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 wave function. For instance, Feher and later Hale and Mieher 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 electron and nuclear spins in semiconductors can be regarded as well-isolated two-level systems: qubits. If the donor electrons are qubits, 29Si nuclei that have spin-1/2 and occupy 4.67% of the lattice sites in natural Si are decoherence sources as their flip-flops produce fluctuations of the local fields. Indeed, 29Si-depleted, isotopically controlled 28Si:P exhibited the coherence time of order of magnitude longer than 31P:P, demonstrating that such nuclear spin-depleted Si would be indispensable for building a practical Kane-type quantum computer. On the other hand, a study of the decoherence caused by the spectral diffusion arising from nuclear flip-flops requires a material of the opposite class, nuclear spin-enriched Si. This novel material is also interesting because of its similarity to III–V materials in that the electrons are localized in a sea of nuclear spins, and more preferable for our purpose owing to the negligibly small spin–orbit interaction in bulk Si, which could otherwise contribute to decoherence.

In this paper, we report the phase relaxation time \( T_M \) for P donor electron spins in isotopically purified 29Si and 31P 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 1 ground state to the \( E_2 \) 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 to 20 K. While \( T_1 \) 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 29Si, 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. 13. A \( ^{31} \)Si:P 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 Elexys 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 29Si nuclei. The line-widths (FWHM) are 0.26 mT for \(^{30} \)Si and 1.2 mT for \(^{30} \)P. In the following experiments, the external magnetic field was set to the center of the line at higher fields \( B_0=348 \) mT. \( T_1 \) was measured using an inversion recovery method \(( \pi-t/\pi/2-\pi-\tau-\tau-\text{echo})\),
and is 16 ms for nat Si and 4.4 ms for nat Si. 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 splitting energy, the difference in T1 between samples could arise in part from a slight difference in the actual sample temperatures. The isotope shift of samples could arise in part from a slight difference in the T1 does not contribute to TM.

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 nat Si and 40-ns steps for 29 Si. The duration of the π/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(−mτ2). A single-exponential term exp(−2βτ) is, if present at all, quite small. Thus, T1 can be defined as the time at which an echo envelope damps to 1/e of its initial value, i.e., T1 = 2m−1/2. We note that our temperature setting and assumption on the T1 effect are justified a posteriori by the fact that the echo decay curves are not single exponential and that T1 for each sample is much shorter than the respective T1.

The orientation dependence of T1 given in Fig. 2 shows T1 to be longest at θ = 0°, and shortest around θ = 50°. The dependence manifests the fact that the phase relaxation is caused by 29 Si nuclei mutually coupled via the dipolar interactions. This can be verified by calculating the second moment M2 of the 29 Si 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% 29 Si crystal is shown in Fig. 2 by a dashed line. Correlations between the electron T 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 13 C diamond, a material similar to 29 Si. As the line shape studies of NMR spectra for 13 C diamond and 29 Si have revealed that they share essentially the same line-broadening mechanism, T2 for 29 Si will show the same tendency as that for 13 C diamond if measured.

Although the comparison with M2 works qualitatively, it provides little information on the actual value of T1. Theoretical estimation of T1 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 wave function |Ψ(r)|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 \(r\), but oscillates due to the multivalley nature of Si. Such a theoretical treatment has been proposed by de Sousa and Das Sarma;\(^{24}\) it is therefore interesting to compare our results with theirs.\(^{25}\) 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 ratio of \(\langle u\rangle\) for \(^{29}\)Si, their calculation is in good agreement with our experiments. Another comparison is to take the ratio of the ESEEM maximum to the ESEEM minimum \(\langle u\rangle\). 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., \(m_I\) 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 \(\nu_e\) and \(\nu_{..}\), and their sum and difference \(\nu_{\pm} = \nu_e \pm \nu_{..}\). 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 \(^{29}\)Si, we treated only the case of \(^{29}\)Si here because the larger modulation depth in \(^{29}\)Si facilitated the analysis. Also, the modulation depth is strongly angle 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.\(^{29}\) 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 \((111)\)-axis pattern.\(^2\) The ENDOR frequencies for an axially symmetric hf tensor with an isotropic g factor are given by\(^{30}\)

\[
\nu_{\pm} = \nu_l \pm \frac{a_{iso} + b(3 \cos^2 \varphi - 1)}{2} + \frac{3b \sin 2\varphi}{4},
\]

where \(\nu_l\) is the nuclear Larmor frequency, \(a_{iso}\) the isotropic hf coupling constant, \(b\) the anisotropic hf coupling constant, and \(\varphi\) the angle between \(B_0\) and the unique axis of the hf tensor. \(\nu_l\) is calculated to be 2.94 MHz as the gyromagnetic ratio of \(^{29}\)Si nuclei is 8.46 MHz/T. \(\nu_{\pm}\) calculated with \(a_{iso}\) = 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,\(^2\) 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 (\(\bar{1}\)1\(\bar{1}\)) sites, respectively. Line C is doubly degenerate, since (1\(\bar{1}\)1) and (11\(\bar{1}\)) sites locate each other at plane symmetric positions with respect to the (1\(\bar{1}\)0) 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 [1\(\bar{1}\)0] axis, most likely due to a small misalignment of the crystal. This assumption is supported by
the fact that the ESEEM in $^{29}$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 $^{28}$Si. We also observed tiny peaks around 5.2 MHz throughout the angles tested. They are assigned to shell B (440), but the detailed angular dependence was untraceable. A three-pulse stimulated echo method would be suitable for a more detailed ESEEM study. From the viewpoint of quantum computing, ESEEM clearly agrees qualitatively with (M) $^{-1/2}$ for a 100% $^{29}$Si crystal calculated 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 nonzero 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 $^{29}$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 $^{29}$Si concentration.

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16This tendency has also been suggested by A. M. Tyryshkin and S. A. Lyon experimentally (unpublished).


20Theoretical values given here were provided by R. de Sousa (private communication).


25Theoretical values given here were provided by R. de Sousa (private communication).


29The present experiments, a step of $t$ = 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.
