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Electron Spin Coherence of Phosphorus Donors in Isotopically Purified ^{29}Si

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We investigate spin coherence time of electrons bound to phosphorus donors in silicon single crystals, employing a pulsed electron paramagnetic resonance technique. The samples were isotopically controlled so that they may possess different concentrations (about 5% and 100%) of ^{29}Si, which is the only non-zero-spin (spin-1/2) stable isotope of Si. Both ^{29}Si-concentration dependence and orientation dependence of the electron spin coherence time demonstrate that the decoherence is caused by spectral diffusion due to mutual flip-flops of the environmental nuclear spins. The detail analysis of spin echo decay curves enables the unique assignment of the host sites responsible for electron spin echo envelope modulation.

KEY WORDS: silicon-based quantum computer; electron spin qubit; coherence time; environmental nuclear spin.

1. INTRODUCTION

A spin degree of freedom has been identified as a robust quantum information carrier (called "qubit" if it forms two-level system) in various solid-state implementations of quantum computation. Nuclear spins [1] or electron spins [2] of phosphorus donors in group-IV semiconductors, or isolated electron spins in III–V based quantum dots [3] are such examples. In those schemes, two-qubit operations are exclusively realized through the exchange interaction between adjacent electron spins. However, electron spins also couple with *environmental nuclear spins* through the hyperfine (hf) interaction. For instance, ^{29}Si nuclei (spin-1/2), which occupy 4.67% of the lattice sites in naturally available Si, cause local fluctuation of the magnetic field due to mutual flip-flops of their spins. This effect, termed as nuclear-induced spectral diffusion (SD), leads to the decoherence of the donor electron spins. In practice, depleting ^{29}Si isotopes from natural Si circumvents this drawback. Unfortunately though, such isotope purification cannot be applied to III–V based implementations since all the naturally available isotopes in III–V materials possess non-zero nuclear spins. While there is a body of theoretical works on the effect of environmental nuclear spins on electron spins [4–8], contributions from the experimental side to date are few and far between. In this work, we provide experimental information on this important and intriguing problem by measuring the electron spin coherence time T_2 of P donors in Si.

Several groups have reported T_2 of P donors in Si. Those studies, however, do not always provide information on the effect of environmental nuclei. We now discuss the necessary condition to study nuclear-induced SD, and outline the previous studies briefly. All the experiments performed so far rely solely on a two-pulse electron spin echo (ESE) method, which is a standard pulsed electron paramagnetic resonance (EPR) technique. The pulse sequence is given by $\pi/2$-τ-Θ_2-τ-echo, where τ is the interpulse delay and Θ_2 is the turning angle of the second pulse. Two experimental conditions that can be readily, but must be carefully, controlled are the temperature T and the number of the spins in a unit volume (1 cm^3), i.e., the net donor concentration N_d. The temperature need be low not only for the donor to capture its

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excess electron, but for the thermal (T_1) effect not to affect T_2. Yablonovitch *et al.* [9] and Tyryshkin *et al.* [10] observed in samples with $N_d \approx 10^{15}$ and 10^{16} that T_1 and T_2 nearly coincide at $T > 10\,K$. This is attributed to an Orbach process, a well-known T_1 effect. In the Orbach process, an electron in the ground state is thermally activated to the first excited state, and flips its spin at a certain probability in returning to the ground state. Below 10 K, T_2 deviates from T_1, and becomes insensitive to temperature, while T_1 still increases exponentially with cooling. Therefore, the temperature must at least be below 10 K to study the effect of nuclear-induced SD. Likewise, the impurity concentration need be kept low in order to suppress the exchange and/or dipole interactions among the donor electron spins. The exchange interaction occurs at relatively high impurity concentrations where the electron wavefunctions overlap. It is known from cw-EPR experiments [11] that at $N_d \approx 10^{17}$ exchange-coupled donor-spin pairs are formed, which turn into clusters at $N_d \approx 5 \times 10^{17}$. Finally, metal-insulator transition occurs at $N_d \approx 10^{18}$ in this system. On the other hand, the dipole interaction is a long-range interaction, and thus expected to be valid at even lower impurity concentrations. An effect related to the dipole interaction is instantaneous diffusion (ID), which is a spurious effect induced by the second pulse in the two-pulse ESE experiment. The reversal of the electron spins by the second pulse causes them to sense electron-dipolar fields different from they used to. In other words, the electron spins instantaneously change their resonance frequencies, and thus SD occurs. The time constant due to ID is given by

$$\frac{1}{T_{ID}} = N_d \frac{\pi}{18\sqrt{3}} \frac{\mu_0 g_e^2 \mu_B^2}{\hbar} \sin^2 \frac{\Theta_2}{2},$$

where g_e is the electron g factor and μ_B the Bohr magneton [12]. Technically, ID can be reduced by the use of the second pulse with small Θ_2. However, it is more convenient to use samples in which T_2 is not affected by ID. For this, we require $T_{ID} > T_2$. Assuming $g_e = 2$ and $\Theta_2 = \pi$, $N_d = 10^{16}$ yields $T_{ID} \approx 240\,\mu s$, and $N_d = 10^{15}$ does $T_{ID} \approx 2.4$ ms. As T_2 values so far reported for natural Si usually fall between 200 and 500 μs, it is necessary to use a sample with $N_d < 10^{16}$. In the first systematic study of T_2 in natural Si conducted by Chiba and Hirai [13], a series of samples with $N_d = 10^{16}$–10^{18} were measured at $T = 1.6$–4.2 K. The temperatures were clearly low enough, while the impurity concentrations were relatively high in light of the criteria above mentioned. In fact, Faciulli *et al.* [14] observed ID in natural Si with $N_d = 4.1 \times 10^{16}$ at 10 K. On the other hand, Yablonovitch *et al.* [9] report that T_2 for samples with $N_d = 10^{15}$ and 10^{16} are nearly the same. It seems $N_d = 10^{16}$ is the border at which ID prevails. The bottom line here is: *to study nuclear-induced SD in natural Si, the impurity concentration should be less than* 10^{16} *cm*$^{-3}$ *and the temperature be below 10 K*. With this condition met ($T = 8$ K and $N_d = 0.8 \times 10^{15}$), the present authors [15] have provided an evidence that nuclear-induced SD dominates T_2 from the orientation dependence of T_2, which will be discussed in detail later.

Another approach to investigate the effect of nuclear-induced SD is to change ^{29}Si-concentration f. This was originally performed by Gordon and Bowers [16]. They measured isotopically purified ^{28}Si (spin-0) with $N_d = 4 \times 10^{16}$ at 1.6 K, and obtained T_2 of 520 μs, which is about twice longer than that of natural Si with similar impurity concentrations ($T_2 =$ 240 μs and $N_d = 3 \times 10^{16}$). The impurity concentration is again relatively high in this experiments. At lower ^{29}Si-concentrations where T_2 is expected to be longer, the impurity concentration need be lower as well. The result is most likely to be limited by ID. It is noteworthy that in this experiment $\Theta_2 = \pi/2$ was used, therefore ID is partially eliminated. Recently, Tyryshkin *et al.* [10] revealed that ID is indeed dominant in isotopically purified ^{28}Si samples ($f = 0.07\%$) with $N_d = 0.87 \times 10^{15}$. They have also demonstrate, by carefully changing Θ_2, that T_2 would be several orders longer (up to 60 ms) in the limit of $\Theta_2 \to 0$. Such ^{29}Si-diluted samples have practical importance on building silicon-based quantum computers, but provide less information on nuclear-induced SD since this effect is absent there. Rather, we are interested more in the regime where ^{29}Si nuclei play a critical role on the decoherence. For this purpose, we prepared two single crystalline samples containing different amount of ^{29}Si isotopes ($f = 4.67\%$ and 99.23%), but nearly the same amount of P donors ($N_d = 0.8 \times 10^{15}$). Hereafter, we refer them as ^{29}Si-5% and ^{29}Si-100%, respectively. The details of the samples can be found in Refs. [15,17].

2. RESULTS AND DISCUSSION

2.1. ^{29}Si-Concentration Dependence

The two-pulse ESE experiments were carried out at 8 K with a Bruker Elexsys E580 X-band

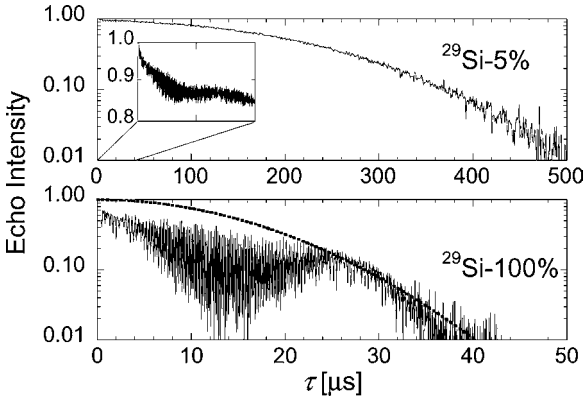

Fig. 1. The ESE decay curves as a function of τ when B_0 is applied along [001]. The dotted curve in the lower panel is a Gaussian fit to the ESE envelope. The inset in the upper panel shows decay behavior at early stages. The beats in the decay curves are ESEEM. See the text.

spectrometer. The duration of the $\pi/2$ pulse was 16 ns. Θ_2 was π, and the pulse length was 32 ns. Echo-detected EPR spectra exhibit a doublet separated by 4.2 mT due to the hf interaction with the ^{31}P nuclei (spin-1/2), and we set the external magnetic field B_0 at the center of the high-field peak. Figure 1 shows the ESE intensities as a function of τ when B_0 is applied along [001]. The envelopes of the decay curves can be expressed by $\exp(-m\tau^2)$, therefore T_2 is determined as $2m^{-1/2}$ by defining it as $1/e$ decay time of an echo envelope. Figure 2 shows T_2 thus obtained. We also plot T_2^*, which is calculated as $2(2\ln 2)^{1/2}\hbar/g_e\mu_B\Delta B$, where ΔB is the inhomogeneous linewidth of the echo-detected EPR peak. ΔB was 0.26 mT for ^{29}Si-5% and 1.2 mT for ^{29}Si-100%. The factor $2(2\ln 2)^{1/2}$ is accompanied due to the Gaussian lineshape of the respective peak. For comparison, $T_2 = 14$ ms and $\Delta B = 0.008$ mT, reported by Tyryshkin [10], are also given in Fig. 2. The former corresponds to intrinsic T_2 (at $\Theta \to 0$) at 8.1 K. It is noteworthy that simple extrapolations of our results roughly coincide with their results.

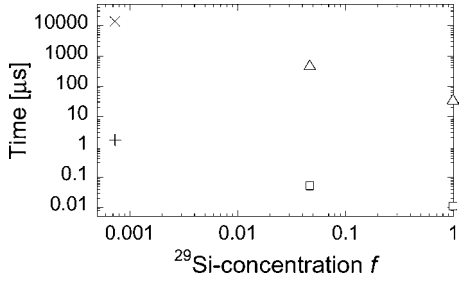

Fig. 2. T_2 (△) and T_2^* (□) as a function of ^{29}Si-concentration f. T_2 (×) and T_2^* (+) reported by Tyryshkin *et al.* [10] are also plotted for the readers' convenience.

The decay curves also exhibit remarkable features known as electron spin echo envelope modulation (ESEEM). The mechanism of ESEEM can be explained briefly as follows: If a nuclear spin close to the electron spin is subject to the moderate hf field in addition to the external magnetic field, the nuclear spin precesses around an effective magnetic field which is tilted from the external magnetic field, i.e., m_I is no longer a good quantum number. Due to this state mixing, formally forbidden nuclear-spin-flip transitions ($\Delta m_S = \pm 1$, $\Delta m_I = \pm 1$) can occur, and interfere with allowed transitions to produce beats in the ESE envelope. In two-pulse experiments for an $S = 1/2, I = 1/2$ spin system, the modulation contains the ENDOR frequencies ν_+ and ν_-, and their sum and difference $\nu_+ \pm \nu_-$. However, in principle, any nearby nuclei can couple with the electron spin. In this case, combination frequencies are also contained. $\nu_\pm$ are given by

$$\sqrt{\left(\nu_I \pm \frac{a_{iso} + b(3\cos^2\varphi_i - 1)}{2}\right)^2 + \frac{(3b\sin\varphi_i\cos\varphi_i)}{4}},$$

where ν_I is the nuclear Larmor frequency, a_{iso} and b are the isotropic and anisotropic hf coupling constants, respectively, and φ_i is the angle between B_0 and the unique axis of the hf tensor [12]. The orientation dependence of the effect will be analyzed in the next section.

2.2. Orientation Dependence

^{29}Si-100% is best suited to test the orientation dependence of T_2 due to nuclear-induced SD, since the effect is most enhanced and other decoherence mechanisms are less significant there. The sample was rotated around the $[1\bar{1}0]$ axis perpendicular to B_0, and θ is defined as the angle between B_0 and [001] (e.g., $\theta = 0°$ when $B_0 \parallel [001]$, $\theta = 55°$ when $B_0 \parallel [111]$, and $\theta = 90°$ when $B_0 \parallel [110]$). The uncertainty in θ is estimated to be less than 5°. Figure 3(a) shows the orientation dependence of T_2 in ^{29}Si-100%. The clear tendency that T_2 is longest when B_0 is along [001] and shortest when [111] is confirmed.

This result demonstrates that the decoherence is caused by ^{29}Si nuclei mutually coupled via the dipolar interactions, since the tendency directly reflects

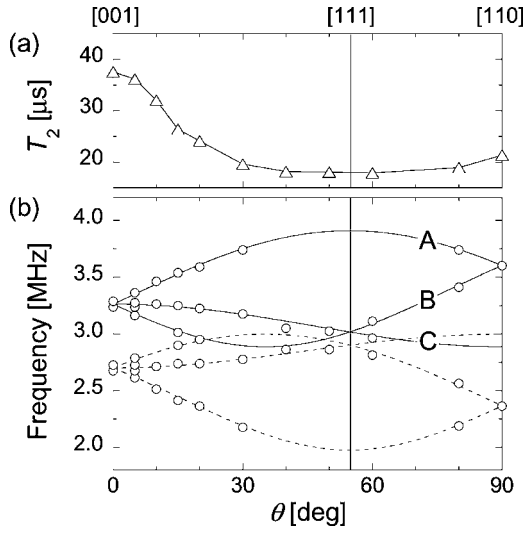

Fig. 3. The orientation dependence of (a) T_2 in ^{29}Si-100%, and (b) ENDOR frequencies around 3 MHz obtained from FT-ESEEM spectra. The solid (dashed) lines are for ν_+ (ν_-). Which lattice site produces lines A, B, and C is explained in the text.

the strength of the nuclear dipolar couplings. That is, when B_0 is along [111], one of the four nearest-neighbor bonds of the Si atoms is parallel to B_0, and this pair of nuclei gives rise to the strongest coupling. With B_0 along [001], all the dipolar couplings between nearest neighbors are frozen since the angle between B_0 and the vector connecting the nearest neighbors is a so-called magic angle. Although not shown, the same tendency was also observed in ^{29}Si-5%, suggesting that nuclear-induced SD is still dominant. It is inferred that this tendency will vanish in a low-f sample where the nuclear-induced SD is no longer effective. This qualitative discussion can be made quantitative by taking the hf interaction between the electron and environmental nuclei into account as well as the nuclear dipolar coupling. Indeed, a stochastic theory proposed by de Sousa and Das Sarma [6] predicts the observed angular dependence correctly, although it overestimates T_2 by about a factor of 3. This already-reasonable agreement becomes even better if we calculate the ratio of T_2 between the samples. Indeed, the theoretical ratio of T_2 for ^{29}Si-5% to 100% falls between 11.2 and 11.8 [18], while the experimental ratio lies between 11.2 and 14.4. This means that their theory also explains the ^{29}Si-concentration dependence as well as the orientation dependence. Coish and Loss [8] have recently studied non-Markovian dynamics of electron spins. Their theory is applicable to this system, but no concrete values of T_2 are reported.

ESEEM can be viewed as a leakage of the qubit information into the environment. An environmental nuclear spin tilts its quantization axis due to the hf field from the qubit electron spin, which implies that the electron-nuclear spin system is entangled. As a result, the qubit information is eavesdropped by the environment through the forbidden transitions. Now our primary task is to pin down the "eavesdropper" among numerous "suspects." The clue is the "fingerprints" left on the ESE decay curves, namely the modulation frequencies. Figure 3(b) shows the angular dependence of ENDOR peaks obtained by usual Fourier analysis. A dc component in the decay curve was subtracted first, then the remaining ac component was Fourier transformed. As the data were taken from $\tau = 320$ ns, all the modulations that decayed within 320 ns cannot be recovered in the frequency domain spectra. $\nu_\pm$ calculated with $a_{\rm iso} = 570$ kHz and $b = 681$ kHz agree well with the experimental results. Comparing with hf constants previously reported [19,20], we assign the observed peaks to shell E, namely four nearest neighbors of the donor. Lines A and B originate from (111) and ($\bar{1}11$) sites, respectively. Line C is doubly degenerate, since ($1\bar{1}\bar{1}$) and ($\bar{1}1\bar{1}$) sites locate each other at plane symmetric positions with respect to the ($1\bar{1}0$) plane. We note that in the pervious cw-ENDOR experiment by Hale and Meiher [19], peaks within the frequency range $\nu_{\rm I} \pm 600$ kHz were not used for the analysis, since a "forest" of ENDOR peaks makes angular dependence of each peak untraceable in this "continuum" region. In fact, this difficulty prevented Feher from determining the hf constants for shell E in his initial ENDOR experiment [21]. On the contrary, ESEEM allows to extract only peaks from the nearest neighbors even at frequencies very close to $\nu_{\rm I}$. Instead, line A disappears when B_0 is along [111] since the directions of B_0 and the anisotropic hf field felt by the (111) nucleus coincide, i.e., the nuclear quantization axis stays the same. In this sense, ESEEM and ENDOR play complementary roles.

As revealed, the nuclei responsible for ESEEM reside close to the donor atom, typically only sub-nanometers apart. On the contrary, the nuclei contributing to flip-flop processes are distributed in the area relatively far from the donor atom, since a flip-flop of a certain pair of nuclei occurs only when the difference of the hf interaction between the pair is small enough to satisfy the condition of energy conservation. In this system, the Fermi contact hf interaction roughly decreases monotonously with receding from the donor atom, and the radius of the

diffusion barrier that prevents the flip-flops within its bounds is estimated to be about 8 nm [18].

3. CONCLUSION

In conclusion, we have measured T_2 of P donor electron spins in isotopically controlled Si single crystals at 8 K, putting emphasis on the ^{29}Si-concentration dependence and the orientation dependence. Frequency domain analysis revealed that ESEEM effects originate mainly from the hf interactions between the donor electron and its nearest neighbor nuclei. It is certainly necessary to add more points on Fig. 2. Such experiments are now underway by the present authors. They have prepared samples with $f = 10\%$ and 50%, using the same crystal growth apparatus as used in Ref. [22]. Those samples will allow us to carry out T_2 measurements of the electron spins as a function of ^{29}Si-concentration.

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