Electron paramagnetic resonance and dynamic nuclear polarization via the photoexcited triplet states of radiation defects in natural and ^{29}Si isotope enriched silicon

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Electron paramagnetic resonance (EPR) of the triplet centers and dynamic ^{29}Si nuclear polarization was studied in irradiated naturally abounded (4.7%) and ^{29}Si isotope enriched (99.3%) silicon crystals. Saturation of the EPR lines of the photoexcited triplet centers with nonequilibrium spin polarization between m_S = +1, 0, and –1 sates leads to the nuclear polarization ≈7000 times higher than equilibrium value. It was shown that the observed dynamic nuclear polarization is a result of the "solid-effect".

1 Introduction Growing interest to the investigation of spin dependent phenomena in silicon is related to the advantages in the production of the isotope enriched silicon crystals and silicon based structures. The possible future applications of these materials in spin electronics and quantum computers require high electron and nuclear spin polarization.

The photoexcited spin S = 1 centers characterized by strong nonequilibrium populations of states with different spin projections m_S = +1, 0, and –1 can be used for dynamic nuclear polarization. The defects with the excited triplet states are produced by electron or γ–irradiation of silicon crystals containing oxygen and carbon impurity atoms [1–4].

In the present paper we report the experimental results of electron paramagnetic resonance (EPR) and dynamic nuclear polarization (DNP) investigations in irradiated silicon crystals containing different amount of the ^{29}Si lattice nuclei.

2 Experimental The experiments were performed with different samples of float zone (FZ) and Czohralski (Cz) grown naturally (4.7 %) abounded silicon and ^{29}Si isotope enriched (99.3 %) Cz n-type silicon crystals [5] doped with phosphorus atoms with the concentration of 5×10^{15} cm^{-3}. The samples were irradiated by1 MeV electrons and γ-rays at room temperature.

The excited triplet states of the neutral charge states of the oxygen + vacancy $(O+V)^0$ (EPR spectrum Si-SL1 [1]) and substitution carbon + interstitial silicon + substitution carbon $(C_S + Si_I + C_S)^0$ complexes (Si-PT1 spectrum [3, 4]) were produced by band-gap illumination from the 100 W halogen lamp. The EPR spectra were detected with a X-band EPR spectrometer at the temperatures 4-100 K. The experiments on DNP of the ^{29}Si nuclei were performed using the EPR spectrometer at the microwave power of 10-200 mW for saturation of the EPR lines. The time of saturation t was changed from 10 min to 6 hr.

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Long nuclear spin lattice relaxation time T_1 > 1 hr for all the samples at room temperature allow us to transfer the sample from EPR to pulse nuclear magnetic resonance (NMR) spectrometers to detect the ^{29}Si NMR signals.

3 Results and discussion The EPR spectra in the naturally abounded and isotope enriched silicon crystals observed after different doses of irradiation are shown in Fig. 1.

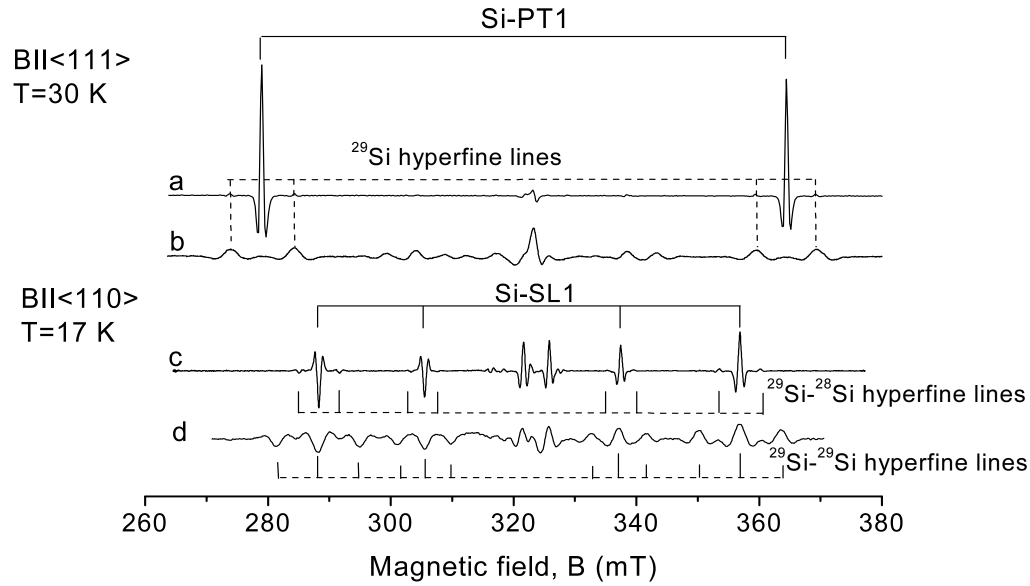

Fig. 1 Second derivative EPR absorption spectra observed in γ-irradiated naturally abounded (*a*) FZ and (*c*) Cz silicon and in (*b, d*) 99.3% ^{29}Si isotope enriched Cz silicon crystals.

In the samples subjected to the low dose, Φ, of γ-irradiation ($\Phi \approx 2\times10^{16}$ cm^{-2}) the concentration of radiation defects is too low to detect the spectra by the usual EPR technique. The EPR spectra shown in Fig. 1(*a,b*) are taken using the spin dependent microwave photoconductivity method [3, 4]. The dominant spectra observed in the investigated samples are the Si-PT1 [3, 4] and Si-SL1 spectra [1]. In the 99.3% ^{29}Si enriched samples (see Fig. 1(*b,d*)) these EPR spectra consist of the inhomogeneously broadened ($\Delta B_{pp} \approx 2.2$ mT) but still resolved lines of hyperfine structure due to one ^{29}Si nucleus (spin I =1/2) for ($C_S + Si_I + C_S$) and two ^{29}Si nuclei for (O+V) centers.

The peak to peak line width (ΔB_{pp}) was measured between the extremes of the first derivative line shape. This is in contrast to the EPR spectra of these defects in natural (4.7 % ^{29}Si) silicon (see Fig. 1(*a,c*)) where the weak hyperfine satellites are observed near the central fine structure lines having the line width of $\Delta B_{pp} \approx 0.2$ mT.

At the higher dose of irradiation ($\Phi \approx 3\times10^{18}$ cm^{-2}, see Fig. 1(*c,d*)) only the Si-SL1 spectrum is observed by usual EPR method. The low- and high-field lines of the Si-SL1 spectrum have different signs showing the nonequilibrium population of the magnetic sublevels with different spin projections. The electron spin polarization P^{+}_{e} between states with m_S = +1, 0 is opposite to polarization P_e^{-} between m_S = 0 and m_S = -1 states and not equal to Boltzmann equilibrium polarization. This nonequilibrium electron polarization has been used in an experiment of ^{29}Si optical nuclear polarization in weak magnetic field corresponding to the anticrossing of the magnetic sublevels m_S = +1 and m_S = 0 at B = 35 mT for Si-SL1 centers [3]. It is expected that the saturation of the EPR transitions of triplet centers will lead to the stronger DNP than in case of DNP under saturation of the phosphorus EPR lines [6] having equilibrium electron polarization. The experimental results of the DNP are shown in Fig. 2.

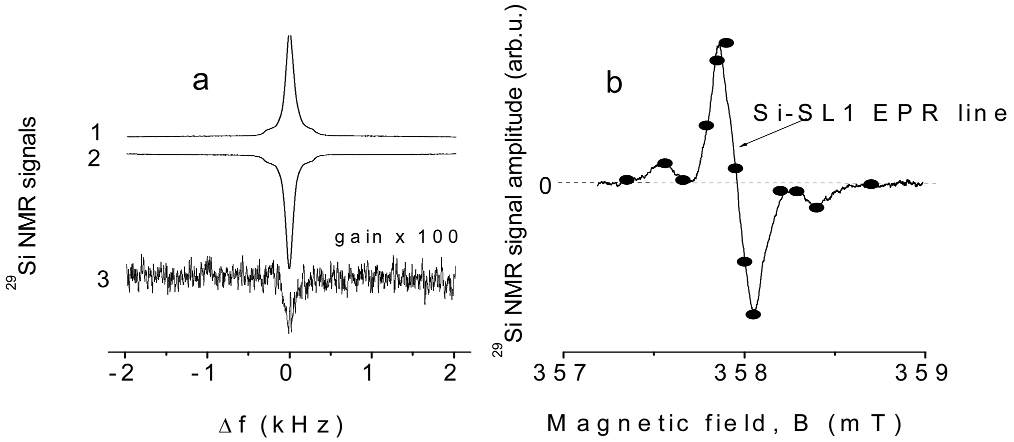

Fig. 2 (*a*) ^{29}Si NMR signals in the naturally abounded Cz electron irradiated ($\Phi \approx 5\times10^{18}$ cm^{-2}) silicon after DNP at 77 K, B =357.85 mT (1), B = 358.05 mT (2) and the equilibrium NMR signal (3) detected at 300 K and B = 7 T; (*b*) - the dependence of the amplitude of NMR signals on B (filled circles) and the first derivative EPR line of the Si-SL1 spectrum (solid curve). All NMR signals are taken after saturation of the Si-SL1 EPR line during t =10 min at 77 K and microwave power of 100 mW.

The strong increase of the ^{29}Si NMR signals of opposite signs corresponds to the extremes of the first derivative shape of EPR line (see Fig. 2(*b*)). This shows that the DNP of the lattice ^{29}Si nuclei is a result of "solid-effect" [5, 6] arising under saturation of the forbidden "flip-flop" or "flip-flip" transitions in the electron-nuclear dipole coupled system when the electron (m_S) and nuclear (m_N) spin projections are changed in opposite ($\Delta m_S + \Delta m_N = 0$) or in the same ($\Delta m_S + \Delta m_N = \pm 2$) directions. The shift, $\Delta B_\pm$, of the forbidden transitions from the center of EPR line at B_0 =358.0 mT is equal to $\Delta B_\pm = B - B_0 = \pm B_0(\gamma_n/\gamma_e)$, where γ_e and γ_n are the electron and nuclear gyromagnetic ratios. For ^{29}Si nuclei $\Delta B_\pm \approx \pm$ 0.09 mT. This is comparable with the EPR line width of Si-SL1 spectrum in the naturally abounded silicon $\Delta B_{pp} \approx 0.2$ mT. This suggests that DNP is a result of the partly resolved "solid-effect". In the 99.3 % ^{29}Si abounded silicon $\Delta B_{pp} \approx 2.2$ mT and the dependence of the DNP on the magnetic field B repeats the first derivative EPR line shape. The degree of the DNP in these samples is lower in accordance with the model of the "differential solid-effect" [7] when the forbidden "flip-flop" and "flip-flip" transitions of different spin packets are saturated at the same time. The exponential growth of the NMR signals with the saturation time t was used to determine the nuclear spin lattice relaxation time under optical excitation and saturation of EPR lines (nuclear polarization time T_1^P) and the DNP degree P_N extrapolated to the infinite time of saturation.

The temperature dependences of P_N in naturally abounded and in ^{29}Si enriched silicon are shown in Fig. 3. These dependences correlate with the temperature dependence of the intensity of the Si-SL1 spectra for all the investigated samples. The time T_1^P = 3 hr was found for electron irradiated ($\Phi = 5\times10^{18}$ cm^{-2}) natural silicon and 1.5 hr for the γ-irradiated ($\Phi = 3\times10^{18}$ cm^{-2}) 99.3% ^{29}Si enriched silicon. The strongest enhancement of nuclear polarization $E = P_N / P_{N0} \approx 7000$ (compare to E = 30 obtained in Si:P [6]) where P_{N0} is the equilibrium nuclear polarization, was obtained at the temperature $T \approx 50$ K in naturally abounded electron irradiated silicon.

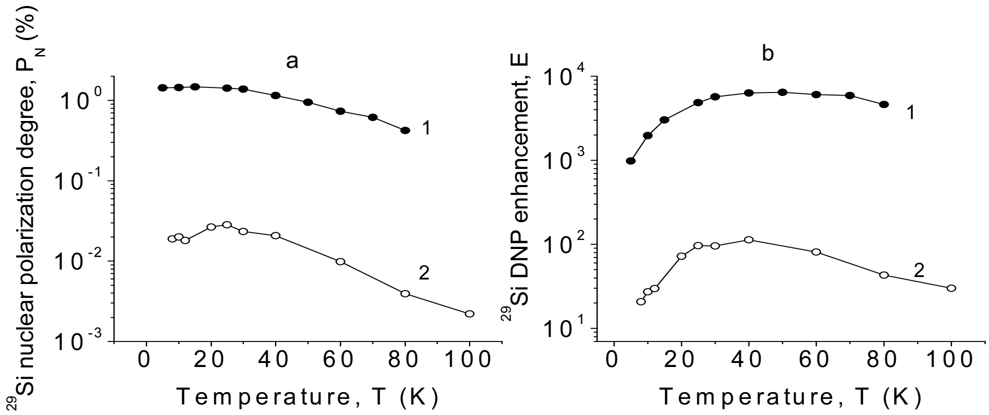

Fig. 3 Dependences of the DNP ^{29}Si degree P_N (*a*) and the enhancement, *E,* of nuclear polarization (*b*) on the temperature for electron irradiated naturally abounded (1) and γ–irradiated 99.3% ^{29}Si isotope enriched silicon (2).

The absolute value of DNP about 1.4 % (see Fig. 3(*a*)) was obtained under saturation of only one EPR line. Remaining 11 lines of the Si-SL1 spectrum [1] act as a leakage of nuclear polarization. Another defects produced by irradiation also increase the DNP degree. The lower DNP degree observed in the 99.3% isotope enriched silicon can be explained by two factors. First is the broadening of the EPR lines. This leads to differential solid-effects decreasing significantly DNP degree. The second reason is ten times lower concentration of radiation defects produced by *γ*-irradiation as compared to electron irradiation at the same doses. Further investigations of DNP in irradiated silicon are needed to optimize the experimental conditions to get stronger nuclear polarization. Prospective and substantial courses to get stronger DNP degree are the increase of the concentration of radiation defects by the increase of irradiation doses, the increase of the amount of the triplet centers which produce the DNP by higher intensity of illumination, and choose of another orientation of crystals in magnetic field, e.g. B||<111>, where the EPR lines of Si-SL1 spectrum are crossed at the same magnetic field.

4 Conclusion We observed the DNP produced by saturation of the EPR lines of the photoexcited triplet states of radiation defects in silicon. It was shown that the DNP was a result of the “solid- effect”. The strongest nuclear polarization was achieved at the temperatures below 30 K.

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References

[1] K. L. Brower, Phys. Rev. B **4**, 1968 (1971).
[2] K. P. O’Donnel, K. M. Lee, J. Weber, and G. D. Watkins, Physica **116B**, 258 (1983).
[3] L. S. Vlasenko, M. P. Vlasenko, V. N. Lomasov, and V. A. Khramtsov, Sov. Phys. JETP **64**, 612 (1986).
[4] L. S. Vlasenko, Yu. V. Martynov, T. Gregorkiewicz, and C. A. J. Ammerlaan, Phys. Rev. B **52**, 1144 (1995).
[5] K. M. Itoh, J. Kato, F. Uemura et al., Jpn. J. Appl. Phys. Pt. 1 **42**, 6248 (2003).
[6] A. Abragam, J. Combrisson, and I. Solomon, Compt. Rend. **247**, 2337 (1958).
[7] C. D. Jeffries, Dynamic Nuclear Orientation (J. Wiley & Sons Interscience Publ., New York/London/Sydney, 1963), chap. 7.

