Electron spin phase relaxation of phosphorus donors in nuclear spin enriched silicon

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(Dated: November 2, 2018)

PACS numbers: 03.67.Lx, 28.60.+s, 76.30.-v, 76.60.Lz

We report a pulsed EPR study of the phase relaxation of electron spins bound to phosphorus donors in isotopically purified $^{29}$Si and natural abundance Si ($^{nat}$Si) single crystals measured at 8 K. The two-pulse echo decay curves for both samples show quadratic dependence on time, and the electron phase relaxation time $T_M$ for $^{29}$Si is about an order of magnitude shorter than that for $^{nat}$Si. The orientation dependence of $T_M$ demonstrates that the phase relaxation is caused by spectral diffusion due to flip-flops of the host nuclear spins. The electron spin echo envelope modulation effects in $^{29}$Si are analyzed in the frequency domain.

Group-V impurities in silicon have been studied extensively in semiconductor physics. Experimental techniques such as infrared absorption, photoluminescence, and electron paramagnetic resonance (EPR) have revealed detailed properties of the impurity centers. EPR is particularly convenient for the identification of defect structures since the hyperfine (hf) interaction is a sensitive probe of the spatial distribution of the electron wavefunction. For instance, Feher and later Hale and Michier applied an electron nuclear double resonance (ENDOR) technique to this system, and measured hf interactions between the donor electron spins and their neighboring host nuclear spins. These experimental works, together with theoretical investigations, have deepened our understanding of shallow donor impurities.

Recently, Kane and others gave a new perspective to the donors in Si, a playground for solid-state quantum information processing, since nuclear and electron spins in semiconductors can be regarded as well-isolated two-level systems: qubits. If the donor electrons are qubits, $^{29}$Si nuclei that have spin-1/2 and occupy 4.67% of the lattice sites in natural Si ($^{nat}$Si) are decoherence sources as their flip-flops produce fluctuations of the lattice sites in natural Si ($^{nat}$Si). The orientation dependence of $T_M$ for $^{nat}$Si measured at 8 K. The temperature was chosen so that $T_M$ would not be affected by the spin-flip time $T_1$. The ground-state electron can be excited by absorbing a phonon if the phonon energy is comparable to the transition energy from the A ground state to the E or T$_2$ excited states. When returning to the ground state, the electron is subject to a spin-flip at a certain probability. This $T_1$ process, known as an Orbach process, also limits $T_M$ over the temperature range from 10 K to 20 K. Since $T_1$ is dominated by the Orbach process down to 6 K, and extends exponentially with cooling, $T_M$ starts to deviate from $T_1$ and becomes insensitive to the temperature below about 10 K. Since our spin echo experiments require each pulse sequence to be repeated at time intervals much longer than $T_1$, we found 8 K to be an appropriate temperature, low enough for $T_M$ not to be limited by $T_1$ but high enough to ensure a reasonable measuring time.

A Cz-grown single crystal of $^{29}$Si, enriched to 99.23%, had a rectangular shape with its long axis in the [110] orientation. The sample contained 1.8 $\times$ 10$^{15}$ P/cm$^3$ with the compensation of 1.0 $\times$ 10$^{15}$ B/cm$^3$. Further information on this crystal is provided in Ref. [12]. A $^{nat}$Si sample was cleaved from a commercial high-quality wafer containing 0.8 $\times$ 10$^{15}$ P/cm$^3$ with a negligible amount of compensation. The net donor concentrations of both samples were kept low so that the dipolar or exchange interactions between donors would be suppressed. Pulsed experiments were carried out using a Bruker Elexsys E580 spectrometer, and samples were kept in an Oxford ER4118CF cryostat. Temperature was controlled with an Oxford ITC503 temperature controller. The echo-detected EPR spectra, in which the intensity of the Hahn echo was measured as a function of the external magnetic field, consisted of two Gaussian-shaped lines separated by 4.2 mT. The splitting is due to the hf interaction with $^{31}$P, and each line is inhomogeneously broadened by the surrounding $^{29}$Si nuclei. The linewidths (FWHM) are 0.26 mT for $^{nat}$Si and 1.2 mT for $^{31}$P.
29Si. In the following experiments, the external magnetic field was set to the center of the line at higher fields (B0 = 348 mT), T1 was measured using an inversion recovery method (π-τ-π/2-τ-π-τ-echo), and is 16 ms for natSi and 4.4 ms for 29Si. As the temperature dependence of the Orbach process is given by 1/T1 = R exp(-Δ/kT), where R is the rate constant and Δ the valley-orbit split energy, the difference in T1 between samples could arise in part from a slight difference in the actual sample temperatures. The isotope shift of Δ is unlikely to cause the difference in T1, since it was not observed in our infrared photocconductivity measurement on the 29Si crystal within the resolution used. 12. The presence of compensation and dislocation (106 cm-2) in the 29Si crystal can alter T1, changing R. However, we can conclude that this difference in T1 has little effect on the difference in T_M presented below, based on the previous assumption that T1 does not contribute to T_M.

The phase relaxation was investigated using a two-pulse spin echo method (π/2-τ-π-τ-echo), where the interpulse delay τ was varied in 800 ns steps for natSi and 40 ns steps for 29Si. The τ/2 pulse was 16 ns.). The samples were rotated around the [110] axis perpendicular to B0. We define θ as the angle between B0 and [001]; therefore, θ = 0° when B0 || [001], θ = 55° when B0 || [111], and θ = 90° when B0 || [110]. Since the echo-detected EPR spectra were independent of the crystal orientation and no other EPR signals were found, the alignment of the crystal from an EPR signal was not applied here. We estimate the uncertainty in θ to be less than 5°. Figure 1 shows the echo decay curves at θ = 0° and 50°. Although so-called electron spin echo envelope modulation (ESEEM) obscures the echo envelope decays, they clearly obey a quadratic decay law, expressed as exp(-mτ^2). A single-exponential term exp(-2bτ) is, if present at all, quite small. Thus T_M can be defined as the time at which an echo envelope damps to 1/e of its initial value, i.e., T_M = 2m-1/2. We note that our temperature setting and assumption on the T1 effect are justified posteriori by the fact that the echo decay curves are not single-exponential and that T_M for each sample is much shorter than the respective T1.

The orientation dependence of T_M given in Fig. 2 shows T_M to be longest at θ = 0°, and shortest around θ = 50° ~ 60°. The dependence manifests the fact that the phase relaxation is caused by 29Si nuclei mutually coupled via the dipolar interactions. This can be verified by calculating the second moment M2 of the 29Si nuclear spin system. M2 calculated with Van Vleck’s method of moment is the sum of squared dipolar fields produced by the nuclei, and its inverse square root is a convenient measure of the nuclear T2. (M2)^-1/2 for a 100% 29Si crystal is shown in Fig. 2 by a dashed line. Correlations between the electron T_M and the nuclear M2 are apparent. As M2 directly reflects the strength of the nuclear dipolar couplings, its orientation dependence is understood qualitatively as follows: When B0 is along [111], one of the four nearest-neighbor bonds of the Si atoms is parallel to B0, and this pair of nuclei gives rise to the strongest coupling; hence, M2 takes its maximum. With B0 along [001], all the dipolar couplings between nearest neighbors are frozen since the angle between B0 and the vector connecting the nearest neighbors is a so-called magic angle; hence, M2 takes its minimum. In fact such an experimental T2 has been reported for NMR of 13C diamond, a material similar to 29Si. As the line-shape studies of NMR spectra for 13C diamond and 29Si have revealed that they share essentially the same line-broadening mechanism, T2 for 29Si will show the same tendency as that for 13C diamond if measured 15,20.

Although the comparison with M2 works qualitatively, it provides little information on the actual value of T_M.
Theoretical estimation of $T_M$ must take the hf interaction between the electron and host nuclei into account as well as the nuclear dipolar coupling. Generally, to characterize a system where the electron phase relaxation is caused by the spectral diffusion due to flip-flops of the host nuclear spins, the diffusion barrier that prevents the flip-flops within its bounds must be considered. As the Fermi contact hf interaction, which is proportional to the density of the electron wavefunction $|\psi(r_i)|^2$, varies from site to site, a flip-flop of a certain pair of nuclei occurs only when the difference of the hf interaction between the pair is small enough to satisfy the condition of energy conservation. The condition must be evaluated for each pair, since $|\psi(r_i)|^2$ does not decrease monotonically with increasing $r_i$ but oscillates due to the multi-valley nature of Si. Such a theoretical treatment has been proposed by de Sousa and Das Sarma, it is therefore interesting to compare our results with theirs. Theory predicts the observed angular dependence correctly, but overestimates $T_M$ by about a factor of 3 for both samples. This already-reasonable agreement becomes even better if we take the ratio of $T_M$ between the samples. Indeed, the theoretical ratio of $T_M$ for $^{29}$Si to that for $^{28}$Si falls between 11.2 and 11.8, while the experimental ratio lies between 11.2 and 14.4. Given the difficulty in determining the precise $T_M$ due to ESEEM, their calculation is in good agreement with our experiments. Another comparison is to take the ratio of the maximum ($\theta = 0^\circ$) and minimum ($\theta \sim 55^\circ$) $T_M$. Theory yields 2.7 for $^{28}$Si and 2.9 for $^{29}$Si, compared with experimental values of 2.0 for $^{28}$Si and 2.1 for $^{29}$Si. The larger values in the theory may indicate the presence of an isotropic contribution to $T_M$, but it is not clear at this stage whether other decoherence mechanisms must be incorporated or an improved theory of nuclear-induced spectral diffusion suffices to explain the discrepancies revealed here. Incorporating non-Markovian nuclear flip-flop processes would certainly be an interesting refinement of the theory, while the stochastic treatment proved valid even for $^{29}$Si. It is also noteworthy that recent multiple-pulse NMR studies in Si provide a glimpse into the complicated behavior of this seemingly-simple dipolar coupled system. Clearly, more experimental and theoretical investigation is necessary for a full understanding of the phenomena.

We now turn our attention to the remarkable feature of the decay curves: ESEEM. The origin of ESEEM can be described briefly as follows: If the nuclear spin feels, in addition to the external magnetic field, the moderate hf field produced by the electron spin, the nuclear spin precesses around an effective magnetic field which is tilted from the external magnetic field, i.e., $m_f$ is no longer a good quantum number. Due to this state mixing, formally forbidden nuclear-spin-flip transitions ($\Delta m_S = \pm 1, \Delta m_I = \pm 1$) can occur, and interfere with allowed transitions to produce beats in the electron spin echo envelope. In two-pulse experiments for an $S = 1/2, I = 1/2$ spin system, the modulation contains the ENDOR frequencies $\nu_+$ and $\nu_-$, and their sum and difference $\nu_+ \pm \nu_-$. When many nuclei are coupled to the same electron spin, some combination frequencies are also contained since the two-pulse ESEEM is the product of individual modulation functions.

We analyzed the ESEEM spectra in the frequency domain. Although ESEEM was also observed in $^{28}$Si, we treat only the case of $^{29}$Si here because the larger modulation depth in $^{29}$Si facilitated the analysis. Also, the modulation depth is strongly angular dependent (Fig. 1), since the degree of state mixing depends on both the position of each nuclear spin and the orientation of the external magnetic field. To obtain a frequency domain spectrum, the slowly decaying part of a time domain spectrum was subtracted first, then the remaining modulation was Fourier-transformed. Figure 3(a) shows the frequency domain spectra at $\theta = 0^\circ$, $50^\circ$, and $90^\circ$. Peaks around 3 MHz are the ENDOR lines, and their angular dependence is shown in Fig. 3(b), from which we see a $\langle 111 \rangle$-axis pattern. The ENDOR frequencies for an axially symmetric hf tensor with an isotropic $g$-factor are given by

$$\nu_{\pm} = \sqrt{\left(\nu_I \pm a_{iso} + b(3\cos^2\varphi_I - 1)\right)^2 + \left(3b\sin 2\varphi_I\right)^2},$$

where $\nu_I$ is the nuclear Larmor frequency, $a_{iso}$ the isotropic hf coupling constant, $b$ the anisotropic hf cou-
pling constant, $\varphi$, the angle between $B_0$ and the unique axis of the hf tensor. $\nu_j$ is calculated to be 2.94 MHz as the gyromagnetic ratio of $^{29}\text{Si}$ nuclei is 8.46 MHz/T. $\nu_2$, calculated with $a_{100} = 570$ kHz and $b = 681$ kHz agree well with the experimental results, as shown in Fig. 3(b). In comparison with hf constants obtained from previous cw ENDOR experiments, the observed peaks are assigned to shell E (111), i.e., four nearest neighbors of the donor. Lines A and B originate from (111) and (111) sites, respectively. Line C is doubly degenerate, since (111) and (111) sites locate each other at plane symmetric positions with respect to the (110) plane. The experimental data corresponding to line C at $\theta = 0^\circ$ and $10^\circ$ split, however. This suggests that the sample was not exactly rotated around the [110] axis but slightly off-axis, most likely due to a small miscut of the crystal. This assumption is supported by the fact that the ESEEM in $^{nat}\text{Si}$ at $\theta = 0^\circ$ did not split (not shown). The strong peak at 5.9 MHz is the sum frequency, but signals from shell A (004) are overlapped. The fourth harmonic is also observed at 11.8 MHz, and the third harmonic is barely visible around 9 MHz. We did not observe the third and fourth harmonics in $^{nat}\text{Si}$. We also observed tiny peaks at 5.2 MHz throughout the angles tested. They are assigned to shell B (440), but the detailed angular dependence is untraceable. A three-pulse stimulated echo method would be suitable for a more detailed ESEEM study. From the viewpoint of quantum computing, ESEEM clearly leads to quantum-gate errors. For this purpose, time domain analysis is highly desirable as recently simulated by Saikin and Fedichkin.

In conclusion, we have measured the phase relaxation time $T_M$ of P donor electron spins for $^{nat}\text{Si}$ and $^{29}\text{Si}$ at 8 K. $T_M$ for $^{29}\text{Si}$ is an order of magnitude shorter than that for $^{nat}\text{Si}$ due to much more frequent flip-flops of the host nuclear spins. The orientation dependence of $T_M$ agrees qualitatively with $(M_2)^{-1/2}$ for a 100% $^{29}\text{Si}$ crystal calculated with the method of moment, and quantitatively with the theory of de Sousa and Das Sarma. Frequency domain analysis revealed that ESEEM effects originate mainly from the hf interactions between the donor electron and its nearest neighbor nuclei, as suggested by Saikin and Fedichkin. Our results also provide insights into the localized electrons in III-V materials, such as GaAs, whose lattice sites are full of nuclei with non-zero spin. Their phase relaxation would be severely controlled by nuclear-induced spectral diffusion, therefore the experimental conditions must be arranged carefully so that the effects of nuclear spins may be suppressed, e.g., high magnetic fields, decoupling pulses, etc. In the near future we plan to prepare a series of samples with different $^{29}\text{Si}$ isotopic composition. Such samples will allow us to carry out systematic relaxation time studies of the electron and nuclear spins as a function of $^{29}\text{Si}$ concentration.

We thank H.-J. Pohl for the $^{29}\text{Si}$ crystal and R. de Sousa for valuable comments and kindly providing his calculation results. This work was supported in part by the Grant-in-Aid for Scientific Research No. 64076215.

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28. This tendency has also been suggested by A. M. Tyryshkin and S. A. Lyon experimentally (unpublished).
29. Theoretical values given here were provided by R. de Sousa (private communication).
30. In the present experiments, a step of $\tau$ was set to 40 ns,
hence the Nyquist frequency is 12.5 MHz. As the data were taken from $\tau = 320$ ns, all the modulation components that decayed within 320 ns cannot be recovered in the frequency domain spectra.