Spin coherence of near-surface ionised $^{125}\text{Te}^+$ donors in silicon

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Impurity spins in crystal matrices are promising components in quantum technologies, particularly if they can maintain their spin properties close to surfaces and material interfaces. Here, we investigate an attractive candidate for microwave-domain applications, the spins of group-VI $^{125}\text{Te}^+$ donors implanted into natural Si at depths of 20 and 300 nm. We examine spin activation yield, relaxation ($T_1$) and coherence times ($T_2$) and show how a zero-field 3.5 GHz ‘clock transition’ extends spin coherence times to over 1 ms and narrows the inhomogeneous spin linewidth to 0.6 MHz. We show that surface band-bending can be used to ionise Te to spin-active $\text{Te}^+$ state, and that coherence times of near-surface donors are comparable to the bulk. We demonstrate initialization protocols using optical illumination to generate excess $\text{Te}^+$. These results show that $^{125}\text{Te}^+$ is a promising system for silicon-based spin qubits and ensemble quantum memories.

INTRODUCTION

Donor spins in nanoscale silicon devices have been shown to be a promising building block for various solid state quantum devices, including atomic qubits [1] and quantum memories with coherence times approaching seconds [2]. Such devices typically contain band discontinuities at silicon/metal and silicon/vacuum interfaces which build electric fields into devices, impacting the charge and spin state of nearby donors. Placing donors close to these interfaces is often important, for example, to increase spin-resonator coupling [3], or couple donor spins to electrostatically-tunable quantum dots [4, 5]. Without control of the surface potential (for example, through a metallic top-gate), this typically limits the minimum donor-interface distance to tens of nanometres for shallow group-V donor electron spins [6] whereas deeper donors could be placed closer to electrodes. There is also evidence that, for deeper donors, the electron spin coherence is less strongly influenced by naturally abundant $^{29}\text{Si}$ spins (as seen by comparing results from P and Bi donors [7, 8]).

Singly ionised group-VI chalcogens ($\text{S}^+$, $\text{Se}^+$, $\text{Te}^+$) possess an electron spin $S = 1/2$, like the group-V donors, but have much larger ionisation energies [9–11] and have attracted recent interest due to their optical transitions [12]. Through continuous-wave electron spin resonance (ESR) studies [9, 13], $^{125}\text{Te}^+$ in silicon is known to have a large isotropic hyperfine coupling of $\sim 3.5$ GHz to the $^{125}\text{Te}$ nuclear spin ($I = 1/2$). Singly ionised double donors such as $^{125}\text{Te}^+$ therefore offer a potential route to maintaining a donor electron spin close to a silicon surface or interface, combined with the presence of a microwave ‘clock transition’ [14] at zero magnetic field.

Here, we present pulsed ESR measurements of the spin coherence properties of implanted $^{125}\text{Te}^+$ in natural silicon, showing how coherence times exceed 1 ms as the zero-field clock transition is approached. We investigate two different methods to singly ionize $^{125}\text{Te}$ — first by co-doping with boron for donors implanted at depths of several hundred nanometres, and second by directly exploiting the band bending arising from Fermi level pinning (FLP) for donors at a depth of $\sim 20$ nm. Infrared illumination of the shallow implanted sample improves the ionisation fraction, surpassing that achieved by co-doping. Overall, our results demonstrate $^{125}\text{Te}$ to be an attractive candidate for achieving strong spin-resonator coupling with donor spins.

RESULTS

The Tellurium donor Spin system

The singly ionised $^{125}\text{Te}$ donor has a single bound electron ($S = 1/2$) coupled to the $^{125}\text{Te}$ nuclear spin ($I = 1/2$) via an isotropic hyperfine coupling $A$, and is described by the following spin Hamiltonian in frequency units:

$$H = AS \cdot I + \gamma_e B_0 \cdot S + \gamma_{\text{Te}} B_0 \cdot I + H_{\text{SI}}.$$  (1)

Here, $B_0$ is the applied magnetic field, while $\gamma_e/2\pi = 28.025(1)$ GHz/T, $\gamma_{\text{Te}}/2\pi = -13.5$ MHz/T are, respectively, the gyromagnetic ratios of the bound electron

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Spin transitions of $^{125}$Te:Si as functions of magnetic field. (A) Spin eigenenergies with $S_x$ and $S_z$ transitions marked in blue and red, respectively. Transitions are labelled by their quantum number $F = S \pm I$ and its projection $m_F$. (B) Frequencies of allowed spin transitions, where the line intensity is proportional to the transition probability. Echo-detected spectra obtained at 9.65 GHz are shown in black. (C) First order magnetic field dependence of the transition frequencies. Dots in (B,C) show fields and transitions, where $T_2$ measurements are performed. (D,E) Echo-detected spectra of $^{125}$Te:Si close to zero magnetic field with the cavity oriented to measure $D_x$ and $S_z$ transitions. A one-pixel Gaussian blur is applied. Solid lines show simulations assuming only a hyperfine constant of 3.4965 GHz to $^{125}$Te nucleus, or, in addition, a SHF interaction with a neighbouring [110]-shell $^{29}$Si nuclear spin. All measurements are taken at 10 K.

The first derivative of the transition frequency with respect to the applied field, $\partial f / \partial B_0$, is an important parameter in determining spin coherence lifetimes and inhomogenous broadening. So-called ‘clock transitions’, where $\partial f / \partial B_0 = 0$, possess extended coherence times [14–16], and narrow linewidths [14]. Like most coupled spin systems, $^{125}$Te$^+$ exhibits an $S_z$ clock transition at zero field (see Fig. 1C). Due to the large hyperfine coupling, the clock transition of $^{125}$Te$^+$ occurs in the microwave domain at 3.4965 GHz. In Fig. 1(D,E) we present echo-detected field sweeps (EDFS) for $S_z$ and $S_x$ transitions respectively whilst varying the frequency of the microwave drive. We resolve the main spin transition as well as the super hyperfine levels shown with the calculated transition frequency overlaid.

**Activation of tellurium spins**

To be spin active, chalcogens must be incorporated into the silicon lattice (as with group-V donors) and also be singly ionised [10, 11]. Using the deeply implanted p-type sample, we first investigated three annealing schedules (5 minutes at 600, 800 and 1000°C in dry nitrogen) to incorporate $^{125}$Te into the lattice after implantation. In these samples, ionisation is achieved by co-doping $^{125}$Te ion implanted at 800 keV with a peak concentration of $10^{17}$ cm$^{-3}$ (profile shown in SI) with boron at a concentration of $2.4(2) \times 10^{16}$ cm$^{-3}$ (Fig. 2A). Using an excess of Te, we aim to ionise the majority of the boron into an electron spin-less B$^-$ state to reduce the impact on the Te$^+$ donor spin coherence through spectral diffusion. This necessarily reduces the fraction of Te$^+$ compared to the overall quantity of implanted Te.

Spin echo measurements at 9.65 GHz show two resonances at the expected magnetic field positions for the $S_z$ transitions shown in Fig. 1B, confirming the presence of $^{125}$Te$^+$. By comparing these echo amplitudes to a reference P:Si sample (see Supplementary Materials for details), we determined the activation yield of Te$^+$. We observed that activation yield increases with annealing temperature (see Table I) and, given that the ionisation mechanism is the same between the samples (B co-doping), we attribute this change to a higher Te incorporation fraction.

We also observe that the electron spin coherence time $T_2$ obtained at X-band increases with annealing temperature (see Table I) likely due to healing of spin-active implantation damage at higher annealing temperature. Secondary ion mass spectrometry (SIMS) depth profiles shown in the Supplementary Materials show that annealing at 1000°C causes $^{125}$Te to diffuse by $\sim 35$ nm in contrast to lower temperature annealing, which causes little diffusion. Further optimization of annealing schedules (e.g. longer anneals) would likely allow higher incorporation fraction, healing of implantation damage and control over diffusion. SIMS profiles (Supplementary Materials) show some Te in the surface SiO$_2$, which is not spin ac-

\[
H_{Si} = \sum_i (S \cdot A_{Si,i} + \gamma_{Si} B_0) \cdot I_{Si,i}.
\]

Here, $A_{Si,i}$ is the SHF coupling to the $i$-th $^{29}$Si nuclear spin, $I_{Si,i}$, with gyromagnetic ratio $\gamma_{Si}/2\pi = -8.5$ MHz/T.

Fig. 1A,B shows the spin transition frequencies ($f$) and probabilities as a function of magnetic field, neglecting the SHF term. Transitions are labelled $S_x$ ($\Delta m_F = 0$) or $S_z$ ($\Delta m_F = \pm 1$), which are, respectively, driven when the microwave magnetic field component is applied parallel or perpendicular to the static magnetic field. Here, $m_F$ denotes the projection of the quantum number $F = S \pm I$. The ESR experiments described below were performed using a copper loop-gap resonator with adjusted orientation depending on the type of the transition, as shown in insets to Fig. 1D,E (see Materials and Methods and Supplementary Materials for experimental details).
Table I. \( \text{T}_2 \) and activation of \( ^{125}\text{Te}^+ \) in different samples.

| Sample         | \( \text{T}_2 \) at X-band (ms) | Activation (%) |
|----------------|----------------------------------|----------------|
| 600°C p-type   | 0.24(2)                          | 7.4(7)         |
| 800°C p-type   | 0.39(2)                          | 9.2(9)         |
| 1000°C p-type  | 0.45(3)                          | 11(1)          |
| 1000°C intrinsic | 0.44(9)                        | 7.3(7)         |

The p- and intrinsic samples were implanted at 800 keV and 20 keV, respectively. Activation is determined by measuring the ratio of echo intensity between a reference P:Si sample and the Te-implanted samples.

**Figure 2. Ionisation of Te.** (A) Cartoons showing the different ionisation mechanisms of Te in silicon. (B) EDFSs performed at X-band for \( S_x \) transitions. The \( ^{125}\text{Te}^+ \)-Si line is present in the 20 keV intrinsic sample and the 800 keV p-type sample but absent in the 20 keV p-type sample. (C-E) Simulated band profiles for the three samples used in this study assuming FLP of 0.4 eV below the conduction band. The simulation results are consistent with EDFSs in (B). (C) Intrinsic wafer with 20 keV implant energy gives all Te singly ionized by surface band bending. (D) p-type wafer with 20 keV implant energy has approximately all Te doubly ionized. (E) p-type wafer with 800 keV implant energy has the Fermi level close to the singly ionized Te level as 1/10th of Te atoms are ionized by sacrificing an electron to the boron acceptors present at 1/10th the density of Te.

**Figure 3. Optical control of charge configuration.** Energy levels and electron transitions under illumination of (A) 4300 nm, (B) 2800 nm and (C) 1050 nm light. The labels of energy levels are marked in (A). Coloured vertical lines show the energy of incident photons supplied by LEDs at cryogenic temperatures and indicate which levels are excited by these photons. Vertical arrows show electron capture. Green arrows indicate population swapping between levels under illumination with arrows indicating the shift of population of Te donors under illumination. (D) Echo intensity from the intrinsic sample as a function of time as LEDs are shone at the sample at 10 K. The labels of energy levels and electron transitions under illumination of (A) 4300 nm, (B) 2800 nm and (C) 1050 nm light. The labels of energy levels are marked in (A). Coloured vertical lines show the energy of incident photons supplied by LEDs at cryogenic temperatures and indicate which levels are excited by these photons. Vertical arrows show electron capture. Green arrows indicate population swapping between levels under illumination with arrows indicating the shift of population of Te donors under illumination. (D) Echo intensity from the intrinsic sample as a function of time as LEDs are shone at the sample at 10 K. With appropriate LED preparation, the echo intensity can be enhanced by a factor of \( \sim 3.5\times \). The inset shows the echo integral as a function of cumulative 2800 nm illumination showing that the echo is suppressed.

In order to understand this behaviour, we self-consistently solved the Schrödinger-Poisson equation in one dimension and simulated different implants and substrates with various FLP levels. FLP in the range of 0.4–0.5 eV give ionisation profiles consistent with the echo amplitudes in Fig. 2B and are in line with literature values for FLP at the silicon/silicon oxide interface. We show simulations of the band profiles with FLP at 0.4 eV below the conduction band in Fig. 2C-E. Fig. 2C shows simulated band profiles of \( 10^{17}\text{cm}^{-3} \) Te extending 20 nm into intrinsic silicon, where all Te is singly ionised. However, for the shallow implant into p-type material (Fig. 2D) the simulation predicts predominantly ESR-silent \( ^{125}\text{Te}^{2+} \), consistent with the lack of observed spin echo from this sample. Finally, in the simulation of deep implanted Te into p-type Si (Fig. 2E) the Fermi level is close to the Te\(^+\) level, resulting in Te ionisation commensurate with the boron codoping concentration. Extended simulations as a function of FLP are presented in the Supplementary Materials for these different samples.

A comparison with the P:Si reference sample gives an estimated Te activation of \( \sim 7\% \) for the shallow-implant (Table I), which arises from a combination of imperfect incorporation of Te into the lattice and less than 100% ionisation into Te\(^+\). Shining light of different wavelengths at our shallowly implanted intrinsic silicon sample allows us to alter the charge configuration and improve the fraction of singly ionized Te. We explore illumination at
three different wavelengths: 1050 nm, sufficient to excite carriers across the Si bandgap; 2800 nm, sufficient to promote electrons from Te$^{+}$ or Te$^{0}$ to the conduction band; and 4300 nm, which excites only the Te$^{0}$ state (see Fig. 3A-C). Illumination at 2800 nm drives the formation of (spinless) Te$^{2+}$, as illustrated by the four-fold reduction of echo intensity as shown in the inset of Fig. 3D.

In Fig. 3D we explore the effects of 4300 nm and 1050 nm, with respect to the initial echo intensity from the sample as cooled from room-temperature to 10 K. Illumination first with 4300 nm results in a small (~20%) increase in echo intensity, indicating there is only a small concentration of Te$^{0}$ in the as-cooled state, consistent with our simulations above. Illumination at 1050 nm results in a complete suppression of the electron spin echo, consistent with driving population from Te$^{+}$ (and Te$^{2+}$) into the neutral Te$^{0}$ state. The echo recovered on the timescale of an hour, similar to Se$^{+}$ recovery after illumination by 1047 nm [10], due to some redistribution of population from Te$^{0}$ to Te$^{+}$. However, as is evident from the large (4×) increase in echo intensity following subsequent illumination at 4300 nm, there remained a substantial fraction of Te$^{0}$, much greater than that present upon cooling the sample. Further rounds of illumination at 1050 and 4300 nm demonstrate the ability to switch between Te$^{0}$ and Te$^{+}$ states. The non-equilibrium Te$^{+}$ population created persists for at least ~16 hours (further data off panel), and represents a spin-activation fraction of ~26%. Similar illumination experiments applied to the deeply implanted p-type sample are described in the Supplementary Material, however, there no increase in echo intensity was observed relative to the as-cooled state.

**Spin linewidth and coherence**

The linewidths (half width half max) of the $S_x$ and $S_z$ transitions largely follow $∂f/∂B_0$, as shown in Fig. 4A, consistent with inhomogeneous broadening from $^{29}$Si nuclear spins, as is commonly seen for donors in natural Si. The linewidth reaches a minimum value of ~0.6 MHz, which is close to the pulse bandwidth limit (π pulse duration 140 ns), but approximately equal to that measured for a clock transition in Bi:$^{nat}$Si doped at similar concentration [21]. The lineshape is well fit by a single Gaussian (see Fig. 4B) with no evidence of additional splitting caused by isotope mass variation of the nearest-neighbour silicon atoms [22] — the low ($I = 1/2$) nuclear spin of $^{125}$Te means the spin transitions are typically less sensitive to shifts in the hyperfine coupling than donors with high-spin nuclei like $^{209}$Bi. The increase in line broadening for $∂f/∂B_0 ≤ 0.03$ (corresponding to $B_0 ≤ 4$ mT), is due to SHF transitions splitting from the main transition as zero magnetic field is approached (see Methods and Supplementary Material).

We studied the spin relaxation time, $T_1$, in the range 6.5–18 K for an $S_z$ transition at 9.65 GHz and close to the $S_x$ clock transition (see Supplementary Figure S10). In both cases, the $T_1 ∝ T^{-9}$ temperature dependence indicated a (phonon-induced) Raman spin-relaxation process, as was also observed for $^{77}$Se$^{+}$ in $^{28}$Si [10]. For temperatures above about 10 K, the spin coherence time, $T_2$, is limited by $T_1$, however, below 8 K, $T_2$ reaches a constant value. We investigate $T_2$ in this low-temperature limit in more detail below, examining the effects of magnetic field, $∂f/∂B_0$, and other factors. We can expect that the naturally abundant $^{29}$Si nuclear spins in these samples pose a limit on the measured coherence times, which can be calculated using the cluster correlation expansion (CCE) method [23], as used for (shallower) group-V donors [7, 8]. We plot this calculated limit (CCE-2, based on two-body correlations of bath spins) along with the experimental results in Fig. 5, with further details of the simulations provided in the Materials and Methods.

From the $T_2$ measurements and simulations, we make three observations. First is that the $T_2$ measured for deep implanted Te$^{+}$ in p-type substrates (ionised by the boron acceptors) is similar to the shallow Te$^{+}$ in intrinsic substrates (ionised by surface band bending). This suggests that neither the effect of the compensation, nor proximity to the surface limit the $T_2$ values measured, consistent with what may be expected (see calculations in the Supplementary Material).

Second, is that the $T_2$ limit from the $^{29}$Si nuclear spin bath predicted by the CCE-2 calculations is almost a factor of two longer than that seen for the shallow donors such as Bi and P [7, 8]. However, as a result, the nuclear spin bath alone does not appear to account for the observed $T_2$ values, and rather instrumental magnetic field noise and sample orientation effects are likely

![Figure 4: Linewidths and lineshape of $^{125}$Te$^{+}$:Si electron spin transitions.](image-url)

**Figure 4:** Linewidths and lineshape of $^{125}$Te$^{+}$:Si electron spin transitions. (A) Half width at half maximum linewidth of the $S_z$ (blue) and $S_x$ (red) transitions of deeply implanted p-type sample as a function of $∂f/∂B_0$ determined by fitting a Gaussian to the frequency-swept echo amplitude. Inset shows the increase in linewidth observed for $S_z$ transition at low $∂f/∂B_0$ arising from unresolved SHF transitions. (B) The lineshape, measured at the narrowest linewidth is fit well by a single Gaussian.
to play dominant roles. We consider additional sources of decoherence such as unhealed damage from ion implantation and spin concentration effects in the Supplementary Materials and conclude that they are unlikely to play a significant role in these measurements. Experimental setups similar to that used here are known to suffer from magnetic field noise that limits the measured $T_2$ to $\sim 1$ ms. This effect can be circumvented by performing single-shot measurements of echo magnitude [24], but this requires a large signal-to-noise ratio not available when measuring these implanted samples using 3D cavities. Such an additional magnetic-field-type decoherence process (rate $\propto \partial f / \partial B_0$) with a corresponding $T_2 = 1$ ms for $\partial f / \partial B_0 = \gamma_e$, is able to well reproduce the observed measurements for $S_x$ transitions (see dashed line in Fig. 5A), however, it does not however adequately explain $S_z$ data. The effect of spectral diffusion from the $^{29}$Si bath spins in natural silicon depends strongly on the orientation of $B_0$ with respect to the principal axes of the silicon host matrix due to the anisotropy of the nuclear dipolar interaction [25], as illustrated in Supplementary Fig. S12. A misalignment from the principal axis of $\sim 15^\circ$ for the $S_z$ measurements (nominally made for $B_0$ oriented along [001]) would be sufficient to bring the CCE-2 simulations in line with the measured $T_2$ data. Additional measurements consistent with such a misalignment are presented in the SI, including a study of the $S_x$ transition $T_2$ as a function of $B_0$ orientation.

Our third observation concerns the $T_2$ behaviour as $\partial f / \partial B_0$ approaches zero in the $S_z$ transitions. A key factor which distinguishes these measurements from those performed on a ‘clock transition’ of Bi donors in natural silicon [14] is that here $\partial f / \partial B_0 \rightarrow 0$ coincides with the static magnetic field $B_0$ approaching zero. Therefore, rather than seeing the $T_2$ towards $\sim 100$ ms (as for Bi: natSi) the CCE-2 calculations predict an (orientation-dependent) limit of $1-2.5$ ms. This can be understood as a ‘melting’ of the ‘frozen-core’ of $^{29}$Si spins around the donor spin, leading to enhanced noise from the spin bath. Furthermore, our measurements reveal an additional decrease in the fitted $T_2$ at the very lowest values of $\partial f / \partial B_0$ corresponding to $B_0 \lesssim 4$ mT, which we ascribe to periodic electron spin echo envelope modulation (ESEEM) from $^{29}$Si nuclei in the crystal matrix. Simulations of the ESEEM performed using EasySpin [26] accounting for this are presented in the Supplementary Materials, and the same effect has been observed recently in Bi:Si [27].

**OUTLOOK AND CONCLUSIONS**

Our results show that $^{125}$Te in silicon is a promising donor for use in quantum technology applications, including qubits and quantum memories. We have demonstrated coherence times in excess of 1 ms, and these times can be expected to reach of order 100 ms or more based on results on similar donor systems [10, 28]. We have also shown a novel approach to ionise shallow implanted chalcogens in nanoelectronic devices using surface band bending, which, when combined with infrared illumination, gives a single ionisation fraction substantially greater than that achieved by co-doping with acceptors, and no visible reduction in coherence time in natural silicon.

Each of the limiting decoherence processes described above can be mitigated by moving to isotopically purified silicon and measuring using superconducting resonators patterned onto implanted silicon. The micro-resonators will enable enhanced the signal to noise ratio (and thus such single-shot measurements) while also providing greater control over the sample alignment with respect to the microwave field. Isotopically enriched $^{28}$Si material will mitigate the effects of the $^{29}$Si bath responsible for the decoherenced captured in the CCE-2 simulations, as well as the ESEEM seen at very low magnetic fields. Use of $^{28}$Si should also substantially reduce the linewidths by removing the broadening from unresolved SHG levels.

The large (3.5 GHz) zero-field splitting of $^{125}$Te makes it suitable for use at low magnetic fields and thus compatible with with field-intolerant systems such as superconducting qubits. The nuclear spin-half of $^{125}$Te give this donor an attractive level structure which can be used, for example, in so-called ‘flip-flop’ qubits [5], and which permit near-complete polarisation of the two-spin sys-

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**Figure 5. Coherence times of $^{125}$Te:Si.** $T_2$ as a function of (A) $\partial f / \partial B_0$ and (B) $B_0$ for different types of ESR transitions, measurement conditions and samples. Points where $T_2$ is suppressed by ESEEM are indicated with increased transparency in (A,B). The solid curves mark the limit to $T_2$ considering nuclear spin dynamics as a function of electron spin $\partial f / \partial B_0$ (A) and static magnetic field (B). Adding in the effects of classical magnetic field noise gives good agreement to experiment at higher fields (dashed curves).
tem at dilution fridge temperatures, even at zero field. The significant second ionisation energy of these donors permit the placement of spin-active $^{125}$Te very close to surfaces and interfaces, which is beneficial for achieving large inductive coupling to microwave circuits [3]. All of these features, combined with the optical transitions of such donors [29], open a host of potential applications in quantum frequency converters, quantum sensors [30], and quantum memories.

**MATERIALS AND METHODS**

**Samples**

We implanted mass-selected $^{125}$Te ions into three samples of 275 µm thick float-zone silicon: two samples were p-type doped with $[B] \sim 2.4(2) \times 10^{16}$ cm$^{-3}$, and one was intrinsic. The intrinsic sample and one p-type sample were ion implanted with $^{125}$Te at 20 keV with a fluence of $1.4 \times 10^{11}$ cm$^{-2}$ forming a shallow layer of dopants centred at a depth of ~20 nm. The second p-type sample was implanted using 800 keV with a fluence $2.2 \times 10^{12}$ cm$^{-2}$ forming a ~200 nm thick layer of Te centred at a depth of ~300 nm. Monte Carlo simulations of ion implantation were performed using SRIM [31], and are shown alongside SIMS depth profiles before and after annealing in the Supplementary Materials. To activate the dopants, samples were annealed at 1000°C for 5 minutes, unless otherwise stated.

**SIMS experiments**

SIMS analysis of the samples was carried out using an IONTOF ToF-SIMS 5 instrument. The analytical ion beam used was a 25 keV Bi$^+$ LMIG. To obtain high resolution mass spectra and good detection limits, high current bunch mode was used with a beam current of about 1 pA. The analytical area was 100 mm$^2$. Depth profiling was performed using a second sputtering Cs ion beam at 500 eV. The ion beam current was about 40 nA, and the sputter area was 300 mm$^2$. Negative secondary ions were collected.

**ESR experiments and analysis**

Pulsed ESR measurements at X-band (~ 9.6 GHz) were performed using a Bruker ELEXSYS E580 spectrometer equipped with a 1 kW travelling wave tube power amplifier and an overcoupled sapphire ring resonator (measured in reflection) resulting in a typical τ-pulse duration of ~ 50 ns. For measurements at S-band (~ 3.5 GHz), we used a home-built spectrometer (similar in design to that described in Ref. [21]) and 3.5–4.5 GHz loop-gap resonators, wire abraded using oxygen-free copper, which were measured in transmission (see Supplementary Materials for details). The loop-gap resonators had as-fabricated quality factors of ~ 200, reducing to ~ 50 when the frequency was tuned by inserting a small (approximately 2x4 mm) piece of intrinsic 275 µm float zone Si wafer into the capacitive gap, giving a window of about 100 MHz for experiments at different microwave frequencies, and had a typical π-pulse duration of ~ 700 ns when using a 30 W solid-state power amplifier. To amplify the weak spin echo signals from these ion implanted samples, we used probeheads with cryogenic low-noise preamplifiers as described in Ref. [32]. Static magnetic fields were applied along principal crystal axes of Si either in-plane with the wafer surface [100] ($S_{e}$ geometry) or perpendicular to the wafer surface [001] ($S_{c}$ geometry).

The EDFS spectra were recorded using Hahn echo pulse sequence. For fields below 4 mT, we fit the $S_{z}$ EDFS spectra using the spin Hamiltonian to determine the centres of Gaussians with contributions from all $^{28}$Si nearest neighbours and also use the (111)$_{0}$ SHF transition leaving the amplitude and width of peaks as free parameters with the fit shown in the Supplementary Materials. The relaxation time $T_{1}$ was obtained by fitting a monoexponential function to the data obtained by the inversion recovery sequence. The electron spin coherence time $T_{2}$ was measured using the Hahn echo sequence. The resulting traces were fit using stretched-exponential decays to extract $T_{2}$ times.

**CCE simulations**

The spins have the interactions

$$H = H_{Te} + H_{Si} + H_{int}, \quad (3)$$

with

$$H_{Te} = \omega_{e} S_{z} + A_{0} S \cdot I_{0} + \omega_{n}^{Te} I_{0}^{z}, \quad (4a)$$

$$H_{int} \approx S_{z} \sum_{i} \xi \cdot k_{i} \cdot I_{i} \equiv S_{z} b_{z}, \quad (4b)$$

$$H_{Si} = \omega_{n}^{Si} \sum_{i} I_{i}^{z} + \sum_{i<j} I_{i} \cdot D_{ij} \cdot I_{j}, \quad (4c)$$

where $S$ is the $^{125}$Te donor electron spin operator, $I_{0}$ ($I_{i}$) is the $^{125}$Te ($^{29}$Si) nuclear spin operator, $\omega_{e}$, $\omega_{n}^{Te}$, and $\omega_{n}^{Si}$ are correspondingly the Larmor frequencies of the donor electron spin, donor nuclear spin and bath nuclear spin, which are related to their gyromagnetic ratios $\gamma$ by $\omega_{e} = \gamma_{e} B_{0}$, and therein $B_{0}$ is the external magnetic field applied along $z$ axis, $A_{0}$ ($A_{i}$) is the hyperfine coupling strength (tensor) between the donor electron spin and the $^{125}$Te ($^{29}$Si) nuclear spins. $D_{ij}$ is the nuclear-nuclear dipole interaction tensor. Eq. 4b is valid in the limit $\omega_{Te} \gg b$ (or equivalently the electron Zeeman energy is much larger than the hyperfine coupling of $^{125}$Te$^{\mp}$ to silicon).

When there is no external field ($\omega_{e} = \omega_{n}^{Te} = 0$), the eigenstates of $H_{Te}$ are the triplet states...
\[ |T_+\rangle = |\uparrow\uparrow\rangle, |T_0\rangle = \left( |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right)/\sqrt{2}, |T_-\rangle = |\downarrow\downarrow\rangle \]
with the eigenenergy \( A_0/4 \) and singlet states \( |S_0\rangle = \left( |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right)/\sqrt{2} \) with \(-3A_0/4\). The existence of magnetic field can mix the singlet state \( |S_0\rangle \) and the triplet state \( |T_0\rangle \) by the Zeeman energy that leads to two new eigenstates

\[
|u\rangle = \cos \frac{\theta}{2} |T_0\rangle + \sin \frac{\theta}{2} |S_0\rangle \quad (5)
\]
\[
|d\rangle = -\sin \frac{\theta}{2} |T_0\rangle + \cos \frac{\theta}{2} |S_0\rangle \quad (6)
\]
with corresponding eigenenergies

\[
E_{u/d} \approx -\frac{A_0}{4} \pm \frac{\Omega + b_z \sin \theta}{2}, \quad (7)
\]
where \( \theta = \arctan \left[ \frac{\omega_e}{A_0} \right] \) and \( \Omega = \sqrt{A_0^2 + \omega_e^2} \). Here, we have omitted \( \omega_e^4 \) since it is much smaller than \( \omega_e \). The other two eigenstates \( |T_{\pm}\rangle \) remain unchanged, but their eigenenergies become

\[
E_{T_{\pm}} = \frac{A_0}{4} \pm \frac{\omega_e + b_z}{2}. \quad (8)
\]

The Hamiltonian can be written as

\[
H \approx |1\rangle \langle 1| \otimes H^{(+)}, \quad |0\rangle \langle 0| \otimes H^{(-)},
\]
where the central-spin-conditional bath Hamiltonians for transition \( |u\rangle \leftrightarrow |d\rangle \) (\( S_z \) transition) are given as

\[
H^{(+)} \approx -\frac{A_0}{4} + \frac{\Omega}{2} + \frac{b_z \sin \theta}{2} + H_{Si}, \quad (9a)
\]
\[
H^{(-)} \approx -\frac{A_0}{4} - \frac{\Omega}{2} - \frac{b_z \sin \theta}{2} + H_{Si}, \quad (9b)
\]
and for transition \( |u\rangle \leftrightarrow |T_-\rangle \) (\( S_z \) transition)

\[
H^{(+)} \approx -\frac{A_0}{4} + \frac{\Omega}{2} + \frac{b_z \sin \theta}{2} + H_{Si}, \quad (10a)
\]
\[
H^{(-)} \approx \frac{A_0}{4} - \frac{\omega_e}{2} - \frac{b_z}{2} + H_{Si}. \quad (10b)
\]

The Hahn echo signal is

\[
A_e \propto \mathcal{L}(2\tau) = \text{Tr} \left( \rho_n e^{iH^{(-)}\tau} e^{iH^{(+)}\tau} e^{-iH^{(-)}\tau} e^{-iH^{(+)}\tau} \right),
\]
where \( \rho_n \) is the initial bath density matrix (which we choose as the infinite high-temperature thermalized state since the nuclear Zeeman energy is much less than 10 mK).

The central spin coherence is calculated using the CCE [23], in which the decoherence caused by a cluster of \( M \) bath spins \((1, 2, 3, M)\) is denoted as \( \mathcal{L}_{1,2,...,M} \). The irreducible correlation of a cluster is defined recursively as \( \tilde{L}_j = L_j, \tilde{L}_{i,j} = L_i,\tilde{L}_i^{-1}\tilde{L}_j^{-1} \), etc., that is, the decoherence function divided by all irreducible correlations of all sub-clusters. For the \( M \)-order truncation (CCE-\( M \)), the calculation takes into account the irreducible correlations up to the clusters of \( M \) spins, \( \mathcal{L} \approx \mathcal{L}^{(M)} \), with

\[
\mathcal{L}^{(M)} = \prod_{i=1}^{M} \tilde{L}_{i_1} \prod_{j_1 < j_2} \tilde{L}_{j_1,j_2} \cdots \prod_{k_1 < k_2 \ldots < k_M} \tilde{L}_{k_1,k_2,\ldots,k_M}. \]

With the secular approximation, the CCE-1 contribution (decoherence due to single-spin dynamics, which also causes the ESEEM for relatively strongly coupled nuclear spins) vanishes.

In the simulation, we place the \( ^{29}\text{Si} \) nuclear spins (with a natural abundance \( p_n = 0.047 \)) randomly on the Si lattice sites and the Te\(^+\) ions randomly substituting one of Si. The bath includes all nuclear spins within a sphere of radius of 5 nm around the central spin. The direction of \( B_0 \) is applied along [001] of the crystal. A larger bath size produces nearly the same result. The simulation is carried out by using an ensemble average over many (100) different spatial configurations. The convergence of CCE is confirmed by the fact that CCE-3 and CCE-2 produce nearly identical results.

Poisson-Schrödinger solver

We used a 1D Poisson-Schrödinger solver which is well documented [19]. Our simulations defined the top surface as a Schottky barrier with 0 V applied across it, where the barrier height was varied and the thick substrate boundary was an ohmic contact to ground. The top layer contained Te donors with the given concentrations.

ACKNOWLEDGEMENTS

The authors acknowledge the UK National Ion Beam Centre (UKNIBC), where the silicon samples were ion implanted, and Nianhua Peng who performed the ion implantation.

FUNDING

The UK Engineering and Physical Sciences Research Council (EPSRC) Skills Hub in Quantum Systems Engineering: Innovation in Quantum Business, Applications, Technology and Engineering (InQuBATE), Grant No. EP/P510270/1; The European Research Council (ERC) via the LOQOMOTIONS grant (H2020- EU.1.1., Grant No. 771493). R.B.L. was supported by Hong Kong Research Grants Council General Research Fund Project 14302121 and S.L. was supported by The Chinese University of Hong Kong Impact Postdoctoral Fellowship.

AUTHOR CONTRIBUTIONS

Conceptualization: MS, JO’S, OWK, RL, JJLM. Data curation: MS, JO’S, OWK, SL. Formal analysis: MS, JO’S, OWK, SL. Funding acquisition: MS, OWK, RL, JJLM. Investigation: MS, JO’S, OWK, SF, CWZ, SL. Methodology: MS, JO’S, OWK, RL, JJLM. Project administration: JJLM. Resources: MS, JO’S, GD, TS, PS,
DATA AND MATERIALS AVAILABILITY

All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors. The custom code that supports the findings of this study is available from the corresponding author upon request.
(2020).
Supplementary Materials for Spin coherence of near-surface ionised $^{125}$Te$^+$ donors in silicon

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SUPPLEMENTARY MATERIALS

A. S-band setup

ESR experiments at S-band are performed using a home-built spectrometer [1] with a 30 W solid-state power amplifier. The spectrometer is connected to a home-built transmission probehead equipped with a loop-gap resonator. The resonator design is presented in Fig. S1A together with the microwave field simulations of the mode used to drive the ESR transitions. The probehead contains a low-noise cryogenic high-electron-mobility transistor (HEMT) preamplifier (Low Noise Factory LNF-LNC6_20C), which is protected from high power microwave pulses by a fast microwave switch (Analog Devices HMC547ALP3E) (see Fig. S1B). The resonator is coupled via a short input and a long output antenna and has a quality factor of \( Q \sim 200 \) (Fig. S1C). The frequency of the resonator can be tuned by about 200 MHz by inserting a small piece of intrinsic silicon in the resonator gap. This lowers the resonator Q-factor to about 50 providing us a sufficiently broad window for ESR experiments at different microwave frequencies (Fig. S1D). Several resonators having different untuned frequencies and similar Q-factors were used in this study to cover \( \sim 3.5-4.1 \) GHz frequency range.

B. Implanting and diffusion

We simulate the distribution of implanted ions using SRIM, a Monte-Carlo simulator, that simulates the random motion of energetic ions incident on samples. We show the SRIM profiles of Te for the 800 keV implantation in Fig. S2A and the 20 keV implantation in Fig. S3. We also directly measure the Te profile using depth profiled SIMS. A diffuse beam of C\(_6\)O ions is directed to the sample where it mills the surface of the sample in a number of milling stages. The ionised species milled from the surface are collected and analysed using mass spectrometry allowing us to count the \(^{125}\)Te in the sample. We normalise the \(^{125}\)Te signal by the Si\(^{3-}\) as this signal is proportional to the ion current and allows us to correct for any instabilities in the ion beam. Measuring the total depth milled allows us to determine the depth milled per stage and thus calibrate the depth.

The SIMS profiles of samples before annealing match well to the SRIM profiles for both samples implanted at 20 and 800 keV. There is an offset in the depth from the SRIM and
Figure S1. (A) Simulation of the electric and magnetic microwave field components of a loop-gap resonator mode used to drive ESR transitions at S-band. Simulations are performed at arbitrary excitation power using CST Studio software. (B) Schematic of the microwave circuit used to amplify the spin signals. A photograph of a loop-gap resonator with inserted Te:Si sample is shown at the bottom in (B). The fast microwave switch is used to protect the low-noise cryogenic HEMT preamplifier from high power pulses. (C,D) $S_{21}$ traces of untuned and tuned resonator.

Figure S2. (A) $^{125}$Te counts in SIMS data normalised to Si$^3$ – counts to account for varying ion current. The faint lines show the data, and solid lines the data after application of a Savitzky-Golay filter to reduce noise. Gaussians (black dashed lines) are fit to the raw data, and their standard deviation is shown in (B). The simulated Te distribution using SRIM Monte Carlo techniques is shown in (A). Slight differences in the centre of the peak may be caused by the depth calibration of SIMS data.
Figure S3. SIMS and SRIM for the (A) intrinsic and (B) p-type samples implanted at 20 keV before and after annealing at 1000°C for 5 minutes.

SIMS profiles with SRIM implying deeper implants than SIMS. The discrepancy is likely due to the non-equilibrium effects in the SIMS depth profiling when milling the surface.

We measure the SIMS profile of Te after annealing the sample at different temperatures (Fig. S2A). The presented profiles were obtained by applying a Savitzky-Golay filter to smooth the noisy data. The Te distribution is well fit by a Gaussian profile for all annealing temperatures. We plot the standard deviation of the Gaussian profile as a function of annealing temperature in Fig. S2B. There is little broadening of the implanted peak at temperatures $\lesssim 800^\circ$C, but the peak broadens by $\sim 35$ nm at 1000°C showing that this annealing schedule allows reasonable diffusion in the sample. In the future, careful simultaneous optimization of donor diffusion, donor $T_2$ and activation yield will provide optimal anneal conditions.

We also measure the SIMS profiles for the samples implanted at 20 keV after annealing and show this data alongside SRIM simulations in Fig. S3. The peak in Te counts that was present before annealing is absent after annealing at 1000°C. This is consistent with Te diffusion seen in the 800 keV sample.

C. Te activation

To determine the activated Te fraction, we measure the echo strength of the implanted samples relative to a reference sample. Both the reference sample and the implanted samples are loaded into the cavity. Experiments are performed at X-band with pulse parameters optimized for the cavity, and the echoes are acquired in the centre of the respective spin.
Figure S4. Echo intensity as a function of time as different wavelength light is shone at the deeply implanted p-type sample at 10 K. The sample starts as-cooled. Red and blue circles indicate 4300 nm and 1050 nm LED illumination, respectively and black crosses are data without illumination.

transitions using pulses with bandwidth larger than the spin linewidth. The reference sample is a small piece of bulk doped P:Si meaning that it contains a significant numbers of spins. The reference sample has resistivity $\rho = 2.2 \ \Omega \cdot \text{cm}$ giving a phosphorous concentration of $2.1(2) \times 10^{15} \ \text{cm}^{-3}$. Weighing the sample allows us to determine the reference spin number, $N_P$.

We measure the number of implanted Te, $N_{\text{Te,total}}$ by multiplying the surface area of the sample by the implantation fluence. The surface area is obtained from the mass of the used sample, the wafer thickness and silicon density.

We correct the amplitudes of Te:Si and P:Si signals by the ratio of the matrix element squared for the two transitions $M_{\text{rat}}^2 = M_P^2/M_{\text{Te}}^2$ and thus measure activation by comparing the echoes amplitudes from the two species denoted $A_{\text{Te}}$ and $A_P$, respectively. We compute the number of active Te as $N_{\text{Te,active}} = N_P \times M_{\text{rat}}^2 \times A_{\text{Te}}/A_P$. We find the activation by $N_{\text{Te,active}}/N_{\text{Te,total}}$.

D. LED illumination of the deeply implanted p-type sample

Fig. S4 shows echo intensity as a function of time as different LEDs are shone at the deeply implanted p-type sample at 10 K. The 1050 nm illumination destroys the echo, while its intensity is recovered to the as-cooled value after the subsequent 4300 nm illumination.
Figure S5. Effect of FLP voltage on the band structure at the surface in the Te doped samples. The top, middle and bottom rows correspond to 20 nm intrinsic, 20 nm p-type and 200 nm p-type samples, respectively. Each profile is colour coded as to whether it yields \( \sim 100\% \) single ionisation (green), a fraction single ionisation (amber) or \( \sim 0\% \) single ionisation (red).

E. Fermi level pinning and band bending

We investigate FLP by solving the 1D Poisson-Schrödinger equation for different implantation profiles considering different bulk doping of the substrate. This allows us to extract the band profile inside the silicon, which determines the charge state of the Te. We perform these simulations with a simulation temperature of 40 K. At lower temperatures, the simulations do not converge. Performing these simulations as a function of temperature shows that the band profiles depend very weakly on the simulation temperature.

We perform the simulations as a function of the FLP level allowing us to investigate how FLP level effects the ionisation fraction of Te. This is shown in Fig. S5. We find that there are regions of FLP, which result in high ionisation efficiency based on surface band bending for the shallow implants. In contrast, the deeper implant has approximately constant ionisation fraction independent of the surface and determined by the boron concentration.
F. SHF levels

SHF effects shift the frequency of the $^{125}\text{Te}^+$ transitions. The SHF coupling contains dipolar and contact terms and depends on the location of $^{29}\text{Si}$ nuclear spins. ENDOR measurements of the coupling parameters for the closest $^{29}\text{Si}$ have been performed in Ref. [2]. In Fig. S6, we overlay experimental EDFS data with the simulated transitions corresponding to the strongest SHF couplings. We colourise the lines by the matrix element squared at the different transitions. Simulations performed using EasySpin [3].

We can see that the $S_z$ transition splits into well resolved levels, and that the different levels are well matched by the SHF levels from the $^{29}\text{Si}$ considered here. The $S_x$ transition is sufficiently broad that the different SHF levels cannot be well resolved. However, for $S_x$ transitions there is asymmetry between the regimes higher and lower in frequency than the zero-field splitting, and the SHF levels are split further from the all-$^{28}\text{Si}$ case at lower frequencies. This is reflected in the linewidth of the $S_x$ transition with $\gamma \sim 3$ MHz at lower frequencies and $\gamma \sim 4$ MHz at higher frequencies with both these points shown in Fig. 4 in the main text.

We fit the 2D-EDFS for $S_z$ transitions considering the $^{28}\text{Si}$ line and the (111)$_2$ lines as described in the main text and show the result in Fig. S7.

G. ESEEM

We use EasySpin [3] to simulate the echo suppression by ESEEM at low magnetic fields. In our simulation, $^{29}\text{Si}$ is randomly distributed according to its natural abundance around $^{125}\text{Te}^+$ centre in Si lattice (see inset in Fig. S8). For $^{125}\text{Te}^+ - ^{29}\text{Si}$ distances of less than 9.5 Å, we use the SHF couplings determined in the previous ENDOR study [2]. For longer distances, we ignore the isotropic contact contribution and calculate the SHF couplings using the point-dipole approximation [4]. The interaction distance is truncated at 30 Å, which proved to be sufficient to achieve a good convergence of the simulation. We average 50 of such realizations to get the final ESEEM traces.

The simulated time domain ESEEM data obtained at different magnetic fields are presented in Fig. S8 revealing ESEEM with the modulation frequency close to the Larmor frequency of $^{29}\text{Si}$. This indicates that ESEEM is mostly dominated by very weakly coupled
Figure S6. Different SHF transitions overlaid on 2D EDFSs. The top (bottom) row shows $S_z$ ($S_x$) transitions. The line colour of SHF levels is proportional to the matrix element squared. There are differences in the number of equivalent subsites for the different shells meaning that the intensity of the different SHF branches in EDFS will be modified.

Figure S7. (A) Repeat of the EDFS from Fig. 1A (main text) showing the SHF levels used to fit the spectrum. (B) The result of the fit using four Gaussians centred at the lines shown in the figure. This fit is used to extract linewidths at low $\partial f/\partial B_0$ in Fig. 4 (main text).

$^{29}$Si nuclei. At magnetic fields below $\sim 1$ mT, the time between the dips in the echo intensity becomes comparable with $T_2$ of $^{125}$Te$^+$ resulting in a much shorter value of the effective apparent $T_2$ below $\sim 5$ mT as demonstrated in Fig. S9. This result is in agreement with our experimental results that show a sudden decrease of the measured $T_2$ in the same field region.
Figure S8. ESEEM modulations at different field magnitudes. We model ESEEM modulation using the model shown in inset, where $^{29}\text{Si}$ nuclei are randomly distributed in the matrix around a central $^{125}\text{Te}$ atom. We calculate the dipolar interaction between $^{29}\text{Si}$ nuclei and the Te and the associated modulation in two pulse ESEEM experiments. At higher fields, ESEEM modulation results in minimal change to echo amplitude, but at lower fields strong ESEEM modulation occurs.

Figure S9. (A) Simulated coherence decay of $^{125}\text{Te}^+:\text{Si}$ at 0.2 mT assuming $T_2 = 1.2$ ms (black). The exponential fit to the data results in a much shorter apparent $T_2$ due to the severe ESEEM suppression. (B) Magnetic field dependence of the apparent $T_2$ obtained by fitting the simulated coherence decays.

H. $T_1$ and $T_2$

We first measure the $T_1$ and $T_2$ of both $S_z$ and $S_x$ transitions. The $T_1$ follows a $T^{-9}$ dependence implying that it is phonon limited as has been widely seen for donors in silicon,
Figure S10. The temperature dependence of $T_1$ and $T_2$ at both a high field $S_x$ transition and a low-field (near clock) $S_z$ transition. The $T_1$ follows a $T^{-9}$ dependence commonly seen for silicon donors.

including selenium, as discussed in the main text. Both $S_x$ and $S_z$ transitions follow the same temperature dependence and within errors have the same values of $T_1$. At high temperatures, $T_2$ is limited by $T_1$, but as the temperature falls, $T_2$ saturates. We ensure that all measurements of $T_2$ are performed at temperatures below the saturation temperature so that no $T_1$ effects become mixed into the signals. We ensure that shot repetition times are longer than $T_1$.

As indicated in the main text, the discrepancy between simulated $T_2$ limits and experimental data suggests an additional decoherence process. We consider different noise mechanisms which could couple to our samples, but ultimately we think are unlikely to cause the extra decoherence we see in these samples. Three possible sources of additional noise we could find in our samples are magnetic noise from the electron spin of uncompensated boron acceptors, magnetic or electric noise from spins or traps, respectively, on the surface of the silicon, and unhealed damage from ion implantation. The first two noise sources will differently affect the samples we use in this work, and we can study the literature to estimate the effect of implantation damage. We found similar $T_2$ times for both the deeply implanted sample (boron present, weakly affected by distant surface) and the shallow sample (no boron, close to surface), which suggests that neither the surface nor the boron are the cause of this additional noise, although we cannot rule out boron acceptors and surface proximity adding the same levels of noise. Recent measurements of the effect of silicon surface on the coherence time of Bi:$^{28}$Si with peak Bi density $\sim$50 nm below the
silicon surface showed that charge noise from the surface limited coherence to \( \sim 300 \) ms and found an effective magnetic field noise from the silicon surface \( \sim 10 \) nT, which would limit coherence times to \( \sim 3.5 \) ms even at the highest values of \( \partial f / \partial B_0 \) [5] both much longer than timescales we measure here. Ion implantation has been widely used to implant \( ^{209}\text{Bi}^+ \), an ion approximately \( 2 \times \) heavier than tellurium, and at higher energies than used here. Despite this, long coherence is routine [6], and studies on the other donors indicate that anneals for the same times as used here at 900°C are already sufficient to heal implantation damage, which also suggests that this is unlikely source of the additional decoherence mechanism.

We compare our results with previous measurements of dilute ensembles of the deep donor \( \text{Se}^+ \) in isotopically purified silicon, where coherence times of \( \sim 80 \) ms were observed even away from clock transitions [7]. The predominant difference between these samples and ours are the spin density (both \( \text{Se}^+ \) and compensating B) and the isotopic purification. A high density of resonant spins causes instantaneous diffusion (ID) \( \propto (\partial f / \partial B_0)^2 \) [4] and direct flip flops (dFFs) [8]. ID should be suppressed at clock transitions and so does not explain rather short coherence we measured here. The active spin concentrations in these samples (\( \sim 10^{16} \) cm\(^{-3} \)) implies, by inference from bismuth coherence times measured at clock transitions [9], that dFFs would limit coherence to \( \sim 8 \) ms, much longer than the coherence time we measured. These considerations suggest that our \( T_2 \) measurements should not be limited by spin concentrations, particularly at the \( S_z \) clock transition.

The \( T_2 \) of donors in natural silicon depends on the orientation of \( B_0 \) with respect to the principal axes of the silicon host matrix due to the anisotropy of the nuclear dipolar interaction [10]. Maximal \( T_2 \) times are observed with \( B_0 \) along one of the principal axes [001] (or equivalent), and a minimum is found along [111] (or equivalent). Simulations of coherence times with respect to the angle of the magnetic field (\( \theta \)) with respect to the principal silicon axes. We measured the dependence of \( T_2 \) upon the angle of \( B_0 \) relative to the silicon crystal axes and present the results in Fig. S11. Despite cubic crystal symmetry, \( T_2 \) is periodic in 180° (rather than 90°) implying some alignment error.

We also show the CCE-2 simulated \( T_2 \) times for an \( S_z \) transition at 10 mT revealing that the coherence times drop quite rapidly as the field is tilted away from principal crystal axes (Fig. S12). This replicates what is seen above in Fig. S11. It implies that there is some misalignment so that when the field is nominally along [100] there is actually a residual angle between the crystal axis and the field resulting in the only partial recovery of \( T_2 \).
Figure S11. Angular dependence of $T_2$ of an $S_x$ transition measured at X-band at 8.5K. $T_2$ does not follow the cubic crystalline symmetry of silicon implying that the surface plays some role in breaking symmetry.

In order to measure $S_z$ transitions, we had to rotate the resonator so that all $S_z$ measurements are performed with an in plane field nominally along [100], whereas $S_x$ measurements are performed with field along [001]. We therefore think that the reduced $T_2$ in $S_z$ transitions relative to the CCE-2 simulations likely arises due to misalignment of the sample to the magnetic field. We consider the $T_2 = 1.18$ ms measured at an $S_z$ transition at 10 mT ($\partial f / \partial B_0 \sim 0.08 \gamma_e$). At this field value the CCE-2 simulation predicts $T_2 \sim 2.2$ ms, but, if we add in the same magnetic field noise as for $S_x$ transitions and a misalignment from the principal crystal axis of $\sim 15^\circ$, we recover the $\sim 1.2$ ms $T_2$. Inspecting our samples where many pieces of the same wafer are packed into a sample tube to maximise filling factor (and consequent signal) we observe a $\sim 5^\circ$ misalignment. More misalignment could occur due to imperfect alignment in the home-built probe used in these experiments and so this total alignment error is plausible in our setup.

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Figure S12. The angular dependence of the $T_2$ simulated by CCE-2 for an $S_z$ transition at 10 mT, well before the onset of ESEEM.

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