Spectral diffusion of phosphorus donors in silicon at high magnetic field

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We characterize the phase memory time of phosphorus donor electron spins in lightly-doped natural silicon at high magnetic field (8.58 T) in the dark and under low-power optical excitation. The spin echo decays are dominated by spectral diffusion due to the presence of the 4.7 % abundant spin-1/2 silicon-29 nuclei. At 4.2 K, the spectral diffusion time (T_{SD}) measured in the dark is 124±7 µs, a factor of 2 smaller than that measured at low magnetic fields (0.35 T). Using a tunable laser we also measured the echo decay as the wavelength of the optical excitation is swept across the band edge from 1050 nm to 1090 nm. Above-bandgap optical excitation is seen to increase the spectral diffusion time of the donor electron spin to 201±11 µs. The physical mechanism underlying both the decrease of T_{SD} at high field and the subsequent increase under optical excitation remains unclear.

Donor and defect electronic spins in solids are promising platforms for quantum technologies [1,2]. Understanding how systems such as donors in silicon or defects in diamond and silicon carbide decohere under different experimental conditions is key to enabling improved materials design and to identifying optimal operating conditions.

The donor electrons in phosphorus-doped silicon (Si:P) have some of the longest coherence times observed in solid-state spin systems [3–4]. Natural silicon consists of 3 isotopes: 28Si, 29Si and 30Si, whose relative abundances are 92.23%, 4.67% and 3.1% respectively. While 29Si is a spin-1/2 nucleus, 28Si and 30Si are spin-0 nuclei. Spectral diffusion due to the 29Si spins is the dominant source of spin echo decay in lightly-doped natural Si:P samples at and below 4 K in low magnetic fields [4–9]. The spin dynamics of the isolated donor spin are determined by its hyperfine interactions with surrounding nuclear spins—an instance of the classic central spin problem [10]. Many-body magnetic dipolar interactions between the nuclear spins induce a fluctuating nuclear magnetic field at the site of the donor electron spin causing the echo decay [11]. The elimination of the spin-1/2 29Si nuclei was seen to dramatically suppress spectral diffusion of the phosphorus donor electron resonance in low-field experiments [4], enabling the development of coherent single and two-qubit devices [12–14].

Here we measure the phase memory time of the donor electron in a lightly-doped (N_D = 3.3 – 3.5 × 10^{15} cm^{-3}) natural abundance Si:P sample at liquid helium temperatures at 8.58 T, both in the dark and with low power optical excitation. The experiments were performed on the 240 GHz electron magnetic resonance setup at the National High Field Magnet Laboratory (NHFML) [17].

At low donor concentrations, the Hamiltonian of the isolated phosphorus donor at high magnetic field is

\[ H = \omega_e S_z + \omega_p I_z^p + \frac{2\pi}{\hbar} AS_z I_z^p \]  

which results in two electron spin resonance (ESR) transitions at frequencies \( \nu_e \pm A/2 \). Figure 1(a) shows the continuous wave ESR spectrum of the sample with the two hyperfine-split transitions separated by 4.2 mT (117.5 MHz). The small central peak is due to contributions from coupled donor pairs [18, 19]. The intensity of the two ESR transitions are nearly equal, indicating a low polarization of the 31P nuclear spins. As these two transitions are well separated in energy, it is possible to address and measure their coherence times individually.

Figure 1(b) shows the measured echo decay in the dark (red) and with 1051 nm (E = 1.18 eV) optical excitation (blue). The optical excitation is clearly seen to extend the timescale of the signal decays. This is a surprising effect as optical excitation—though typically at higher intensities—has been shown to dramatically reduce both T_1 and T_2 relaxation times for donors in silicon [20, 22]. Each data point is an average over 16 scans. The signal intensity is calculated from the total area of the echo using both in-phase and quadrature channels.

The inset to the figure shows a schematic of the two-pulse spin echo experiment. The durations of the π/2 and π pulses were 500 ns and 980 ns respectively. The echo delay \( \tau \) was incremented from 2 μs to 100 μs in 2 μs steps. The repetition time of the experiment was set to 1 s, which is much longer than the electron spin T_1 (~ 20 ns [23]), but still short compared to any nuclear spin T_1 time (typically several hours [24]). Laser excitation (when used) was applied continuously to the sample throughout the experiment. The echo decay measured in the dark was acquired immediately after the conclusion of the experiment with optical illumination. The size of the Si:P sample was about 5 × 5 × 3 mm. The orientation of the crystal in the magnetic field is unknown in our experiments.

In general, there are different phenomena that contribute to the decay of a spin echo signal in systems such as Si:P. The echo intensity at time 2\( \tau \)

\[ S(2\tau) = S_0 e^{-2\tau/T_1} e^{-2\tau/T_2} e^{-(2\tau/T_{SD})^n} \]  

(2)
includes contributions from instantaneous diffusion (ID), spectral diffusion (SD) and the $T_2$ coherence time of the spins. In silicon the parameter $n$ has been observed to be in the range from $2-3$. Instantaneous diffusion describes the decay observed due to dipolar-induced spin-flips with surrounding electron spins that are also excited by the microwave pulse. For $10^{15}$ electron spins/cm$^3$ the characteristic time $T_{1\text{ID}}$ for instantaneous diffusion is about 1.2 ms. At high fields the $T_1$ relaxation time is known to shorten considerably and has been measured to be on the order of 20 ms in the dark in a similarly doped sample. In the absence of coupling to other spins – which is accounted for by the instantaneous diffusion and spectral diffusion terms – we expect $T_2 \sim T_1 \sim 20$ ms. $T_2$ and $T_{1\text{ID}}$ are thus both significantly longer than the timescales on which the decays are observed and do not play a significant role in these experiments. Fitting the echo decays to the spectral diffusion component of Equation 2 using $n = 2.3$ as measured both theoretically and experimentally for Si:P, we obtain $T_{\text{SD}} = 124 \pm 7 \mu$s in the dark and $T_{\text{SD}} = 201 \pm 11 \mu$s under 1051 nm excitation. At low field $T_{\text{SD}}$ was found to range from 270 $\mu$s to 620 $\mu$s depending on the orientation of crystal in the magnetic field. The $T_{\text{SD}}$ observed in the dark is thus more than a factor 2 smaller than that measured at lower magnetic fields. Under optical excitation $T_{\text{SD}}$ is seen to increase and is closer to the value of $T_{\text{SD}}$ measured in the dark at low magnetic fields. Figure 1(b) also shows the simulated echo decay calculated using the pair correlation approach of Witzel et al. which was found to be in excellent agreement with low-field experiments.

In an effort to better understand these surprising experimental results, it is useful to examine the microscopic origins of the $T_{\text{SD}}$ variations. Following [8, 10, 25, 26] we can cast this problem in terms of a qubit-bath Hamiltonian with the donor electron as the spin qubit and the nuclear spins as the bath. Since we are exploring the coherence properties of a single ESR manifold, we can treat this as a single spin and ignore the donor nucleus. The Hamiltonian describing the interaction of this electron spin with the surrounding $^{29}$Si spins can be expressed as

$$H = \omega_0 S_z + S_z \sum_i A_i I^z_i + \omega_n \sum_i I^z_i + \sum_{i<j} h_{ij}$$

(3)

consisting of the electron Zeeman, electron-nuclear hyperfine, nuclear Zeeman and nuclear dipolar interactions respectively. The pairwise nuclear dipolar interaction is given by

$$h_{ij} = d_{ij}(I^z_i I^z_j + I^y_i I^y_j - 2I^z_i I^z_j)$$

where

$$d_{ij} = \left( \frac{\gamma_n^2}{2r_{ij}^3} \right) (3\cos^2 \theta_{ij} - 1)$$

The hyperfine interactions $A_i$ contain both contact and dipolar contributions. The electron and nuclear Zeeman interaction terms can be dropped as they independently commute with all other terms in the Hamiltonian and play no role in the decay of the electron spin coherence in a Hahn-echo experiment. The qubit-bath Hamiltonian can be re-written as

$$\mathcal{H} = |\uparrow\rangle\langle\uparrow| \otimes H^+ + |\downarrow\rangle\langle\downarrow| \otimes H^-$$

(4)

where $H^\pm = \pm \frac{1}{2} \sum_i A_i I^z_i + \sum_{i<j} h_{ij}$ are different bath Hamiltonians that depend on the qubit state ($|\uparrow\rangle$ or $|\downarrow\rangle$) [10]. If the bath nuclear spins are initially in a state $|J\rangle$ – a random thermal equilibrium nuclear spin configuration, then an initial coherent superposition state of the qubit

$$|\psi(0)\rangle = (\alpha |\uparrow\rangle + \beta |\downarrow\rangle) \otimes |J\rangle$$

(5)
evolves into a state
\[
\psi(t) = a|\uparrow\rangle \otimes e^{-iHt}|J\rangle + \beta|\downarrow\rangle \otimes e^{-iH\tau}\tau|J\rangle
\] (6)
at time \(t\), entangling the spin and bath. Evaluating the state of the spins at time \(t = 2\tau\) in a Hahn echo experiment and tracing over the nuclear spins gives us the magnitude of the electron spin echo
\[
S(2\tau) = \langle J| e^{iH\tau}e^{iH\tau}e^{-iH\tau}e^{-iH\tau}|J\rangle
\] (7)
For a mixed state of the nuclear spin bath \(\rho = \sum_{j} p_{j}|J\rangle\langle J|\), we average equation (6) over the different bath states. The magnetic field dependence of this expression for the spectral diffusion only arises from the probabilities for the different bath configurations. At \(T = 4\) K and \(B = 8.58\) T we have a thermal equilibrium \(^{29}\text{Si}\) nuclear spin polarization of \(4\times 10^{-4}\) which indicates that the nuclear spins are effectively at infinite temperature and all bath configurations are equally likely. The resulting echo amplitude
\[
S(2\tau) = \text{Tr}\left[ e^{iH\tau}e^{iH\tau}e^{-iH\tau}e^{-iH\tau}\right]
\] (8)
is independent of magnetic field in contrast to our experimental result, as long as the Hamiltonian parameters of the system remain unchanged.

Different approaches have been used to estimate the decay due to this many-body dynamic [10]. For a 2-pulse spin echo experiment the pair correlation function approach has been shown to give very good agreement to experimental results at low magnetic fields [8, 9]. The resulting echo intensity is
\[
S(2\tau) = \exp \left( -\sum_{i<k} \frac{d_{ij}^2(A_i - A_j)^2}{4\omega_{ij}^2} \cos \omega_{ij}\tau - 1\right)
\] (9)
where \(\omega_{ij} = \frac{1}{2}\sqrt{(A_i - A_j)^2 + 4d_{ij}^2}\). Figure 1(b) compares numerical simulations of this model to the experimental data acquired at high field. The simulated curve has been multiplied by an decaying exponential to account for instantaneous diffusion effects \(T_{SD} = 1.2\) ms. Details of the simulation are provided in the Supplementary Information.

Ultimately the observed changes in \(T_{SD}\) indicate changes in the local magnetic field fluctuations seen by the donor electron. The decrease in \(T_{SD}\) in the dark suggests that either the magnitude of the magnetic noise has increased or that the fluctuations have become more rapid leading to imperfect refocusing by the spin echo. One possibility is that the Kohn-Luttinger wavefunctions [27, 28] are perturbed by the high-field conditions used here so that the magnitudes of the \(^{29}\text{Si}\) hyperfine interactions become larger, thus increasing the strength of the magnetic noise seen by the electron spin. While the ESR conditions are a sensitive probe of the phosphorus donor hyperfine interaction strength and were not observed to change under optical excitation, they do not tell us about the \(^{29}\text{Si}\) hyperfine coupling strengths, which would require electron-nuclear double resonance (ENDOR) experiments under the same conditions.

In order to further understand the enhancement of spectral diffusion time under light excitation, we repeated the experiment with a tunable laser (O/E Land OETLS-300-1060 electrically-tunable external-cavity fiber laser) that could be tuned across the band edge from 1050 nm to 1090 nm (corresponding to the energy window 1.1375 – 1.18 eV). Silicon is an indirect band-gap material with a band-gap of 1.17 eV at 4.2 K [29]. The first optical absorption edge at \(E = 1.174\) eV (1056 nm) is mediated by the emission of 18.2 meV TA phonons and the creation of a free exciton [30]. The power of the tunable laser varies between 250 \(\mu\)W and 2 mW - depending on the wavelength as shown in the Supplementary Materials. The optical linewidth is specified to be below 0.04 nm. We also ran the experiment with 650 nm (\(E = 1.91\) eV) and 980 nm (\(E = 1.27\) eV) excitation, using free space lasers coupled into the fiber.

Figure 2 shows the measured spectral diffusion time at different laser wavelength for both the high-field and the low-field phosphorus peaks of Figure 1(b). The signal decays are fit to just the \(T_{SD}\) term using \(n = 2.3\). The error bars are calculated by the 95 percent confidence interval of the \(T_{SD}\). The data show that \(T_{SD}\) increases as the energy of the optical excitation is increased above the silicon band-gap, and that the change in spectral diffusion time is the same for both the high-field and low-field phosphorus peaks. The longer \(T_{SD}\) is also observed with the 980 nm laser, but falls off again at 650 nm, likely...
due to the limited penetration depth into the sample. It should be noted that the signal measured in these inductively detected pulsed ESR experiments arises from the entire sample. At cryogenic temperatures the optical penetration depth of light into silicon is known to be strongly wavelength dependent \[31\]. For wavelengths of 1050 nm and longer the optical penetration depth is several centimeters, while it reduces to about 100 µm at 980 nm and to 2-3 µm at 650 nm. Thus the 3 mm thick sample is expected to be uniformly illuminated at the longer wavelengths, fairly inhomogeneously illuminated at 980 nm and only the very surface of the sample is optically excited by the 650 nm wavelength. The photo-excited carriers can travel further into the sample, with free excitons traveling up to a millimeter in silicon under these conditions \[32\].

Figure 3 shows the change in T\(_{SD}\) as a function of nominal laser power (measured at the output of the optical fiber) with the 980 nm laser for the high magnetic field transition. The fit indicates that T\(_{SD}\) saturates to a maximum of 208 µs with increasing laser power. This is close to the value measured at low magnetic fields.

The increase in T\(_{SD}\) indicates either that the magnitude of the noise reduces, or the spectral features change - either slowing down and enabling better refocusing by the spin echo or fluctuating rapidly enough to enable a "motional narrowing" of the noise \[33\]. For NV centers in diamond, polarizing the spin bath (electronic P1 centers) has been shown to suppress spectral diffusion and increase T\(_{SD}\)\[34\]. While above bandgap illumination has been shown to hyperpolarize the phosphorus donor spins at high field and low temperature \[21\] \[35\] \[36\], only weak optical hyperpolarization of the silicon spins has been observed to date at high magnetic fields \[21\]. Verhulst et al. observed a \(^{29}\)Si spin polarization of 0.25% at 500 mW after 30 minutes of laser irradiation at 7 T and 4.2 K. With 1024.8 nm excitation, they initially observed a reduction in T\(_1\) of the silicon spins at low optical power (< 1 mW) and a growth of \(^{29}\)Si hyperpolarization at higher optical power (> 1 mW). The 1-2 mW optical power coming out of the fiber in our experiments is just on the threshold of when \(^{29}\)Si hyperpolarization was observed, so it is unlikely that the \(^{29}\)Si nuclear spins polarization is sufficiently high to change T\(_{SD}\) significantly. More importantly, given the long T\(_1\) of the silicon nuclear spins, the enhanced T\(_{SD}\) should persist for several hours. However, as shown in Figure 4(b), the enhanced spectra diffusion times were not observed when the experiment was repeated in the dark 15 minutes later.

Alternatively, spectral diffusion effects can also be reduced if the effective strength of either the inter-nuclear dipolar coupling or the hyperfine coupling are reduced or acquire rapid random rapid fluctuations that lead to motional narrowing of the local field fluctuations. One possibility is that modulation of the donor electron wavefunction by mobile carriers modulates and reduces the silicon hyperfine couplings. While noise spectroscopy \[37\] \[38\] could be used in principle to directly measure the spectrum of magnetic noise seen by the donors, the lack of phase control on the 240 GHz instruments does not permit robust multiple-pulse dynamical decoupling experiments. Disentangling the different potential sources of magnetic field fluctuations in the presence of light is a non-trivial task. Optical excitation creates a dynamically rich environment for the spins as can be seen from the schematic in Figure 4.

At the absorption edge, the electrons and holes are primarily in the form of free excitons (the exciton binding energy is 15.01 ± 0.06 meV \[39\]), while at higher optical excitation energies above 1.19 eV, it is possible to generate free electrons and holes - which in turn form free excitons as they lose energy. The optical generation of free excitons is followed by continuous interconversion between free and bound excitons, and both radiative recombination of free excitons and non-radiative Auger recombination of bound excitons \[39\]. A 1 mW excitation with 1 eV photons would result in \(6 \times 10^{15}\) photoelectrons/excitons generated per second if all the power is deposited in the sample. Given the penetration depth of 1 eV photons in silicon only about 10% of the photons are absorbed. Since the free exciton lifetime at 4.2 K is on the order of 1 µs \[39\], this results in an estimated exciton density of about \(8 \times 10^{13}\) cm\(^{-3}\) in the sample - significantly lower than the donor concentration. However, the excitonic Bohr radius is about 5 nm \[40\] - larger than that of the donor electron - and they are known to have extremely high mobilities \[32\]. It is possible that that exciton dynamics contributes to the observed increase in T\(_{SD}\) as the electrons and holes comprising these excitons can have fairly strong hyperfine couplings to the silicon...
FIG. 4: Schematic of the effects following optical absorption in silicon.

nuclei in the lattice [41].

In conclusion, the spectral diffusion time measured in the dark at high field (8.59 T) was observed to be more than a factor of 2 shorter than the values measured at 0.35 T, though the simple theory outlined here would suggest that the values should be identical. In the presence of weak above band-gap optical excitation, T\text{SD} was observed to increase by almost a factor of 2 suggesting a motional narrowing of the spectrum of magnetic field fluctuations seen by the donor.

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