Electrically detected magnetic resonance of phosphorous due to spin dependent recombination with triplet centers in $\gamma$-irradiated silicon

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A B S T R A C T

Electrically detected magnetic resonance (EDMR) of phosphorus in silicon was detected in weak magnetic fields at low resonance frequencies of 200–400 MHz before and after irradiation of samples by $\gamma$-rays. EDMR spectra were detected by measuring dc-photoconductivity of samples under band-gap illumination. Phosphorus ($P^0$) EDMR lines are accompanied always with the single line ($S$-line) with $g$-factor $\approx 2.01$ originated most likely from the surface recombination centers. Strong, about 10 times, increase of the $P^0$ and $S$ signals was found in the same samples after irradiation with the doses of $(3-6) \times 10^{15} \gamma/$cm$^2$. For these doses of irradiation we were also able to see the ESR transition between entangled states of phosphorous formed at low magnetic field. This shows the higher efficiency of spin dependent recombination (SDR) process in irradiated samples. In addition, several new EDMR lines emerged after irradiation. Some of them arose from the spin dependent recombination through the photoexcited triplet states of A-centers (oxygen+vacancy complex).

1. Introduction

Electrically detected magnetic resonance (EDMR) is a powerful and sensitive method for investigating spin dependent recombination (SDR) processes involving different recombination centers in semiconductors. The change in conductivity and photoconductivity of silicon under magnetic resonance of phosphorus ($P^0$) donor centers was observed and investigated many years ago [1]. It was argued that the processes of spin dependent scattering of the conducting electrons from paramagnetic donor centers [2] and spin dependent capture of electrons by neutral shallow donors [3] are responsible for the change in conductivity under magnetic resonance. Suggested mechanisms of spin dependent conductivity require high electron spin polarization achieved at low temperatures below 4.2K and strong magnetic fields used in standard electron paramagnetic resonance (EPR) spectrometer. Since the observation of SDR effect in silicon at room temperature, reported by Lepine [4], many experimental and theoretical investigations of SDR were performed.

The most significant feature of SDR is the independence or weak dependence of EDMR signals on the magnetic field strength. Independence of the EDMR signals on the strength of magnetic field was explained by the model of SDR [5] taking into account the exchange-interaction coupled electron-hole pairs in the triplet spin $S = 1$ state. A similar SDR model considering exchange-interaction coupled donor-acceptor pairs was suggested to explain the broadening of magnetic resonance lines detected optically [6]. This weak dependence of EDMR signals on magnetic field allows us to observe magnetic resonance transitions of paramagnetic recombination centers in weak magnetic fields at low frequencies. The first low frequency observation of EDMR spectra of $P^0$ centers and of the excited spin $S = 1$ states of the neutral A-centers (oxygen+vacancy complex) in low dose irradiated silicon has been reported in [7]. An additional line with $g$-factor $g \approx 2$ was observed but not identified at that time. Similar EDMR spectra were observed in irradiated and post annealed samples almost 8 years later [8] and it was pointed out that no EDMR spectra of shallow donors were observed in as-grown n-type silicon and that the $g \approx 2$ line originated from thermal donors and from A-centers.

EDMR method using detection of conductivity by applying electrical contacts provide the opportunity to observe EPR signals of recombination centers in small samples with electrical contacts. In addition, complementary information concerning the properties of paramagnetic centers and SDR processes can be obtained from the EPR spectra in weak magnetic fields because the additional EDMR lines due to the mixing of spin states, magnetic level crossing, and anticrossing can be observed.

In the present paper we report the results of experimental detection of EDMR signals in weak magnetic fields monitoring the...
change in dc-photoconductivity of silicon samples under magnetic resonance. We also report the effects of etching the samples with hydrofluoric acid (HF) and γ-irradiation on the EDMR signal of phosphorus atoms in silicon.

2. Experimental

Ohmic contacts for the EDMR measurement were made by ion-implantation and post-implantation annealing of arsenic on Fz-Silicon wafers doped with phosphorous (1 × 10^{15} \text{cm}^{-3}). Samples were irradiated by γ-rays emitted from a 60Co source at room temperature with the dose of irradiation from 10^{14} to 6 × 10^{15} \text{cm}^{-2}. The EDMR measurements were performed at low magnetic field \(B<50 \text{mT}\) with \(B/\langle 110 \rangle\) and at temperature between 6–20 K. Radio frequency used for the measurement was applied by a coil wrapped around the sample. 100 W halogen lamp was used for creating photoexcited carriers. Prior to each measurement, the surface oxide from the surface was removed with dilute hydrofluoric acid (HF) solution to reduce the concentration of surface defects. A lock-in detector tuned to the second harmonic of \(g\)-irradiation on the EDMR signal was used for creating photoexcited carriers. To measure the EDMR signals, the sample with and without the surface oxide layer. Here the decrease of S-line intensity observed after the etching is attributed to the increase of radiation defects that take away from phosphorus donors increasing the concentration of positively charged phosphorus atoms being effective capture centers of photoexcited electrons increasing the efficiency of the spin dependent recombination process. Also, the spin dependent transfer of the captured electrons from phosphorus to another radiation defects localized near phosphorus atoms can increase the efficiency of SDR in the bulk of the sample. Unlike the case for the surface centers serving exclusively as spin dependent recombination centers, the recombination centers created by the γ-ray are distributed uniformly throughout the bulk sample. Therefore, the SDR occurs not only near the surface but throughout the bulk region leading to much larger change in the conductivity.

Fig. 2 compares the EDMR spectra of the irradiated sample with and without the surface oxide layer. Here the decrease of S-line intensity observed after the etching is attributed to the reduction in the surface recombination centers. However, the EDMR signal intensity of phosphorous remains unchanged showing that the SDR is occurring throughout the bulk region. Fig. 3 shows the EDMR spectrum from irradiated sample at lower modulation frequency (1 KHz). We can observe an additional EDMR signal, marked by an arrow in the figure, which is not visible for not irradiated samples doped with phosphorous. This signal is due to the transition between the entangled states of phosphorous formed at low magnetic field. Inset in Fig. 3 shows the phosphorous energy level at low

3. Results and discussion

EDMR spectra observed with the resonance frequency of 200 MHz in a Si sample before and after irradiation are shown in Fig. 1. The positive sign of signals corresponds to the increase of the recombination rate and decrease of photoconductivity in the sample. The EDMR spectrum of phosphorus donor atoms is detected together with the line labeled S-line (surface recombination center) with \(g\)-factor about 2.01. In the sample without irradiation the intensity of S-line decreases together with the intensity of phosphorus lines when the surface oxide was removed with HF. This allows us to conclude that S-line arises from the surface recombination centers and SDR process includes the spin dependent electron transfer from phosphorus to surface paramagnetic centers. This is consistent with the previous report where EDMR of phosphorous in silicon has been attributed to the spin dependent recombination between neutral donor (P0) and paramagnetic states at the Si/SiO2 interface [9].

Fig. 1b shows the EDMR spectrum from the sample after γ-irradiation. The increase about 10 times of the P0 and S-line intensities is observed at the irradiation doses of (3–6) × 10^{15} \text{cm}^{-2}. The concentration of radiation defects created in silicon by γ-rays at these doses of irradiation cannot exceed 10^{14} \text{cm}^{-3} which is 10 times lower than the concentration of phosphorus atoms. It is the remarkable result that the creation of 10 times lower concentration of defects increases 10 times the intensity of phosphorus EDMR signals. At higher doses of irradiation the intensity of the P0 EDMR lines decreases.

The increase in the efficiency of SDR process after irradiation can be attributed to the increase of radiation defects that take electrons away from phosphorus donors increasing the concentration of positively charged phosphorus atoms being effective capture centers of photoexcited electrons increasing the efficiency of the spin dependent recombination process. Also, the spin dependent transfer of the captured electrons from phosphorus to another radiation defects localized near phosphorus atoms can increase the efficiency of SDR in bulk of the sample. Unlike the case for the surface centers serving exclusively as spin dependent recombination centers, the recombination centers created by the γ-ray are distributed uniformly throughout the bulk sample. Therefore, the SDR occurs not only near the surface but throughout the bulk region leading to much larger change in the conductivity.

Fig. 2 compares the EDMR spectra of the irradiated sample with and without the surface oxide layer. Here the decrease of S-line intensity observed after etching is attributed to the reduction in the surface recombination centers. However, the EDMR signal intensity of phosphorus remains unchanged showing that the SDR is occurring throughout the bulk region. Fig. 3 shows the EDMR spectrum from irradiated sample at lower modulation frequency (1 KHz). We can observe an additional EDMR signal, marked by an arrow in the figure, which is not visible for not irradiated samples doped with phosphorous. This signal is due to the transition between the entangled states of phosphorous formed at low magnetic field. Inset in Fig. 3 shows the phosphorous energy level at low

![Fig. 1. EDMR spectra recorded with 200 MHz in silicon before irradiation (a) and after irradiation (b) by γ-rays with the dose of 2 × 10^{15} \text{cm}^{-2}.

![Fig. 2. EDMR spectra detected in the irradiated sample before (a) and after (b) removal of the surface oxide by HF.](image-url)
magnetic field, were the hyperfine interaction between electron and phosphorus nuclear spins is comparable with Zeeman term in spin Hamiltonian.

Moreover, additional EDMR lines were detected in the irradiated sample as shown in Fig. 4. Positions of these lines depend on the orientation of the crystal in magnetic field. Analysis of the line positions of the spectrum in Fig. 4 shows that this spectrum arises from the excited spin $S = 1$ state of oxygen+vacancy complex (A-center) which give the Si-SL1 EPR spectrum observed by traditional EPR method [10] and by EDMR [7,8,11]. The line positions calculated for orientation $B \parallel \langle 110 \rangle$ using the spin Hamiltonian parameters determined in Ref. [10] are shown by triangles in Fig. 4. The line at $B = 35$ mT corresponds to the anticrossing point of magnetic sublevels with spin projections $m_S = +1$ and $m_S = 0$. The position of this line does not depend on the resonance frequency and the line is observed even without resonance field. The negative line marked by X in Fig. 4 is not identified. The mechanism of SDR responsible for Si-SL1 EDMR spectrum is well established [11] and caused by spin-selective transitions from excited triplet states of A-centers to ground singlet state which leads to non-equilibrium populations of triplet magnetic sublevels with spin projections $m_S = +1, 0,$ and $-1$, and to different signs of lines detected by traditional EPR technique [10]. The excitation of magnetic resonance transitions between magnetic sublevels in the excited triplet state increases the recombination rate and photoconductivity of samples [11].

4. Summary

Electrically detected magnetic resonance (EDMR) of phosphorus donors, surface defects, and photoexcited Si-SL1 centers has been detected for relatively low resonance frequencies ($< 400$ MHz) and magnetic fields ($< 50$ mT).

The comparison of the phosphorus and surface EDMR lines intensities in the sample before and after \( \gamma \)-ray irradiation shows convincingly that the defects created throughout the bulk region by the \( \gamma \)-ray are effective spin dependent recombination centers and they lead to strong enhancement of the phosphorus EDMR signal even at the concentration of radiation defects 10 times lower than concentration of phosphorus atoms.

EDMR signal from the entangled states of phosphorous in silicon can also be observed in irradiated samples. The EDMR S-line with $g \approx 2.01$ was identified as arising from surface recombination centers. The photoexcited triplet states of A-centers were also observed.

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