Spin Echoes in the Charge Transport through Phosphorus Donors in Silicon

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The electrical detection of spin echoes via echo tomography is used to observe coherent processes associated with the electrical readout of the spin state of phosphorus donor electrons in silicon near a SiO_2 interface. Using the Carr-Purcell pulse sequence, an echo decay with a time constant of 1.7 ± 0.2 μs is observed and discussed in terms of decoherence and recombination times. Electrical spin echo tomography thus can be used to study the dynamics of the spin-dependent transport processes, e.g., in realistic spin qubit devices for quantum information processing.

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A detailed understanding of the dynamics of charge carriers in semiconductors is of fundamental importance for the basic physical understanding of charge transport, relaxation, and recombination processes. However, a correlation of the dynamics observed to specific microscopic states generally remains a challenge. In indirect semiconductors such as silicon, electrically detected magnetic resonance (EDMR) is uniquely capable of microscopically identifying electronic states participating in the charge transport with a sensitivity approaching single spin detection [1–3]. On the other hand, the dynamics of paramagnetic states such as the spin relaxation and decoherence can be determined via the observation of spin echoes. In this Letter, we demonstrate that pulsed EDMR experiments using the Carr-Purcell pulse sequence in combination with echo tomography [4] can selectively monitor the dynamics of electronic transitions between two distinct paramagnetic states. We use these electrically detected spin echoes exemplarily to study spin-dependent recombination involving phosphorus donors in crystalline silicon and Si/SiO_2 interface states which have recently been proposed as a technique to read out the spin state of donor electrons [5] and quantitatively discuss this result taking into account decoherence and recombination processes. The echo dynamics found here provide a critical test for the applicability of donor qubits in the framework of quantum information processing [6]. More importantly, this work shows that with the help of advanced pulse sequences combined with echo tomography valuable new information on the complex charge carrier and spin dynamics can be obtained by EDMR.

To detect the donor spin information electrically, we use a spin-to-charge conversion method based on the Pauli exclusion principle. The P donor and a so-called P_{b0} center [7,8], a paramagnetic interface state at the Si/SiO_2 interface in close vicinity to the donor, form a correlated spin pair as shown in Fig. 1(a). Since a doubly occupied, negatively charged P_{b0}^- state as the final state of the spin-to-charge conversion has a total spin $S = 0$, the transition of the electron from a P donor to a neutral P_{b0} center is forbidden for triplet pairs, while for singlet P-P_{b0} pairs the transition can occur [9]. Under spin resonance conditions the spin pair can be changed coherently, e.g., from the triplet to the singlet configuration, resulting in a change of the rate of the spin-dependent transition sketched in Fig. 1(a), which in turn is observable as a resonant change of the conductivity [5].

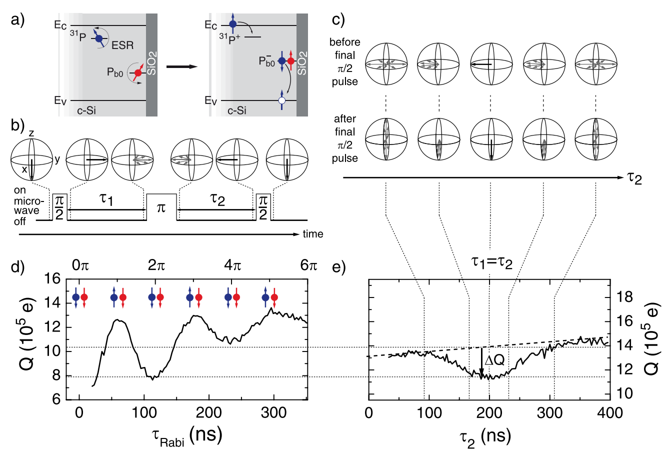

FIG. 1 (color online). (a) Spin-dependent transition involving the electron spin of a ^{31}P donor and a paramagnetic state P_{b0} at the interface between crystalline Si (c-Si) and SiO_2. (b) Carr-Purcell echo for an ensemble of identical spins plotted on a Bloch sphere. The echo in the x-y plane is rotated to an eigenstate by the final "echo tomography" $\pi/2$ pulse, necessary for the electrical detection of the echo. (c) The effect of a change in the second evolution time τ_2 with respect to τ_1 on the same spin ensemble before and after the final $\pi/2$ pulse. (d) Charge Q obtained from the integration of the current transients after microwave pulses of length τ_{Rabi} resonant with the high-field resonance of the ^{31}P donor spin ensemble (Rabi oscillations). The color code for the P-P_{b0} pair is identical to (a). (e) Charge Q after application of a Carr-Purcell pulse sequence including the final tomography pulse, again detected on the high-field ^{31}P resonance. The sign and the amplitude of the echo signature agree well with the corresponding Rabi oscillations as discussed in the text.

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Spin decoherence is usually studied with the help of a Carr-Purcell echo experiment with a $\pi/2 - \tau_1 - \pi - \tau_2 -$ echo pulse sequence, where $\pi/2$ and π denote the rotation angle of the spin system induced by resonant microwave pulses and τ_1 and τ_2 are the free evolution periods between the pulses [10]. Such a Carr-Purcell echo is shown in Fig. 1(b) for an ensemble of identical spins (e.g., the spins of phosphorus donors) plotted in a Bloch sphere, starting, e.g., with the spin ensemble in the "down" eigenstate $|\downarrow\rangle$ [11]. The microwave pulses are assumed to rotate the spins around the x axis of the Bloch sphere. The echo develops in the x-y plane of the Bloch sphere, giving rise to a pulse in the transverse magnetization or coherence, which is easily detectable in conventional electron spin resonance (ESR). However, the spin-to-charge conversion process employed here is sensitive to the singlet-triplet symmetry of a spin pair. A successful detection of such echoes via charge transport therefore requires so-called echo tomography [4], where after the second free evolution period τ_2 a final $\pi/2$ pulse rotates the spin system back into singlet or triplet eigenstates of the pair, shown in Fig. 1(c) in more detail. For $\tau_2 \ll \tau_1$ and $\tau_2 \gg \tau_1$, no echo has developed in the x-y plane so that after the final $\pi/2$ pulse, the spins of the ensemble point to all directions in the x-z plane of the Bloch sphere. Both triplet and singlet configurations will therefore be found in ensembles of P-P_{b0} spin pairs. However, for $\tau_2 = \tau_1$, an echo has developed, so that after the final $\pi/2$ pulse, the spin ensemble is in the original $|\downarrow\rangle$ eigenstate again. If the P_{b0} partner in the spin state is also in the $|\downarrow\rangle$ state, we find only the triplet configuration $|\downarrow\downarrow\rangle$ for the P-P_{b0} spin pairs. Therefore, echoes can be formed also in the singlet-triplet symmetry of spin pairs and are accessible to purely electrical detection.

In EDMR, until now only rotary spin echoes have been reported [12], where the spin system is continuously driven by the microwave and the echo develops when the microwave-induced rotation is canceled out by an equally long reversed rotation realized by a 180° phase shift in the microwave. While these echoes in principle are also able to quantitatively measure decoherence [13], the use of pulse sequences including free evolution periods together with echo tomography is more versatile and in principle allows other properties such as the exchange interaction in the P-P_{b0} spin pair or the superhyperfine interaction with ^{29}Si to be investigated by double electron electron resonance (DEER) [14] and electron spin echo envelope modulation (ESEEM) [15] pulse techniques, respectively.

Because of RC time constants of the experimental system consisting of the sample and the measurement electronics, echoes cannot be observed in real time. Rather, current transients after the application of the microwave pulse sequence are measured, where the excited spin system relaxes back into the steady state. However, theory shows that the amplitudes of the multiexponential decay are proportional to the deviation of the singlet-triplet configuration of the spin system at the end of the pulse sequence from the steady-state configuration [16]. To increase the signal-to-noise ratio, the current transients are integrated in a boxcar type of analysis, yielding a characteristic charge Q as the primary result of the experiment. As shown in Fig. 1(d) for the coherent manipulation of the P spin by a microwave pulse of varying time τ_{Rabi}, Q is small if the manipulation brings the spin system back into the steady state (corresponding to 2π, 4π, ... pulses). In contrast, the current transient and therefore Q is large when the spin system has been brought out of equilibrium by the microwave pulse [5]. Because of the Zeeman interaction, the spin state $|\downarrow\downarrow\rangle$ is the energetically lowest state of the P-P_{b0} spin pair and is therefore indicated as the steady-state configuration in Fig. 1(d).

We can now predict the experimental signature of the echoes. The pulse sequence $\pi/2 - \tau_1 - \pi - \tau_2 - \pi/2$ contains microwave pulses with a total length of 2π. Ideally, we therefore expect a value of Q after a Carr-Purcell echo sequence with $\tau_1 = \tau_2$ equal to the Q found after a rotation by 2π in a Rabi-flop experiment as shown in Fig. 1(e). For $\tau_2 \gg \tau_1$ and $\tau_2 \ll \tau_1$, the spin-pairs are not in the steady-state configuration. Rather, the ensemble of spin-pairs will contain singlet and triplet configuration in about equal contributions and therefore a larger Q corresponding to Rabi oscillations by $3\pi/2$ and $5\pi/2$ is expected as the result of such Carr-Purcell sequences, as shown in Fig. 1(e).

The sample investigated was grown by chemical vapor deposition and consists of a 15 nm thick silicon layer with natural isotope composition and $[\mathrm{P}] = 10^{17}$ cm^{-3} covered with a native oxide on top of a 500 nm thick nominally intrinsic buffer on a Si:B wafer (30 Ω cm) [17]. The measurements are performed at 9.765 GHz with a maximum peak power of 1 kW in a dielectric microwave resonator between 5 K and 15 K under illumination with white light. Interdigit Cr/Au contacts with a periodicity of 20 μm covering an active device area of 2×2.25 mm^2 are used, so that $\approx 10^{10}$ P spins are probed. The sample is biased with 22 mV resulting in a current of ≈ 50 μA measured by a current amplifier. To record the current transients the output of the amplifier (500 kHz bandwidth) is connected via a passive Butterworth high-pass filter (7th order, $f_{3\ \mathrm{dB}} = 400$ Hz) and a video amplifier (20 MHz bandwith) to a digital storage oscilloscope. The photocurrent transients detected consist of a fast (characteristic time constant $t = 3$ μs) rise of the conductivity, a slower ($t = 11$ μs) fall overshooting the steady-state value followed by a very slow ($t = 140$ μs) rise back to the steady-state conductivity. As the discussion will show below, an assignment of the experimental time constants to singlet and triplet recombination times from measurements of the transients alone is not possible, but is also not required for the detection of decoherence and the determination of the relevant time scales. Control experiments showed that the results obtained were not influenced by the repetition time of 350 μs used to accumulate the transients. The boxcar type integration was performed over the positive part of the overall photocurrent transient from 2–22 μs. The Rabi oscillations shown in Fig. 1(d) detected on the high-field P resonance were used to determine the $\pi/2$-pulse time to 31 ns at the specific microwave power employed corresponding to a microwave B_1 field of 0.3 mT.

Figure 2 shows the Carr-Purcell echo tomography data ΔQ at a temperature of 6.5 K obtained after substraction of a constant background. A first evolution period $\tau_1 =$ 200 ns was selected and τ_2 as well as the magnetic field B_0 were varied. As expected, a single echo with $\Delta Q < 0$ is found for $\tau_1 = \tau_2 = 200$ ns for the 4.2 mT hyperfine split P resonances with the central g factor $g = 1.9985$ at $B_0 =$ 351.2 mT and $B_0 = 347.0$ mT and a broad P_{b0} resonance. Because of the high excitation power used for the pulses and their large inhomogeneous linewidth the two P_{b0} resonances expected for the magnetic field oriented along the [110] axis of the Si sample [7,8] are not resolved in Fig. 2, but rather appear as a single feature at $B_0 = 347.9$ mT. The full-width-at-half-maximum temporal extent $\Delta\tau_{1/2}$ of the echo is correlated with the inhomogeneous Gaussian linewidth $\Delta B_{1/2}$ via $\Delta\tau_{1/2} = (2h)/(g\mu_B \Delta B_{1/2})$, where g is the g factor, μ_B is the Bohr magneton, and h is Planck's constant [18]. For an inhomogeneous linewidth of 0.4 mT for the high-field P resonance at $B_0 = 351.2$ mT, a $\Delta\tau_{1/2}$ of 170 ns is expected, in good agreement with the value of 130 ns determined from the experimental echo data Q for this resonance shown in more detail in Fig. 1(e) [19]. A quantitative comparison of Q observed on the high-field P resonance during the echo [Fig. 1(e)] to the Q observed in the Rabi oscillation [Fig. 1(d)] demonstrates that the echo amplitude ΔQ is indeed as large as expected. However, the absolute values of Q are higher in the echo experiment and correspond to Q found in the Rabi oscillations at high τ_{Rabi}. This is most probably caused by the limited attenuation of the single microwave switch used in the ''off'' state, which leads to a weak but continuous disturbance of the spin system also during the free evolution periods.

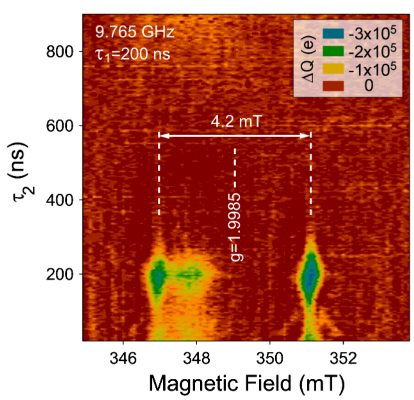

FIG. 2 (color online). Electrically detected Carr-Purcell echoes at 6.5 K for a first free evolution period of $\tau_1 = 200$ ns. A clear signature in the integrated charge ΔQ appears at $\tau_1 = \tau_2$ for all spin resonance lines, while no further features are resolved up to 900 ns. The features at $\tau_2 \lesssim 60$ ns are so-called Ramsey fringes, which are observable for evolution periods τ_2 below the dephasing time of the system.

To determine the echo decay time in this system, the echo sequence is measured as a function of τ_1. In all cases, the echo is observed at $\tau_1 = \tau_2$; however, its intensity decreases for longer τ_1, τ_2. Figure 3 shows ΔQ as a function of the total free evolution period $\tau_1 + \tau_2$ for the high-field P resonance obtained after substraction of a linear background. The echo amplitude decays monoexponentially with the time constant $\tau_{\text{echo}} = 1.7 \pm 0.2$ μs (solid line in Fig. 3). The same time constant is observed on the P_{b0} echo. The transients as well as the echoes and their decay are independent of temperature up to 12 K. Above 12 K, no echo is observed due to the decrease in the amplitudes of the underlying current transient.

At least two physical processes can contribute to the decay of the echo: namely, (i) the actual decoherence usually denoted by the transverse relaxation time T_2 and (ii) the loss of spin-pairs through recombination.

Let us first assume that the echo decay is caused by fast T_2 processes. In conventional pulsed ESR performed at low doping concentrations ($< 2 \times 10^{16}$ cm^{-3}), in isotopically pure ^{28}Si and in bulk samples to ensure the isolation of the phosphorus spins, T_2 as long as 60 ms have been found [20,21]. However, already at $[\text{P}] = 1 - 2 \times 10^{17}$ cm^{-3} similar to the doping concentration used in our experiment, T_2 decreases to 5 μs [22], similar to the τ_{echo} determined here. Additionally, in our experiment the P donors are on purpose particularly close to the Si/SiO_2 interface simulating device structures required for donor-based quantum information processing, where the SiO_2 is needed to electrically isolate gate electrodes used to address the donor qubits [6,23]. The effect of magnetic noise from Si/SiO_2 interface states on the T_2 of donor states has been described theoretically [24] and already been observed for Sb implanted to relatively large depths [25]. Taking into account the distance to the interface studied here and the larger P_{b0}

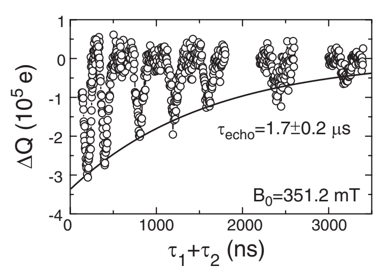

FIG. 3. Electrically detected Carr-Purcell echoes observed on the isolated high-field P resonance at $B_0 = 351.2$ mT for different evolution times τ_1. The solid line represents a monoexponential decay with a time constant of 1.7 ± 0.2 μs.

density of 10^{12} cm^{-2} of native oxides [26] our τ_{echo} could similarly be accounted for well by de Sousa's prediction [24].

Alternatively, the echo decay could also be due to recombination. Rate limiting for Carr-Purcell echoes would be the singlet recombination rate r_S [16]. Since the singlet content of the spin pair during the evolution periods of our echo experiment is 1/4, $\tau_{echo} = 4/r_S$ in the case of slow T_2 processes. For P-P_{b0} spin pairs, the singlet recombination time has not been determined independently. However, effective lifetimes of photogenerated charge carriers can be as short as 1 μs, as has been studied for P-doped emitters in crystalline Si solar cells [27], structures very similar to our test device. The value of τ_{echo} found would in this case correspond to $r_S = 2.3 \times 10^6$ 1/s, a rate significantly higher than observable directly from the current transients. Since we experimentally find that EDMR on the identical structures using the inversion recovery pulse sequence is limited by the same r_S [28], we conclude that, at the densities of P and P_{b0} in our sample, indeed recombination determines the echo decay. Identical values of τ_{echo} are expected in this case on both resonances as indeed observed. Furthermore, the inversion recovery EDMR results suggest that microwave phase noise can be excluded as the origin of the echo decay.

As discussed, the P-P_{b0} pair interaction allows the purely electrical detection of the spin states of donor qubits [5]. Irrespective of the actual microscopic mechanism, the echo decay time determined by pulsed EDMR is the relevant time scale on which such pairs can be used for quantum information processing. The τ_{echo} found here allows to apply around 30 π pulses of 60 ns length. While this is below the standard DiVincenzo requirement [29], this should be sufficient to demonstrate the basic usability of P donors in quantum information processing. Still, a variation of the phosphorus density, the density of the interface states, the isotopic composition of the host lattice, and the illumination intensity should allow us to increase the recombination times and reduce the decoherence processes in such structures, extending the time scale on which P-P_{b0} pairs can be used for quantum logic.

In conclusion, we have electrically detected Carr-Purcell echoes using P-P_{b0} pairs via echo tomography, demonstrating that charge carrier dynamics such as the singlet recombination rate can be monitored even on time scales shorter than the *RC* time constant of the detection system. This technique will allow a more detailed understanding of the complex charge carrier and spin dynamics in pulsed electrically detected magnetic resonance and opens the possibility to apply pulse sequences such as DEER and ESEEM including free evolution times to study spin-spin interactions in Si with unprecedented sensitivity.

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