC wafers grown by the Lely method and SSM with $(N_D - N_A) \approx 10^{17}$ cm^{-3} have been studied by pulsed EPR spectroscopy in the 10–40 K temperature range.

For $N_{k1,k2}$ donors in both types of the samples, the temperature dependence of SLR in the 10–40 K temperature range was described by the direct one-phonon and two-phonon relaxation processes via acoustic phonons proportional to T and to T^9, respectively, and it exceeds 204 ms in 6H SiC grown by SSM and 163 ms and the Lely grown 6H SiC at 10 K. The temperature behavior of the T_1^{-1} for donor electrons of N_h in both samples was explained by the cross-relaxation process between N_h and fast-relaxing centers. The T_1 time for N_h donors at 10 K becomes three times longer in 6H SiC grown by SSM ($T_1 = 244$ ms) as compared with that found in the Lely grown 6H SiC ($T_1 = 82$ ms).

The observed enhancement of the T_m^{-1} with the temperature increase for the N_h in both samples and $N_{k1,k2}$ in the Lely grown 6H SiC samples was explained as being caused by the exchange scattering of free electrons, which has a temperature-dependent concentration, on the N donors.

In contrast to the N_h donors, the time decay of the ESE signal amplitude for the $N_{k1,k2}$ donors in 6H SiC grown by SSM has a single-exponential behavior. The key new result is that the decay rate of the T_m^{-1} strongly increases with the temperature lowering. Such behavior was explained by the hopping motion of electrons between occupied and unoccupied sites of the $N_{k1,k2}$ and N_h centers with the variable jump length occurring in 6H SiC grown by SSM. At the same time with the increase of the temperature up to 40 K, when the low temperature hopping conduction process is not significant anymore, the spin decoherence time for the $N_{k1,k2}$ donors becomes comparable ($T_m = 20\,\mu s$) with that for the N_h donors at 10 K ($T_m = 21.79\,\mu s$) in 6H SiC grown by SSM. Thus, the presence of the hopping conduction process leads to the different spin dynamic process for the N_h and $N_{k1,k2}$ donors in 6H SiC. As a result, a small contribution of the $T_{m,f}^{-1}$ in T_m^{-1} for $N_{k1,k2}$ and N_h donors in the Lely grown 6H SiC was explained by only a minor hopping conduction process in this sample. The drastic reduced hopping conduction in the Lely grown 6H SiC can be explained by the formation of the distant donor pairs between N_h and $N_{k1,k2}$ donors, which reduce the concentration of the isolated N donors and prevent the hopping motion of the donor electrons between occupied and unoccupied sites of the $N_{k1,k2}$ and N_h centers. On the other side, the presence of the distant donor pairs between N_h and $N_{k1,k2}$ donors gives rise to the decrease of the spin lattice relaxation and spin decoherence time in the Lely grown 6H SiC. Thus, following the obtained results, we are able to conclude that the longer spin decoherence time for N donors may be achieved by reduction of the concentration of the donor clusters (pairs, triads, distant donor pairs) formed in SiC wafers during the growth. Therefore, from the technology point of view, the n-type 6H SiC wafers grown by SSM look more prospective for realizing the potential of N donors as a mainstay donor spin system in SiC for the engineering of spin qubits.

ACKNOWLEDGMENTS

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