Pulsed EPR studies of shallow donor impurities in SiC

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Abstract

Spin-lattice relaxation time ($T_1$) and phase memory time ($T_M$) of shallow donors in 3C-, 4H- and 6H-SiC have been measured in time domain by using pulsed EPR technique. The temperature dependence of $T_1$ suggests that the Orbach process should be frozen at relatively high temperatures. Shallow donors in SiC are promising in attaining a sufficiently long phase memory time at temperatures much higher than Si:P.

\section{1. Introduction}

Both electron and nuclear spins, which comprise two-level systems in the magnetic field, are potential candidates of quantum bits (qubits). The implementation of quantum algorithms has been demonstrated in liquid-phase NMR [1]. However, for practical information processing, liquid-phase NMR quantum computers (QC) are limited in increasing the number of qubits. Scalable solid-state QCs using spins in shallow donors of semiconductors have been proposed [2,3]. It is proposed that the modification of the donor wave function by the gate bias on each qubit should control both addressing through tuning of resonant frequency and qubit–qubit interaction for quantum logic operations through activation of exchange interaction [2]. While a long spin coherence time is easily achieved in nuclear spins, electron spins have advantages in terms of higher sensitivity for readout and feasibility to couple adjacent qubits. A critical issue in electron spin QCs is to achieve a sufficiently long phase coherence time.

Time-dependent fluctuations of local fields which lead to migrations of resonant frequency (spectral diffusion) cause dephasing of the electron spin precession. Thus, phase memory decay is usually much shorter than spin-lattice relaxation which involves changes of spin orientation. To attain a long phase memory time ($T_M$), the spin-lattice relaxation time ($T_1$) needs to be sufficiently long. In the electron spin of Si:P, $T_1$ is dominated by the Orbach process due to thermal excitation of donor state,

\begin{equation}
\frac{1}{T_1} = A \exp(-A/T),
\end{equation}

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where $\Delta$ is the energy separation between $1s(A_1)$ and $1s(T_2)$ \[4\]. Thus, in Si:P, a sufficiently long $T_M$ requires low temperatures at which the Orbach process described above is effectively frozen.

The motivation of our present work is to search for donor electrons in which the Orbach process is frozen at relatively higher temperatures. Spin relaxations of shallow donors in 3C-SiC ($E_g = 2.40$ eV), 4H-SiC ($E_g = 3.28$ eV), 6H-SiC ($E_g = 3.10$ eV) have been studied by using the pulsed EPR technique.

In pulsed EPR, transient signals produced by coherent excitation using strong and short microwave pulses are observed in the time domain. The microwave pulse is characterized by the turning angle $\theta_p$ through which the microwave field $B_1$ turns the electron spins. The free induction decay (FID), which is the decay of the transverse magnetization after a single pulse (normally with $\theta_p = 90^\circ$), would reflect the spin coherence time only if the signal should consist of a single spin packet. In solid state, EPR signals are usually inhomogeneously broadened, consisting of many overlapping spin packets with different resonant frequencies. Since the distribution of the frequencies causes destructive interference, FID decays rapidly. While FID corresponds to the Fourier-transform (FT) of the inhomogeneous broadening, the time domain signal which corresponds to FT of the spin packet is the 2-pulse echo decay in which the echo signal created by 2-pulse Hahn sequence ($90^\circ \cdots \tau \cdots 180^\circ \cdots \tau \cdots$ echo) is measured as a function of the interpulse delay $\tau$. The 2-pulse echo decay (the time constant of the decay is $T_M$) method does measure the spin coherence time by overcoming the inhomogeneous broadening. The measurement of $T_M$ for the ensemble of a large number of spins is useful in estimating the coherence time that a single spin should have.

2. Experimental

Nitrogen shallow donors were studied by using 6H-SiC crystal (Nippon Steel), 6H-SiC crystal (AIST), 4H-SiC crystal (Nippon Steel), and 3C-SiC film (HOYA). Phosphorus shallow donors were studied by using 6H-SiC crystal (Nippon Steel) which had been implanted with phosphorus ions ($5 \times 10^{13}$ cm$^{-2}$ at each of the nine stages of energy from 9 to 21 MeV at 800°C) and had been annealed at 1650°C \[5\].

Pulsed EPR measurements were carried out by using a Bruker ELEXYS 580 X-band EPR spectrometer.

3. Results and discussion

In 4H-SiC, each of silicon and carbon has two inequivalent sites with either hexagonal ($h$) or quasicubic ($k$) character. In 6H-SiC, each of silicon and carbon has one hexagonal ($h$) and two quasicubic sites ($k_1, k_2$). In both 4H-SiC:N and 6H-SiC:N, the signal from the hexagonal site overlaps with the central hyperfine line of quasicubic site(s). In 6H-SiC, spectra of the two quasicubic sites 6H-SiC:N($k_1, k_2$) were not resolved at the external magnetic field along [0 0 0 1]. The $P_{\alpha}, P_{\beta}$ spectra corresponding to two quasicubic sites of 6H-SiC:P are observed \[5–7\]. Our time-domain measurements were carried out with the magnetic field fixed at the high-field component of $^{14}$N($I = 1$) or $^{31}$P($I = \frac{1}{2}$) hyperfine structure of the quasicubic sites with $B//[0 0 0 1]$. Our measurements of $T_1$ and $T_M$ were carried out without distinguishing the $k_1, k_2$ sites in 6H-SiC.

3.1. Spin-lattice relaxation time

A pulse sequence of inversion recovery ($180^\circ \cdots \tau \cdots 90^\circ \cdots \tau \cdots 180^\circ \cdots \tau \cdots$ echo; $\tau$ is fixed; $t$ is scanned) was used to measure $T_1$. The first pulse creates a non-equilibrium population. The Hahn echo generated by the second and third pulses monitors the recovery to the thermal equilibrium population.

The inversion recovery curve of 6H-SiC: N($k_1, k_2$) and 4H-SiC:N($k$) was well fitted by a single exponential function. The inversion recovery curve of 6H-SiC:P($k_1, k_2$) obtained suggests a considerable distribution of $T_1$, which is likely to be arising from a variation of environment such as differences in the local concentration of phosphorus donors and in the kinds and the distances of nearby defects. Here, we used the shorter one of
the two time constants obtained by fitting to the inversion recovery curve to a biexponential function, since the part of the spins contributing to the slower recovery might come from the overlapping nitrogen spectrum. Temperature dependence of $T_1$ is shown in Figs. 1 and 2. In Fig. 1, $T_1$ of Si:P [4,8] is included. It is noted that the curves of the temperature dependence of $T_1$ of SiC:N and SiC:P are significantly shifted to a higher temperature range compared to that of Si:P. Thus, in the shallow donors in SiC, it is expected that the temperature range, where the 2-pulse echo decay is dominated by the spin lattice relaxation, should be shifted to higher temperatures compared to that of Si:P.

As seen from Fig. 2, the temperature dependence of $T_1$ is described by the Orbach process (Eq. 1). The donor energies $(E_{CB} - E_D)$ are 110 meV ($k_1, k_2$) for 6H-SiC:P [9], 137.6 meV ($k_1$) and 142.4 meV ($k_2$) for 6H-SiC:N, 91.8 meV ($k$) for 4H-SiC:N [6]. The valley-orbit splittings [1s(A1)-1s(E)] determined from the IR measurements are 62.3 meV ($k_1$) and 61.1 meV ($k_2$) for 6H-SiC:N, 45.5 meV ($k$) for 4H-SiC:N [6]. The values of $\Delta$ obtained from the temperature dependence of $T_1$ are 77 meV ($\Delta_1$, high-temperature range) and 44 meV ($\Delta_2$, low-temperature range) for 6H-SiC:N($k_1, k_2$), 59 meV for 4H-SiC:N($k$), and 52 meV for 6H-SiC:P($k_1, k_2$). If we assign $\Delta$ of the $T_1$ measurements to the valley-orbit splitting, we note some discrepancy between those estimated from $T_1$ measurements and those from IR.

3.2 Phase memory time

The 2-pulse echo decay at low temperatures was dominated by instantaneous diffusion effect [10,11], since $T_M$ in our case was long. Among various sources of inhomogeneous broadening, one arising from dipole–dipole interactions among the electron spins within $\sim B_1$ of resonance does contribute to the echo decay, since the flipping of electron spins induced by 180° pulse instantly changes the sign of the local field. Since a random distribution of dilute electron spins gives a Lorentzian line broadening in the frequency domain; the single-exponential decay is observed in the time domain. The instantaneous diffusion effect is decreased by using a second pulse of a smaller flipping angle. The echo decays measured by using a pulse sequence $(\theta_p/2 \cdots \tau \cdots \theta_p \cdots \tau \cdots \text{echo}, \tau \text{ scanned})$ are described by [11]

$$E(2\tau) = E_0 \exp(-2b(\theta_p)\tau),$$  

(2a)

$$b(\theta_p) = 1/T_M + \gamma <\Delta B_{\text{dip}}> \sin^2(\theta_p/2),$$  

(2b)
where \( \langle \Delta B_{\text{dip}} \rangle \) is the average magnitude of the dipolar field. At each temperature, the echo decay was measured for 10 different values of \( \theta_p \) between 180° and 40°. From the plot of \( b(\theta_p) \) against \( \sin^2(\theta_p/2) \), \( T_M \) and \( \langle \Delta B_{\text{dip}} \rangle \) were determined. At high temperatures, the contribution of instantaneous diffusion to the 2-pulse echo decay becomes negligible with the decrease of \( T_M \).

In Fig. 3, temperature dependences of \( T_1 \) and \( T_M \) of 6H-SiC:N\((k_1, k_2)\) are plotted. It should be noted that \( T_M \) of 6H-SiC:N\((k_1, k_2)\)-NS exceeds 100 \( \mu \)s at 50 K (125, 333, 588 \( \mu \)s at 50, 40, and 20 K respectively). While \( T_1 \) is similar between two samples of 6H-SiC:N\((k_1, k_2)\), \( T_M \) of 6H-SiC:N\((k_1, k_2)\)-AIST is significantly shorter than that of 6H-SiC:N\((k_1, k_2)\)-NS. In 4H-SiC:N\((k)\), \( T_M \) was 69, 94, 103 \( \mu \)s at 40, 30, and 20 K, respectively.

Site-to-site variation in the local fields, arising either from dipolar interactions with the nearby electron spins or from those with the neighboring nuclei is a source of inhomogeneous broadening. The local field is determined by both the spatial arrangement of nearby spins and their \( M_S(m_1) \) values. The resonance frequency is changed from one spin packet to another by the local field fluctuations caused by electron spin flips, electron spin flip-flops, nuclear spin flips, and nuclear spin flip-flops [12]. When samples of natural isotope abundance are used, the variation of \( T_M \) among the same shallow donors in the same host crystals is likely to be caused by the difference in the donor concentration and by the difference in the kind and the concentration of paramagnetic impurities and defects.

The microwave pulses (pulse width \( \sim 32 \) ns for 180° pulse) excited only one component of the hyperfine structure. From \( \gamma \langle \Delta B_{\text{dip}} \rangle (\sim 3 \times 10^{14} \text{s}^{-1}) \) (Fig. 4), the concentration of donors is estimated to be \( \sim 1 \times 10^{17} \text{cm}^{-3} \) for 6H-SiC:N\((k_1, k_2)\)-NS, 4H-SiC:N\((k)\). In Si:P at 1.6 K, \( T_M \) decreases drastically when the donor concentration \([P]\) increases (100, 5, and 0.02 \( \mu \)s for 1.3 \( \times \) \( 10^{17} \), 2.0 \( \times \) \( 10^{17} \) and 3.1 \( \times \) \( 10^{17} \) \text{cm}^{-3} \), respectively) and is independent of \([P]\) for \([P]< \sim 7 \times 10^{16} \text{cm}^{-3} \) [13]. Thus, it is expected that \( T_M \) of 6H-SiC:N\((k_1, k_2)\) and 4H-SiC:N\((k)\) should be increased if the donor concentration is lowered.

In 3C-SiC:N, \( T_M \) was 168 \( \mu \)s at 20 K. 6H-SiC:P\((k_1, k_2)\) has a distribution in both \( T_1 \) and \( T_M \). The concentration of phosphorus donors of the region with high local concentration was estimated to be \( \sim 2.4 \times 10^{17} \text{cm}^{-3} \) from \( \gamma \langle \Delta B_{\text{dip}} \rangle \) by using a relatively high repetition rate of pulse sequence in accumulation at 5 K.

4. Summary

The shallow donors in SiC are promising in attaining long spin coherence time at temperatures higher than those required for Si:P, since the temperature range in which Orbach-type spin-lattice relaxation dominates the phase memory decay is shifted to higher temperatures.
References