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Linewidth of Low-Field Electrically Detected Magnetic Resonance of Phosphorus in Isotopically Controlled Silicon

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The linewidth of the low-field electrically detected magnetic resonance (LFEDMR) of phosphorus electrons in silicon is investigated using samples with various ^{29}Si nuclear spin fractions and is compared to that of X-band electron paramagnetic resonance (EPR). The linewidths of LFEDMR and EPR are the same even though LFEDMR signals are obtained based on spin-dependent recombination, suggesting that the interaction between electron spins of phosphorus and recombination centers is strong enough for the LFEDMR detection but weak enough not to affect the linewidths. This favorable balance makes LFEDMR an attractive method to elucidate the low-field behavior of paramagnetic defects in semiconductors.

Electron paramagnetic resonance (EPR) has received wide recognition as an indispensable technique for the characterization of defects in solids. Typical EPR measurements are conducted at X-band frequencies $\omega_0/2\pi$ of around 9.5 GHz and external fields B_0 of about 3 kG. Higher frequencies and fields are often desired to achieve larger spectral separation and electron spin polarization. On the other hand, a number of paramagnetic defects exhibit zero-field splittings and/or level (anti-) crossing near zero field, which carry important information on the nature of the defects. While the operation of EPR spectrometers in the rf regime is technologically less demanding and thus advantageous, the signal detection poses a challenge because the EPR intensity theoretically scales as ω_0^2.[1)] One route to improve the sensitivity is to use a spin-dependent recombination (SDR) process. For instance, the spin resonance of particular defects in silicon (Si) is accompanied by a change in the electrical conductivity of a sample due to SDR, which in turn induces a detectable change in the reflection from a microwave resonator. This method has served for the determination of anti-crossing points, hyperfine constants, and exchange interaction constants of oxygen-vacancy photoinduced defects and carbon-related irradiation defects at low fields.[2,3)] More recently, some of the present authors have developed a method to directly measure the conductivity for detection, which we term here as low-field electrically detected magnetic resonance (LFEDMR), and applied it to phosphorus donors in Si (Si:P), A-centers in Si, and P_b centers near Si/SiO_2 interfaces.[4,5)] Despite these successes, a capability of LFEDMR which has as yet not been investigated thoroughly is its spectral resolution. This is not an obvious task, since the observation of LFEDMR is found to require rf powers higher than conventional EPR and the high power operation is known to cause an artificial broadening of the spectra. The intrinsic linewidth itself contains a wealth of information on the spin–spin interactions present in the defects and therefore any extrinsic effect must be eliminated wherever possible.

The present paper reports on the LFEDMR linewidths of P donors in isotopically controlled Si single crystals with different ^{29}Si fractions $f = 0.047$, 0.012, and 50 ppm. ^{29}Si is the only spin-carrying stable isotope of Si. The donor concentrations of the three samples were approximately the same ($\approx 10^{15}$ cm^{-3}). The motivation for the choice of materials is twofold. First, Si:P is a prime example of dopants and defects in semiconductors and thus allows for the detailed comparison with conventional EPR studies.[6,7)] A reduction of f leads to, as we will show below, a drastic decrease of the both EPR and LFEDMR linewidths, providing an opportunity to test the limit of the spectral resolution achievable in LFEDMR. The second motivation is related to Kane's scheme for a silicon-based quantum computer.[8)] SDR in Si:P is mediated by P_b centers. P and P_b electrons form a triplet pair that prevents the P electron from moving to the P_b center. This Pauli spin-blockade is lifted when the spin resonance transforms the pair into a singlet, and the subsequent electron–hole recombination leads to the change in the conductivity. The use of Pauli spin-blockade is essentially the same as the spin detection method proposed by Kane, and therefore LFEDMR in Si:P may provide information on the feasibility of his scheme.

The spin-Hamiltonian for Si:P is described, in angular frequency units, as

$$\mathcal{H}_0 = \gamma_e B_0 S_z - \gamma_n B_0 I_z + a\boldsymbol{S}\cdot\boldsymbol{I}, \tag{1}$$

where $\gamma_e/2\pi = 2.8$ MHz/G and $\gamma_n/2\pi = 1.72$ kHz/G are the gyromagnetic ratios of electron and nuclear spins, respectively, $a/2\pi = 117.5$ MHz is the contact hyperfine constant, and $\boldsymbol{S}$ and $\boldsymbol{I}$ are the $S = 1/2$ and $I = 1/2$ spin operators for electron and nuclear spins, respectively. Sweeping B_0 under continuous wave irradiation with $\omega_0/2\pi$ leads to the observation of a doublet signal at $B_{h,l} = 2\omega_0(\omega_0 \pm a)/[(2\omega_0 \pm a)\gamma_e]$. At fields above 200 G, the high (low) field resonance B_h (B_l) corresponds to the

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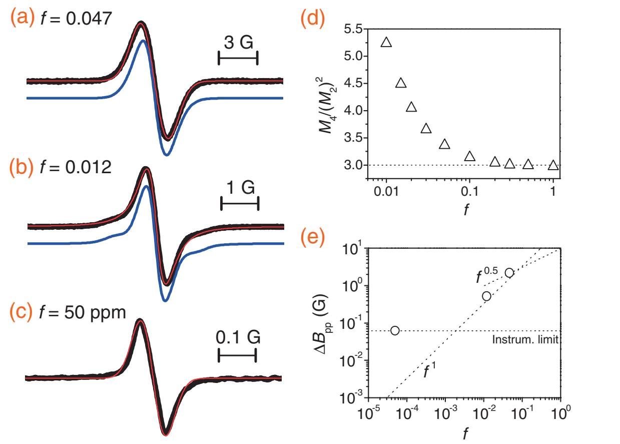

Fig. 1. (a–c) High-field lines of the Si:P EPR spectra in the ^{29}Si fraction $f = 0.047$ (a), 0.012 (b), and 50 ppm (c) samples. The measurement temperature was 10 K. The red curves superposed on the experimental data are the fits by the first-derivative Gaussian for (a) and (c), and by the first-derivative Lorentzian for (b). In (a) and (b), simulated curves are shown in blue. (d) Ratio $M_4/(M_2)^2$ obtained from simulation. (e) f dependence of the peak-to-peak linewidth ΔB_{pp}.

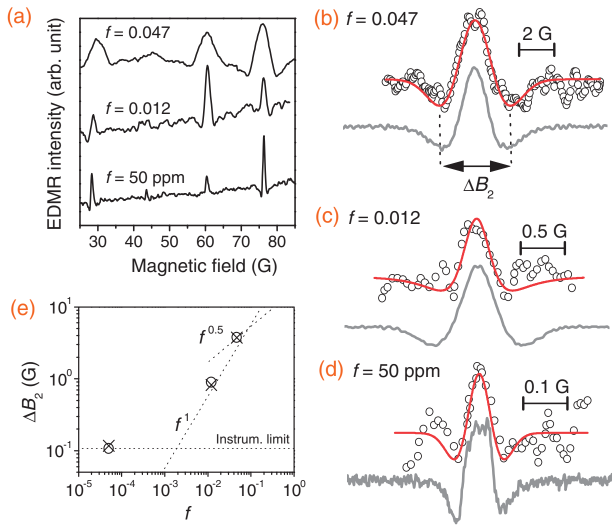

Fig. 2. (a) LFEDMR spectra under 170 MHz rf irradiation. Measurement temperatures were 5 K. (b–d) The high-field lines of the Si:P LFEDMR spectra in the ^{29}Si fraction $f = 0.047$ (b), 0.012 (c), and 50 ppm (d) samples. The red curves superposed on the experimental points are the fits by the second-derivative Gaussian for (b) and (d), and by the second-derivative Lorentzian for (c). Shown in gray are the numerical derivatives of the EPR spectra in Fig. 1. (e) f dependence of ΔB_2. The points in $\times$ (○) are ΔB_2 for LFEDMR (EPR).

transition involving $|\pm 1/2, -1/2\rangle$ ($|\pm 1/2, +1/2\rangle$), where the states are labeled in the $|m_S, m_I\rangle$ basis.

We first discuss the results from conventional EPR. Figures 1(a)–1(c) show the high-field lines (B_h) of the Si:P doublet, collected by commercial X-band spectrometers. The peak-to-peak linewidths ΔB_{pp} for $f = 0.047$ and 0.012 are 2.2 and 0.52 G, respectively, demonstrating the linear dependence of ΔB_{pp} on f in this regime. The line shape for the former is Gaussian, while that for the latter is Lorentzian. Due to the relatively large Bohr radius of its wave function, each donor electron experiences a random Fermi contact hyperfine field from the ^{29}Si nuclei within its extent, leading to inhomogeneous broadening of the EPR lines. These observations have been made and analyzed recently, where the linewidth for a Gaussian curve is given as $\Delta B^{G}_{pp} = 9.85\,\text{G} \times f^{0.5}$, and that for a Lorentzian curve as $\Delta B^{L}_{pp} = 33.3\,\text{G} \times f$.[7,9,10] From Fig. 1(e), we verify a good agreement between these formulae and experiments in the $f = 0.047$ and 0.012 samples. Here, we reinforce the argument in ref. 7, using a simple simulation, the details of which we describe in a footnote.[11] We carried out the simulation for 10 different values of f, ranging from 0.01 to 1.0, and the results for $f = 0.012$ and 0.047 are shown for comparison with the experiments. The simulation reproduces not only the linewidths but also the line shapes, including the humps observed in the tails of the spectrum in the $f = 0.012$ sample. Figure 1(d) shows $M_4/(M_2)^2$ extracted from all the simulated lines, where M_2 (M_4) is the second (fourth) moment of the line. In general, Gaussian curves have $M_4/(M_2)^2 = 3$, and as they approach Lorentzian curves the quantity becomes larger than 3. The departure from 3 is clearly seen at $f < 0.1$, in accordance with the experimental observation. We have also confirmed that the linewidths of the simulated lines obey the aforementioned formulae (not shown).

It is apparent that the $f = 50$ ppm sample behaves in contrast to the expectations from the above discussion. The line shape is Gaussian, not Lorentzian, and the observed ΔB_{pp} of 62 mG is much broader than expected from theory (1.7 mG). At this stage, the linewidth is limited by the inhomogeneity in the electromagnet we use. It is, however, worth pointing out that in the $f = 50$ ppm sample, an individual donor electron has on average less than one ^{29}Si nucleus within its wave function, which encompasses a few tens of thousands of Si atoms. Therefore, the contact hyperfine field from ^{29}Si nuclei is not necessarily the dominant mechanism for line broadening in this regime of f, and the dipolar hyperfine interactions between the electron spin and the ^{29}Si nuclei can be a more relevant source of broadening. This contribution is estimated as about 0.1 mG at $f = 50$ ppm using the method of moments for unlike spins.[13] This value is far below our field homogeneity limit, and we did not expect to see this effect.

Having understood the mechanism of line broadening in the EPR spectra, we are in a position to discuss the results from LFEDMR. The experiments were carried out with a custom-built LFEDMR system, in which a 170 MHz rf field was applied to drive the spin resonance, and cw white light was used to maintain the sample photoconductivity.[4] Ohmic contacts required for electrical detection were prepared by ion-implantation of arsenic, followed by annealing and deposition of thin palladium and gold films.[4] The changes in the photoconductivity, accompanied by spin resonance, were detected by a lock-in amplifier synchronized with the double frequency of the magnetic fieldmodulation. This second-harmonic detection was employed here in order to minimize the effect of magnetoresistance when scanning B_0.[14]

Figure 2(a) shows wide-range scans of LFEDMR exhibiting four peaks in the respective samples. From the analytical expressions of $B_{h,l}$, we are able to assign the peaks appearing around 29 and 76 G to B_l and B_h, respectively. The peak around 34 G is the forbidden transition involving states

$|1/2, -1/2\rangle$ and $|-1/2, 1/2\rangle$. At low fields, the transitions are mixed and become observable. We attribute the peak around 60 G to P_b centers.[4] The 34 G peak is unique in the low-field regime, while the 60 G peak was not detected in X-band EPR. Therefore, the observation of these peaks demonstrates the utility of our LFEDMR method. Although all four peaks in Fig. 2(a) clearly show a drastic decrease of the linewidth with reducing f, these spectra were taken with a relatively large fieldmodulation and a high rf power, making it difficult to deduce the correct linewidth unaffected by these artificial experimental parameters. We found that only the B_h lines remain clearly visible even under the operation with smaller modulation and lower power, allowing for the close comparison with the corresponding EPR spectra. Figures 2(b)–2(d) are the LFEDMR spectra for B_h, together with the numerical derivatives of Figs. 1(a)–1(c) (with their signs inverted to facilitate comparison). As the line shapes take the form of the second derivative of the absorptive lines, we define the linewidth ΔB_2 as the distance between the two local minima [see Fig. 2(b)]. In both Gaussian and Lorentzian lines, the relation $\Delta B_2 = \sqrt{3}\,\Delta B_{pp}$ is satisfied. Despite unsatisfactory signal-to-noise ratios in LFEDMR, we observe that the line shapes and linewidths are essentially the same in EPR and LFEDMR. The fits for LFEDMR are thus given by the same functions as those for EPR (i.e., a second-derivative Gaussian for $f = 0.047$ and 50 ppm, and a second-derivative Lorentzian for $f = 0.012$). We emphasize that the number of spins contributing to the LFEDMR signal is on the order of 10^5, which has been deduced from the assumption that only donors locating within 4 nm from the Si/SiO_2 interface can form pairs with P_b centers,[15] while in EPR all the donors in the bulk contribute to the signal and the number of spins is on the order of 10^{13}. We also note that, in addition to the difference in the detection methods, these two measurements have been carried out in very different magnetic fields (3220 and 76 G).

Figure 2(e) shows the direct comparison of the EPR and LFEDMR linewidths (in terms of ΔB_2) as a function of f. For $f = 0.012$ and 0.047, the inhomogeneous hyperfine field from ^{29}Si nuclei is the dominant source of line broadening even at low fields. Again, the LFEDMR linewidth in the $f = 50$ ppm sample is limited by the inhomogeneity in B_0.[16] Nevertheless, from the observed linewidth, we determine the inhomogeneous coherence time T_2^*, crudely defined here as $(\gamma_e \Delta B_{1/2})^{-1}$ and giving the lower limit of coherence time T_2, to be 9 µs, where $\Delta B_{1/2} = \sqrt{\ln 2/6}\,\Delta B_2 = 40$ mG is the half width at half maximum of the Gaussian line. The major limiting factor for T_2 in EDMR is believed to the recombination process, which is unlikely to be affected significantly by the density of ^{29}Si isotopes if the donor concentrations are kept constant.[17] Hence, T_2^* obtained here could also be the lower limit of T_2 in natural Si with 10^{15} cm^{-3} P donors. While T_2 of 1 µs has been reported for natural Si with 10^{17} cm^{-3} P donors using pulsed X-band EDMR,[15,18] our observation raises hopes that T_2 much longer than 1 µs is achievable at lower donor concentrations. It is expected that the recombination time is independent of B_0,[19] and becomes longer as decreasing the donor concentrations.[20] This suggests that the electrical detection of spin states in Si:P holds promise for future application in silicon-based quantum computers.

In summary, we have shown that the ^{29}Si fraction dependence of the linewidths of Si:P are the same between LFEDMR and conventional X-band EPR. The narrowest LFEDMR linewidth discriminable in our system, only limited by the inhomogeneity in the external field, is determined as $\Delta B_{1/2} = 40$ mG, which is already sufficient for the investigation of a variety of paramagnetic centers in solids, and could be improved by the use of a magnet with better homogeneity.

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