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Identification of paramagnetic spin dependent recombination centers on surface of silicon wafers

© L.S. Vlasenko, I.S. Fedosov

Ioffe Institute, St. Petersburg, Russia
E-mail: Leovlas@solid.ioffe.ru

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Electron paramagnetic resonance spectra of centers localized on (111), (110), and (100) oriented surface of silicon wafers were observed and studied using spin dependent microwave photoconductivity. The wafers were not subjected to high temperature oxidization, but oxidized on air at room temperature. The optimal experimental conditions for detection the surface recombination centers, having the sensitivity by order of magnitude greater in comparison with usual electron paramagnetic resonance technique, were discussed.

Keywords: Silicon, surface centers, electron paramagnetic resonance.

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Scientific information about the structure and properties of surface centers in semiconductors and centers at the oxide/semiconductor boundary [1,2] is important for the technology of manufacturing of semiconductor devices and their operating conditions, since such centers significantly affect the processes of carrier recombination, the parameters of various semiconductor devices and processes of their degradation. The main method of studying such centers is the method of electron paramagnetic resonance (EPR), which allows not only establishing their microstructure, but also studying the behavior of the centers in case of various surface treatments [3–6]. However, the EPR method requires a fairly high surface density of paramagnetic centers (of the order $10^{12}-10^{13}\,\mathrm{cm}^{-2}$), which is achieved in case of high-temperature ($600-800^{\circ}\mathrm{C}$) oxidation of the silicon surface [3]. Samples composed of 10–20 thin silicon wafers are usually used in EPR-experiments, as well as the accumulation of spectra during repeated magnetic resonance passage [3,6]. The EPR spectra of spin centers $S = 1/2$ such as centers P_b on the surface (111) and centers P_{b0} and P_{b1} on the surface (100) associated with broken bonds silicon atoms at the Si/SiO_2 boundary were discovered and studied in detail [5].

A significant (by several orders of magnitude) increase of the sensitivity of the EPR method was demonstrated using methods for recording EPR spectra by resonant changes in the microwave photoconductivity of crystals [7] using spin-dependent recombination (SDR) effects. The free path of photoexcited carriers is comparable to the thickness of the plates in thin ($100-300\,\mu\mathrm{m}$) plates of pure high-resistance silicon, and their recombination is determined mainly by surface centers. A change of the spin state of these centers during magnetic resonance shortens the lifetime of nonequilibrium carriers, which results in a decrease of microwave photoconductivity detected by absorption of the electric component of the microwave field in the crystal volume and an increase of the Q-factor of the cavity of the EPR-spectrometer. New recombination centers (P_m-centers) were discovered on (100)-surface of silicon using this technique [8]. Experiments on the detection of the SDR–EPR spectra of recombination centers on the surfaces of (111) and (110) silicon wafers were not been carried out before.

This paper presents the results of the study of the SDR–EPR spectra of surface centers in silicon wafers with orientations (111), (110) and (100), not subjected to high-temperature oxidation, when the spectra of surface centers are not observed using the traditional EPR method.

The experiments were performed using silicon samples cut from industrial silicon wafers of *n*- and *p*-type with a resistivity of $\rho \sim (2-3)\cdot 10^3\,\Omega\cdot\mathrm{cm}$ and a thickness of $h \approx 0.25-0.3\,\mathrm{mm}$. The SDR–EPR spectra were recorded using X-band EPR-spectrometer with a maximum microwave field power of 80 mW. Samples with a size of $3.5\times 8\times h\,\mathrm{mm}$ with a long edge directed along the axis of the crystal of $\langle 110\rangle$ were placed along the axis of the cylindrical cavity into the antinode of the magnetic component of the microwave field H_1. The photoconductivity was excited by the light of 100 W incandescent lamp. The absorption of the electrical component E_1 by free carriers was also observed at the same time, which manifested itself in a decrease of the Q-factor of the cavity when the light was turned on. The signals were recorded as the second derivative of absorption on a magnetic field for improving the resolution of the SDR–EPR spectra. The EPR lines of Mn^{2+} ions in MgO were used for calibrating the magnetic field.

Figure 1 shows the SDR–EPR spectra of the recombination centers on surfaces (111), (110) and (100) with the orientation of the magnetic field **B** along the axis of crystals $\langle 111\rangle$. It should be noted that the signs of the

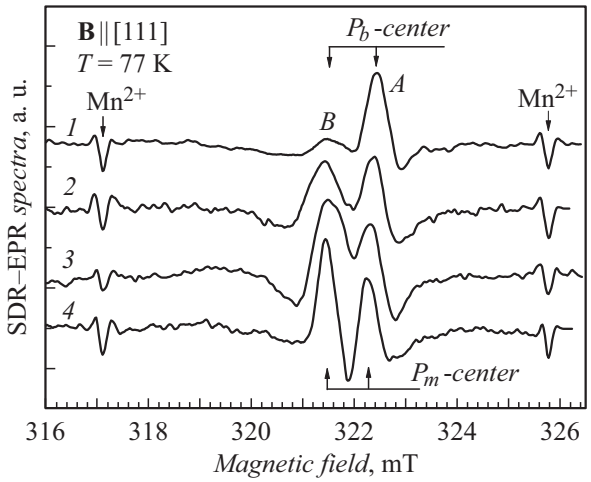

Figure 1. The SDR–EPR spectra of recombination centers P_b and P_m, recorded by changes in microwave photoconductivity in silicon wafers with different surface orientations. Spectrum *1* — (111), spectrum *2* — (110), the spectra of *3* and *4* — (100) (*3* — in the original sample, *4* — after etching the sample in HF). *A* and *B* — lines in the spectra of P_b-centers. The usual EPR absorption signals are shown for two of the six lines of the hyperfine structure of Mn^{2+} ions in MgO.

SDR–EPR lines are opposite to the signs of the usual EPR lines of Mn^{2+} ions in MgO, shown in Fig. 1, and correspond to an increase of the Q-factor of the cavity of the EPR-spectrometer at magnetic resonance, which indicates an increase of the recombination rate of light-excited carriers and a decrease of the photoconductivity of samples recorded by the absorption of the electric component of the microwave field E_1. In addition, the amplitude of the SDR–EPR signals linearly depends on the power of the microwave field P up to $P_{\max} = 80$ mW, while the amplitude of conventional EPR absorption signals is proportional to $P^{1/2}$ at low power levels. The amplitude of the SDR–EPR signals first increases with the increase of light intensity, and then decreases, which is associated with a decrease of the Q-factor of the cavity of the EPR-spectrometer.

The SDR–EPR spectra of samples with surface orientations (111) and (110) (spectra *1* and *2* in Fig. 1, respectively) are not observed immediately after surface treatment in HF for 1 min, which is attributable to passivation of broken silicon bonds by hydrogen atoms [6]. The spectra are restored after 12–14 days of oxidation in air at room temperature, when the oxide layer on the surface is on the order of 5 Å [9]. The etching of the surface (100) in HF does not result in the complete disappearance of the spectrum, but only leads to its simplification (spectra *3* and *4* in Fig. 1). This suggests the different nature of recombination centers on the surface (100) in contrast to surfaces (111) and (110) and manifests itself in the difference in the angular dependences of the position of the lines in the spectra when the samples are rotated in a magnetic field.

The angular dependencies of the positions of the lines *A* and *B* shown in Fig. 1 are represented by lines *1* and *2* in Fig. 2, respectively. P_b-centers having trigonal (C_{3v}) symmetry g-tensor along the axis ⟨111⟩ are recombination centers on the surfaces (111) and (110) of Si/SiO_2. Calculated dependencies for values $g_{\parallel} = 2.00136$, $g_{\perp} = 2.0088$ are shown by solid lines in Fig. 2, *a* and *b* [3]. The P_b — centers are oriented mainly perpendicular to the (111) surface which corresponds to the most intensive line *A* in Fig. 1 (spectrum *1*). The P_b-centers localized on the surface (110) oriented in two directions ⟨111⟩ in the plane (110) which is perpendicular to the surface. This results in the appearance of two lines in the SDR–EPR spectrum. The angular dependence of these lines is shown in Fig. 2, *b*.

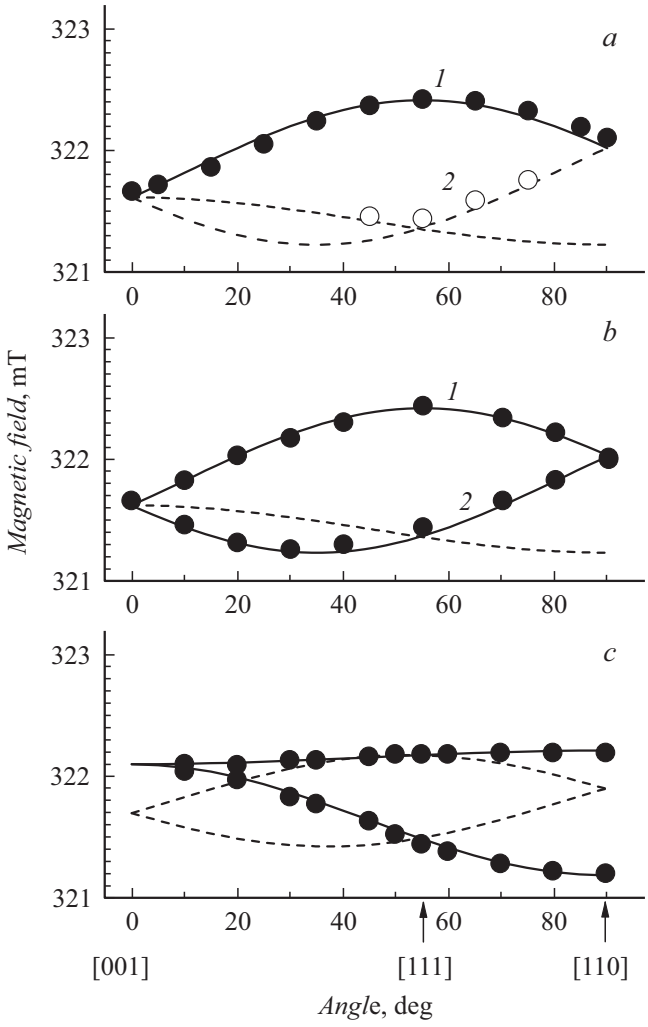

Figure 2. Angular dependences of the line positions in the SDR–EPR spectra of silicon wafers with orientations of surface (111) (*a*), (110) (*b*) and (100) (*c*). Points — experiment data, lines — calculated dependencies for the centers P_b (*a*, *b*) and P_m (*c*). Lines *1* and *2* correspond to the signals of *A* and *B* of P_b-centers shown in Fig. 1. The dashed lines correspond to the equivalent orientations of the centers that would be observed for centers in the volume of crystals, but are not observed on the surface.

The recombination centers on the surface (100) have orthorhombic symmetry (C_{2v}), but only two lines corresponding to centers oriented in two mutually perpendicular directions ⟨110⟩ are observed on this surface of the sample. The angular dependence of the position of these lines when the sample rotates in a magnetic field is shown in Fig. 2, *c* by solid lines. The main recombination centers on (100)-surface of silicon are P_m-centers [8], which are pairs of dangling bonds of adjacent silicon atoms. The angular dependence of P_m-centers calculated for the values of the components of g-tensor $g_1 = 2.0093$, $g_2 = 2.0029$ and $g_3 = 2.0036$ [8] is shown in Fig. 2, *c*.

Unlike traditional EPR-experiments, when samples composed of 10−20 plates were used, the spectra shown in Fig. 1 were obtained on a single plate without using signal accumulation during repeated scanning of the magnetic field. This allows making a conclusion that the sensitivity of the technique used is at least an order of magnitude higher than for the conventional EPR method in the study of surface centers in silicon.

Thus, the use of spin-dependent recombination methods makes it possible to record with high sensitivity the EPR spectra of centers occurring in case of oxidation in air at room temperature on silicon wafers with different surface orientations, and to study the effect of various surface treatments on the properties of these recombination centers.

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Conflict of interest

The authors declare that they have no conflict of interest.

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