High-frequency ESR measurements and ESR/NMR double resonance experiments of lightly phosphorous-doped silicon

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Abstract. We studied lightly doped Si:P with high-frequency (80–120 GHz) ESR and ESR/NMR double magnetic resonance techniques in the temperature range down to 1.4 K. We found dynamic nuclear polarization of ³¹P from steady-state ESR measurements with approximately 3.6 T. We derived the nuclear spin relaxation time, T₁N, of ³¹P by analyzing the time-evolution of ESR spectra utilizing the dynamic nuclear polarization effect. We derive temperature and magnetic field dependence of T₁N and compare with experimental data. Furthermore, from our ESR measurements, we modulate the nuclear polarization of ³¹P by applying an RF field.

1. Introduction

A quantum computer design using phosphorous-doped silicon (Si:P) proposed by B. Kane [1] has been attracting much interest, since it is one of the best practical quantum computer designs reported thus far. The model uses phosphorus (P) nuclear spins embedded regularly in silicon crystal as qubits, where for quantum computer operations, electron spins should be completely polarized by high fields (a few Tesla) and low temperatures in the range of 100 mK. Experimental demonstrations, however, have not yet been successful. In this study, we study an ensemble of ³¹P nuclear spins in phosphorous-doped silicon (Si:P), rather than detecting the state of a single ³¹P nuclear spin, as required in Kane’s model. In Si:P, the donor electrons are well localized around the donor ions if the donor concentration is below the critical doping concentration, n_c = 3.7 x 10¹⁸ cm⁻³, while they are delocalized above n_c. The P atoms in lightly doped Si:P are in a similar environment to those in Kane’s model, and therefore, it is important to study ³¹P nuclear spin state and spin dynamics by NMR especially to measure the coherence time of nuclear spins. Until now, however, it has been difficult to observe the ³¹P NMR
signal directly because the critical concentration of P atoms to keep donors in their proper separation for quantum computation is too low.

Recently, we found that $^{31}$P nuclear spin polarization is enhanced by two or three orders of magnitude over the thermal equilibrium value using dynamic nuclear polarization (DNP) caused by microwave irradiation (~80 GHz) [2]. Since the NMR signal would be enhanced following enhancement of the nuclear spin polarization, it may be possible to observe the $^{31}$P NMR signal from low concentration Si:P sample with the assistance of DNP. With this aim, we constructed an ESR/NMR double-resonance system.

We report here on $^{31}$P nuclear spin dynamics measured by cw-ESR with the assistance of DNP. Further, we show that the magnitude of the nuclear spin polarization was changed when applying NMR pulses using an ESR/NMR double resonance system. We used Si:P samples in the insulating regime with P-concentration $n = 6.5 \times 10^{16}$ cm$^{-3}$ where doped P atoms in Si crystal are isolated impurities.

2. Experimental – ESR/NMR double resonance system

The isolated donor electron spin system was studied using cw-ESR at the frequency of $\omega/2\pi = 80$–120 GHz and at temperatures from 20 K to 1.4 K with field modulation. The experimental setup (see figure 1) was basically the same as that in our previous report [2], except for the position of the sample. To add an NMR system to the ESR system, we made a new probe for the NMR/ESR double resonance experiment. Inside the waveguide we placed a coil for NMR, with its axis perpendicular to the magnetic field. The resonance frequency for NMR was tuneable with a capacitor on the probe and was adjustable from outside the probe. It should be noted that the microwaves are perpendicular to the magnetic field at the sample position in this system, whereas they were parallel to the magnetic field in the previous system. This different microwave propagation direction may cause a different excitation efficiency of electron spin.

A Si:P crystal sample with the size $3 \times 3 \times 0.3$ mm$^3$ was set inside the cylindrical waveguide. To observe the absorption signal, a simple transmission method was adopted without a cavity resonator. We optimised the microwave frequency and phase and the field modulation as described in references 2 and 3.

Figure 1: Block diagram of the high-frequency ESR/NMR double resonance apparatus. The microwave source is a Gunn oscillator that is phase-locked by a Millimetre-wave Vector Network Analyser (MVNA). The microwave signal is measured by an InSb hot electron detector operating at 4.2 K. The coil for the field modulation is wound on a plastic holder and fixed around the sample. The NMR coil is fixed inside the waveguide.
3. Results and discussions

3.1. DNP effect and $T_{1N}$ measurement by cw-ESR

Electron spin $S$ and nuclear spin $I$ are coupled by an isotropic hyperfine constant $A$ ($A/h = 117.5$ MHz) in an isolated donor in Si:P. The Hamiltonian for this two-spin system under the magnetic field $B_0$ along the z-axis is given by

$$
\mathcal{H} = -\gamma_e h S^z B_0 + AS \cdot I - \gamma_N h I^z B_0,
$$

where $\gamma_e$ and $\gamma_N$ are gyromagnetic ratios for electron and nuclear spins, respectively. ESR spectra at low temperatures consist of two resonance lines separated by approximately 4 mT. We refer to an ESR absorption signal appearing at the lower (higher) field as the L-line (H-line). From equation (1), the intensity of the L-line (H-line) is almost proportional to the population of up (down) state of the $^{31}$P nuclear spin. Therefore, if $^{31}$P nuclear polarization is enhanced over thermal equilibrium by the DNP effect, we expect to observe an asymmetric ESR spectrum where the L-line is more intense than the H-line.

We measured the spectra at 1.44 K that is lower than our previous work [2]. After 67 minutes irradiation on the H-line, the ESR spectrum exhibited the expected asymmetry (see figure 2(a)). Note that these ESR spectra were recorded with extremely small microwave power (approximately 14dB attenuation). Approximately 20% nuclear polarization was obtained by DNP, where the intensity of each line was evaluated from the integrated intensity of the line. We repeated the measurements by sweeping the magnetic field, and obtained the time $t$ evolution of the ESR spectra, showing the nuclear polarization $P$ relaxing to its thermal equilibrium (see figure 2(b)). The nuclear relaxation time, $T_{1N}$, was found from the best fit of

$$
P = P_0 + a \exp(-t/T_{1N}),
$$

and was obtained as $24 \pm 7$ min at 3.65 T and 1.44 K, where $P_0$ and $a$ are also fitting parameters.

The values of $T_{1N}$ were derived similarly for above 3 K and under 8.58 T [4], and below 2.2 K and under 4.6 T [5]. In ref. 5, the relaxation times were attributed to two components: the faster one originated in the dynamic polarization of $^{29}$Si nuclear spins ($I=1/2$) located nearby the P atom, and the slower one was observed $t \gtrsim 500$ s. In this work, we observed the longer relaxation time. It is worth comparing $T_{1N}$ data taken across a wide range of the magnetic field. Figure 3 shows $1/(T \cdot T_{1N})$ vs. $1/T$, including data from these references. To analyse these data, we start with a general formula for $T_{1N}$

Figure 2: (a) ESR spectra recorded at less than 1 min, and 77 min after switching off the irradiation on the H-line for 67 minutes at 1.44 K. Only signals in-phase with the modulation field are shown. (b) Time dependence of $^{31}$P nuclear polarization after switching off the irradiation. The solid line shows the best fit to the data of equation (2).
which is expressed in terms of fluctuating local field caused at the nucleus:

\[ \frac{1}{T_{1N}} = \frac{\gamma_N^2}{2} \int_{-\infty}^{\infty} \left\langle \left\{ H_{\text{loc}}^{-}(0), H_{\text{loc}}^{+}(t) \right\} \right\rangle \exp(i\omega_N t) dt, \]

where \(\omega_N\) is the nuclear Larmor angular frequency, \(H_{\text{loc}}^{\pm}\) is the local field caused at \(^{31}\text{P}\) nucleus perpendicular to \(B_0\), and \(\{a,b\} = (ab+ba)/2\). Assuming an exponential correlation function with a correlation time \(\tau\), \(\left\langle H_{\text{loc}}^{-}(0), H_{\text{loc}}^{+}(t) \right\rangle \sim \exp(-t/\tau)\), we obtain,

\[ \frac{1}{T_{1N}} = \frac{\tau M_2}{1 + \omega_N^2 \tau^2}, \]

where \(M_2\) is a relevant second moment for the hyperfine coupling between \(^{31}\text{P}\) and donor electrons. Because the \(H_{\text{loc}}^{\pm}\) originates from \(S^x I^x\) and \(S^y I^y\) terms in the Hamiltonian (1), \(T_{1N}\) is associated with the cross relaxation which involves the electron-nuclear flip-flop transition. Let us put \(\tau\) as the cross relaxation time \(T_{1e} \sim 1/(B_0^2 T)\) [6]. For the relevant situation, \(\omega_N = \gamma_N (B_0 + B_{\text{HF}})\) where \(B_{\text{HF}} = A/\gamma_N\) is the hyperfine field, and \(\omega_N \tau \gg 1\). Taking into account the effect of saturation of electron magnetization [7], we finally derive the following equation:

\[ \frac{1}{T_{1N}} = C B_0^2 (B_0 + B_{\text{HF}})^{-2} \left(1 - P_e^2\right), \]

where \(P_e = \tanh(\gamma_e B_0/2k_B T)\) is the polarization of the electron spin; and \(C\) is a constant, independent of the magnetic field and temperature. Here, the activation-type temperature dependence of \(T_{1N}\) comes from the saturation effect of the magnetization. In figure 3, the dashed lines are the best fits of equation (5) to the experimental data, where the only fitting parameter is the prefactor \(C\). For our data at 3.6 T, we used the same value of \(C\) with that for 4.6 T. The fitted results agree reasonably well to the experimental data. The obtained values of \(C\) for different conditions of temperature ranges and magnetic fields are nearly equal with each other, suggesting that the above discussion correctly accounts for \(^{31}\text{P}\) nuclear relaxation process in lightly doped Si:P. It should be noted here that if the hyperfine coupling has anisotropy, the correlation function \(\langle S^z S^z \rangle\) may contribute to \(T_{1N}\) [8]. For this case, \(\tau\) is put as \(T_{1e}\) and then \(T_{1N}\) is proportional to \(T_{1e}\). However, because of \(B_0^2\) dependence for the direct process of \(T_{1e}\) relaxation [2,9], the field dependence of the experimental data of \(T_{1N}\) can not be

Figure 3: \(1/(T \cdot T_{1N})\) as a function of \(1/T\) for 3.6 T (solid circle, this work), 4.6 T (open triangle) [5], and 8.6 T (open square) [4]. The dashed line shows the best fit of equation (5) for each data set.

Figure 4: ESR spectra recorded after irradiating H-line for 20 minutes at 1.5 K. Only in-phase signals are shown. The lower spectrum was recorded with RF pulses of 107.1 MHz. The background signal was subtracted from the raw data for each spectrum. The dotted lines are drawn to show the intensity of L-line.
explained. We tentatively consider that the anisotropic component of the hyperfine coupling is negligible.

3.2. cw-ESR with RF pulses
To control nuclear spin polarization by NMR, we performed cw-ESR measurements with and without RF pulses using the ESR/NMR double resonance system. In preparation, microwave of about 102.1 GHz were irradiated on H-line for 20 minutes. Just after the preparation, ESR spectra were recorded with or without RF pulses at 107.1 MHz, of 3–5 µs, applied every 2 s. Without RF pulses, ESR spectrum exhibited asymmetry because of DNP (see Fig. 4). With RF pulses, the intensities of the two lines were nearly the same, suggesting that the distribution of nuclear spin states returned to nearly thermal equilibrium. This technique would be useful to obtain a thermal equilibrium state much faster than $T_{1N}$.

4. Summary
We studied the spin dynamics of lightly doped Si:P with the concentration $n = 6.5 \times 10^{16}$ cm$^{-3}$. High-frequency steady-state ESR experiments of the donor electron spin in this sample were performed at 3.6 T and 1.44 K. We observed the $^{31}$P nuclear spin-lattice relaxation time $T_{1N}$ from the DNP enhanced state to thermal equilibrium. We proposed an analysis based on that the nuclear relaxation is caused by the fluctuation of electron spins associated with nuclear-electron flip-flop transition. The equation from this analysis correctly accounted for the behaviour of $T_{1N}$ across a wide range of temperatures and magnetic fields. We also showed that the nuclear polarization can be changed by NMR pulses. We plan to measure at further lower temperatures for large Zeeman splitting because perfect nuclear polarization is required to realize quantum computation.

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