Electron spin relaxation times of phosphorus donors in silicon

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Donor electron spins in phosphorus-doped silicon (Si:P) are a candidate two-level system (qubit) for quantum information processing. Spin echo measurements of isotopically purified ^{28}Si:P are presented that show exceptionally long transverse relaxation (decoherence) times, T_2, at low temperature. Below $\sim$10 K the spin decoherence is shown to be controlled by instantaneous diffusion and at higher temperatures by an Orbach process. T_2 for small pulse turning angles is 14 ms at 7 K and extrapolates to $\sim$60 ms for an isolated spin, over 2 orders of magnitude longer than previously demonstrated.

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Spin-based quantum information processing has recently occupied the attention of a considerable number of researchers. In the past few years several physical implementations of a spin quantum computer have been proposed, with both electron and nuclear spins, as well as combinations of the two suggested as qubits (quantum bits). Nuclear magnetic resonance (NMR) of small molecules has demonstrated a seven-qubit quantum computer.[1] Fullerene structures with trapped nitrogen and phosphorus atoms,[2] and shallow donors and quantum dots in semiconductors[3] have been proposed.

A long coherence time is the feature that makes spins attractive as qubits. Decoherence limits the number of elementary gate operations that can be performed, and while error-correction algorithms partially circumvent the effects of decoherence, it has been estimated that at least 10^4 operations must be performed within a coherence time.[4] Electrons bound to shallow donors in silicon were reported over 40 years ago to have long spin relaxation times[5,6] with phosphorus donors (Si:P) being the most extensively studied. At low donor concentrations ($<10^{16}$ P/cm^3), the longitudinal (spin-lattice) relaxation time, T_1, in Si:P was found to be independent of the phosphorus concentration, and it varies from microseconds at 20 K to thousands of seconds at 2 K.[5,7] The more relevant time for quantum information processing is the transverse relaxation time, T_2, which if measured for isolated spins can be associated with the decoherence time. In isotopically purified ^{28}Si:P, $T_2\sim 500\ \mu$s was previously reported.[6] It has been argued that maintaining the fidelity of gate operations requires that they be no shorter than a few microseconds,[8] thus implying $<10^3$ operations in the 500 μs. A less conservative estimate of the gate times would allow more operations, but it is important to have the longest possible coherence time to minimize the error-correction overhead.

Here we report a detailed study of T_1 and T_2 for P donors in ^{28}Si and natural Si over the temperature range 7–20 K using pulsed electron paramagnetic resonance (EPR). The key result is that the intrinsic T_2 (T_2 of an isolated spin) in ^{28}Si:P is determined to be at least 2 orders of magnitude longer than the earlier reports. After taking into account instantaneous diffusion (an effect arising from the dipole-dipole interactions of neighboring spins[9,10]), and overcoming some instrumental limitations, we have measured the intrinsic T_2 to be approximately 60 ms for a phosphorus donor in ^{28}Si at 7 K. These results show that electron spins in doped, isotopically pure ^{28}Si have long enough coherence times to be considered for quantum computation, including reasonable estimates of the time required for elementary gate operations.

Four silicon samples with different phosphorus concentrations were studied: two samples with 0.8×10^{15} and 1.7×10^{16} P/cm^3 in natural silicon (referred in the text as "Si:P-10^{15}" and "Si:P-10^{16}," respectively), and two samples with 0.87×10^{15} and 1.6×10^{16} P/cm^3 in isotopically purified ^{28}Si (referred as "^{28}Si:P-10^{15}" and "^{28}Si:P-10^{16}," respectively). Pulsed EPR measurements at X band (9.7 GHz) were done on a Bruker Elexsys 580 EPR spectrometer using a flex-line resonator (EN-4118MD4). Measurements at C band (4.7 GHz) and K_u band (16.3 GHz) were done on a multifrequency pulsed-EPR spectrometer described elsewhere.[11] Low temperatures were achieved using helium-flow cryostats (Oxford CF935). Temperature was controlled with a precision of better than 0.05 K using calibrated temperature sensors (Lakeshore Cernox CX-1050-SD) and Oxford ITC503 temperature controllers. This precision was required because of the strong temperature dependence of the relaxation times (for example, T_1 varies by five orders of magnitude between 7 K and 20 K).

An inversion recovery experiment and a two-pulse echo experiment were used to measure the longitudinal, T_1, and transverse, T_2, relaxation times, respectively. In the inversion recovery experiment (π-T-π/2-τ-π-τ-echo) the delay, T, after the first (inversion) pulse was varied while τ was kept constant, and the amplitude of the primary echo signal formed by the second and third pulses was measured. In the two-pulse echo experiment (π/2-τ-π-τ-echo), the amplitude of the echo signal was measured as a function of the interpulse delay, τ. The π/2 and π pulses in both experiments were 16 and 32 ns, respectively, allowing full excitation of the EPR lines.

The EPR spectrum of phosphorus donors in silicon consists of two lines centered at $g=1.9992$ and split by 41.94 G due to the hyperfine interaction with the ^{31}P nucleus.[12] At 15 K and below the EPR lines have a Gaussian shape, both in Si:P and ^{28}Si:P. This indicates that an inhomogeneous line

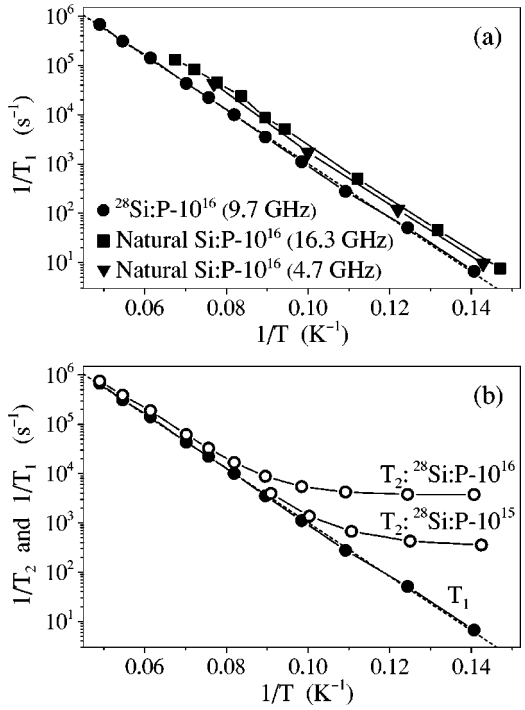

FIG. 1. Temperature dependence of the longitudinal, T_1, and transverse, T_2, relaxation times in (100)-oriented Si:P. (a) T_1 is shown at three microwave frequencies: in isotopically purified ^{28}Si:P-10^{16} at 9.7 GHz (●), and in natural Si:P-10^{16} at 16.3 GHz (■) and 4.7 GHz (▼). (b) T_2 is shown (○) for two samples, ^{28}Si:P-10^{16} and ^{28}Si:P-10^{15}, at 9.7 GHz. For reference, the T_1 dependence for ^{28}Si:P-10^{16} (●) is reproduced from (a).

broadening due to hyperfine interaction with ^{29}Si nuclei is the main source of the spectral linewidth in both samples. From comparing the EPR linewidths in Si:P-10^{16} and ^{28}Si:P-10^{16} ($\Delta B = 2.5$ and 0.08 G, respectively[13]), we estimate that the residual ^{29}Si concentration in ^{28}Si:P does not exceed 50 ppm. Most of the relaxation measurements were done on the high field component of the donor EPR spectrum, though essentially identical relaxation decays were seen at the low field component.

The longitudinal relaxation time in Si:P has already been studied in detail. A strong temperature dependence observed in the 2–20 K range was suggested to arise from an Orbach relaxation process.[7] An energy splitting, $\Delta E = 123$ K, was derived from fast-passage experiments using continuous wave (cw) EPR and shown to be a measure of the valley-orbit energy splitting of the P donor. Below 2 K T_1 was observed to stay approximately constant, limited by direct phonon processes.[5]

In the inversion-recovery experiments both the Si:P and ^{28}Si:P samples showed monoexponential decays, and T_1 was obtained by fitting to a simple exponential. The temperature dependence of $1/T_1$ obtained for ^{28}Si:P-10^{16} at 9.7 GHz is shown with filled circles in Fig. 1(a). The same temperature dependence was seen for the other samples. This confirms the previous observation that T_1 is independent of P concentration (at $<10^{16}$ P/cm^3), and also shows that T_1 does not change beyond typical run-to-run variations upon ^{29}Si depletion.[5,6] Quite remarkably, T_1 varies by 5 orders of magnitude over the temperature interval 7–20 K. In Arrhenius coordinates, $\ln(1/T_1)$ vs $1/T$, the dependence is linear which is consistent with an Orbach mechanism dominating the relaxation process at these temperatures [$1/T_1 \propto \exp(-\Delta E/kT)$ (Ref. 14)]. From the slope in this plot the energy gap to the excited state involved in the relaxation process is found to be $\Delta E = 126.1 \pm 0.5$ K, in good agreement with $\Delta E = 123$ K derived from the cw measurements.[7]

The measured dependence of T_1 extends over a significant temperature range, 7–20 K, and as a consequence a good fit of the experimental data cannot be obtained assuming a two-phonon Raman process with a power-law dependence of $1/T_1 \propto T^7$.[15] In principle, the Raman and Orbach mechanisms may contribute jointly to the T_1 relaxation processes. To evaluate a possible contribution of a Raman process, experiments were done at two additional microwave frequencies, $\nu_{mw} = 4.7$ and 16.3 GHz. The Raman process is expected to show a quadratic frequency dependence ($1/T_1 \sim \nu_{mw}^2$),[15] and its contribution should differ by an order of magnitude at these two frequencies. The T_1 data for Si:P-10^{16} included in Fig. 1(a) do not show a significant variation between 4.7 and 16.3 GHz (the slight differences most likely arise from offsets in the temperature calibrations). Thus, we may conclude that the contribution of the Raman process to T_1 is negligible, and the T_1 relaxation in Si:P is dominated by the Orbach process over the temperature range 7–20 K.

No detailed temperature dependence study of T_2 has been reported, but data from several authors show that T_2 also varies over a wide range, from 0.3 μs at 25 K to 0.6 ms at 1.6 K.[16,17] It was shown that T_2 saturates at considerably higher temperatures than T_1 and at considerably lower values (i.e., $T_2 = 0.6$ ms vs $T_1 = 3 \times 10^3$ s at 1.2 K).[5,17] The mechanism of this saturation has not been explained. In natural Si:P (4.7% ^{29}Si), nonexponential electron spin echo (ESE) decays were observed, best described by $V(t) = \exp(-t/T_2 - t^3/T_S^3)$.[6,17] The cubic exponential term was explained as being caused by spin diffusion in the nuclear ^{29}Si system.[17] This suggests that in isotopically purified ^{28}Si the term with T_S should vanish and pure exponential decays, presumably very long, should be observed. However, in their original work Gordon and Bowers reported only about a factor of 2 increase in T_M (defined as the $1/e$ point of the nonexponential echo decays) for ^{28}Si:P over natural Si:P at 1.4 K.[6]

The T_2 relaxation decays in the present study were measured using a conventional two-pulse ESE sequence. At long interpulse delay τ (>0.3 ms), we observed significant fluctuations in the phase of the detected echo signal with respect to the phase of the microwave source. These fluctuations originate from nonideal characteristics of the spectrometer and may result from phase instability of the microwave source or from fluctuations in the external magnetic field during the two-pulse experiment (these two types of fluctuation are indistinguishable in their effect on the relative phase of the echo signal). Because of this instrumental phase noise, repetitive summation of the echo signal using a conventional quadrature receiver (where the echo intensity is detected with

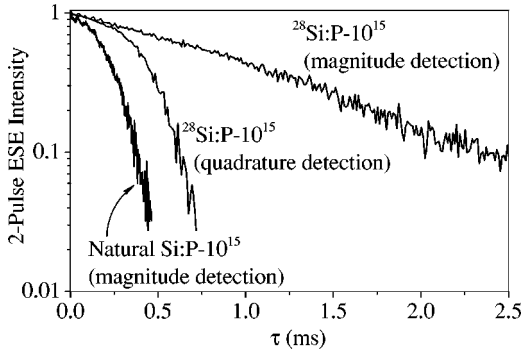

FIG. 2. Semilog plot of two-pulse ESE decay as a function of the interpulse delay, τ, for Si:P-10^{15} and ^{28}Si:P-10^{15} at 9.7 GHz. Two traces for ^{28}Si:P-10^{15} were measured as marked: by averaging the phased echo signal (using conventional quadrature detection) and by averaging the echo magnitude (i.e., disregarding the phase of the echo signal). The faster decay seen in the ''quadrature detection'' approach results from non-ideal characteristics of the pulse EPR spectrometer (phase fluctuations of the microwave source and/or fluctuations of the external magnetic field).

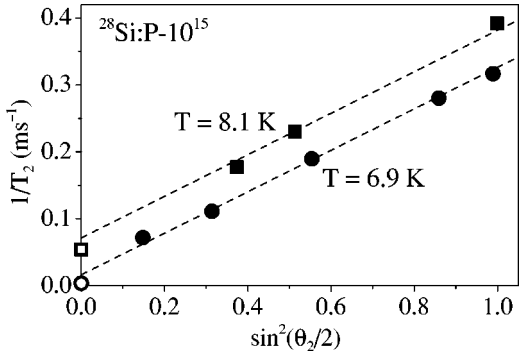

FIG. 3. Demonstration of the instantaneous diffusion contribution to T_2 in ^{28}Si:P-10^{15}, at 9.7 GHz and temperatures 8.1 and 6.9 K. $1/T_2$ (solid symbols) is plotted as a function of the turning angle (θ_2) of the second microwave pulse in a two-pulse ESE experiment. Open symbols on the y axis indicate $1/T_1$ at the respective temperatures. The slope of the linear fit (dashed lines) is proportional to the P concentration and the intercept corresponds to the intrinsic T_2 of an isolated donor-electron spin.

respect to the phase of the microwave source) resulted in distorted echo decays, with a strongly nonexponential behavior (see trace labeled ''quadrature detection'' in Fig. 2). To avoid this instrumental problem, we implemented a different approach of signal accumulation consisting of repetitive summation of the *magnitude* of the echo signal calculated as $[(\text{in phase})^2+(\text{out of phase})^2]^{1/2}$, where ''in-phase'' and ''out-of-phase'' are the signals from the two channels of the quadrature receiver. As a result, nearly exponential decays were recovered in ^{28}Si:P over the entire range of τ (labeled ''magnitude detection'' in Fig. 2).[18]

Figure 2 compares the two-pulse ESE decays in isotopically purified ^{28}Si:P-10^{15} and in natural Si:P-10^{15} (both measured with the magnitude detection approach). While the decay is nearly exponential in ^{28}Si:P, it is nonexponential in the natural Si:P, well described by $\exp(-t/T_2-t^3/T_S^3)$.[17] With B_0 oriented along a (100) axis of the Si crystal, $T_S = 0.63$ ms is estimated from the fit, and this T_S is found to be temperature independent over the range 7–12 K. A shorter T_S (0.36 ms) was reported in the earlier study by Chiba and Hirai[17] but in that work the crystal was oriented differently. We found that T_S is orientation-dependent in natural Si:P, and the longest T_S is seen for a (100) orientation. The orientation dependence of T_S will be discussed in more detail elsewhere.[19]

The linear term in the exponential, T_2, can also be derived from the fit $\exp(-t/T_2-t^3/T_S^3)$ of the decays in natural Si:P, and it is found to be the same as T_2 in isotopically purified ^{28}Si:P, measured at the same temperature and P concentration.[20] Thus, it is the presence of the cubic T_S term that makes the difference between two-pulse echo decays in Si:P and ^{28}Si:P. It is seen in Fig. 2 that in Si:P the T_S term dominates at $\tau > 0.2$ ms and results in complete suppression of the two-pulse echo signal within first 0.5 ms.

Figure 1(b) shows the temperature dependence of T_2 in two ^{29}Si-depleted samples, ^{28}Si:P-10^{16} and ^{28}Si:P-10^{15} at 9.7 GHz. The measurements at 4.7 and 16.3 GHz gave similar T_2 dependences (not shown). For comparison, the T_1 data are also included in Fig. 1(b). Two temperature ranges are clearly seen in the T_2 data. At high temperatures, 12–20 K, T_2 follows closely and nearly coincides with T_1. Apparently, the T_1 relaxation process (the Orbach process) makes the major contribution to T_2 over this temperature range. However, at temperatures lower than 12 K in ^{28}Si:P-10^{16} and lower than 10 K in ^{28}Si:P-10^{15}, T_2 diverges from T_1. While T_1 continues to grow, approaching to 3×10^3 s at 1.2 K,[5] T_2 becomes temperature-independent and saturates at 0.27 and 2.8 ms in ^{28}Si:P-10^{16} and ^{28}Si:P-10^{15}, respectively. The fact that the limiting value of T_2 is greater in the sample with smaller P concentration suggests that T_2 at low temperatures is mostly determined by the dipole-dipole interaction between neighboring P donors via instantaneous diffusion.[9] This effect is known to be temperature-independent, given that the T_1 of the spins involved is long compared to the total duration of the two-pulse experiment.[10]

To test this hypothesis, two-pulse echo experiments ($\pi/2$-τ-θ_2-τ-echo) with a variable rotation angle, θ_2, of the second microwave pulse were performed. The results obtained at 6.9 and 8.1 K are plotted in Fig. 3. It is seen that $1/T_2$ varies linearly with $\sin^2(\theta_2/2)$, indicating that, indeed, instantaneous diffusion contributes significantly to the observed T_2 relaxation rates at these temperatures. Linear fits were obtained assuming the same slope for both data sets, since the slope is determined only by the doping density. The resulting slope was $(3.2\pm0.2)\times10^2$ s^{-1}, which is close to 3.5×10^2 s^{-1} as expected for a homogeneous P distribution at 0.87×10^{15} P/cm^3.[21] Extrapolation to $\theta_2=0$ (to eliminate the contribution of instantaneous diffusion) gives $1/T_2 = 0.072\pm0.008$ and 0.016 ± 0.007 ms^{-1} at 8.1 K and 6.9 K, respectively. The corresponding intrinsic T_2 values (of the isolated donor-electron spins in ^{28}Si:P) are 14 ± 2 ms at 8.1 K and 62 $(+50/-20)$ ms at 6.9 K and approach the T_1 values at these temperatures (18.5 and 280 ms, respectively, shown with the open symbols in Fig. 3).

In summary, we demonstrate that the observed low-

temperature T_2 relaxation time in ^{28}Si:P is controlled by at least two processes, the T_1 relaxation mechanism and instantaneous diffusion, and that the intrinsic T_2 of isolated P donors in Si approaches T_1 at temperatures as low as 6.9 K. At this temperature we find that the intrinsic $T_2 < T_1$, but it is not yet clear whether this difference is just experimental error or if it is indicative of a new decoherence mechanism. Recent theoretical study predicts that spin diffusion (induced by flip-flops between like electron spins) may become important at low temperatures and moderate doping concentrations.[22] A resolution of this question and the possibility of finding even longer intrinsic T_2's in ^{28}Si:P at lower temperatures is currently limited by signal-to-noise considerations arising from the necessity to use magnitude detection at donor concentrations below 10^{14} P/cm^3.

The observation of an extremely long T_2 (>60 ms) has important implications for efforts to use bound electron spins in Si as qubits for quantum information processing. While decoherence is inevitable, we have shown experimentally that electrons bound to phosphorus donors have a long enough coherence times to satisfy the requirements for quantum error correction. To achieve this long electron spin decoherence time (in any candidate spin system), some conditions must be satisfied. To obtain decoherence times of 60 ms or longer, the bound electrons must be at least several tenths of a micron apart (doping density $\sim 10^{13}$/cm^3) to suppress the dipole-dipole interactions. Another condition is that the electrons should be strongly bound. The electrons bound to phosphorus donors are only able to show long decoherence times because the lowest excited state is far away and the Orbach relaxation process can be frozen out. Quantum dots or other bound systems will either need to be no larger than a few nanometers in size, or much lower temperatures will be necessary to freeze out the Orbach process.

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