Photoelectrically Detected Magnetic Resonance Spectroscopy of the Excited Triplet States of Point Defects in Silicon

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Highly sensitive methods of the detection of the electron paramagnetic resonance (EPR) spectra based on the spin-dependent microwave photoconductivity were applied for investigation of the structural defects in irradiated silicon. The parameters of the EPR spectra of the excited triplet states of radiation defects were determined and several models of the carbon related defects were supposed.

Electron paramagnetic resonance (EPR) is one of the main methods for investigation the microscopic structure of various point defects in solids, particularly in semiconductors. Among semiconductor materials the most significant results were achieved in silicon. Using the EPR technique about three hundreds different EPR spectra of impurity atoms, their complexes, radiation and thermal defects in silicon were observed [1]. A part of them were identified and described in reviews [2,3]. Further progress of magnetic resonance spectroscopy of defects in semiconductors was related to the development of the new highly sensitive methods based on the effects of spin dependent recombination (SDR) when the recombination rate of nonequilibrium carriers depends on the spin orientation of the recombination centers [4]. These methods allow us to detect EPR spectra by measuring the intensity of the recombination luminescence or the photoconductivity of samples in magnetic field under saturation of the EPR transitions by the resonance microwave magnetic field.

The detection of microwave photoconductivity of silicon samples by the absorption of the electric component of the microwave field due to the resonance change of the concentration of photoexcited carriers increases the sensitivity of the method by four orders of magnitude [5]. It was found that the main channel of SDR is the recombination through the excited triplet states of the recombination centers. Several new SDR detected EPR spectra of the excited triplet states of different defects have been found in irradiated silicon. Some of them were identified as arising from the excited spin $S=1$ state of Substitutional carbon–Interstitial silicon–Substitutional carbon (C_S–Si_I–C_S) complex (spectrum Si–$PT1$ [5,6]), divacancy (spectrum Si–$PT5$ [7]), and complex phosphorus + vacancy (spectrum Si–$PT3$ [5,8]).

In the present paper the advantages and some applications of the SDR–EPR methods for investigation the structure of the recombination centers in irradiated silicon will be described.

1. Excited Triplet States of Defects

The irradiation of silicon crystals by fast electrons or γ-rays gives rise to various structural defects containing the dangling bonds which can form the molecular orbitals. Each of the latter can be occupied by one electron or by two electrons with opposite spins. If the defects contain even number of electrons their ground state will be nonparamagnetic with spin $S = 0$. Under band gap illumination and recombination process the defects can be in the excited spin $S = 1$ state when two unpaired electrons occupy different atomic or molecular orbitals.

Let us consider the Hamiltonian of two interacting electrons in magnetic field **B**

$$H = \mu_B \mathbf{B} \mathbf{g}_1 \mathbf{S}_1 + \mu_B \mathbf{B} \mathbf{g}_2 \mathbf{S}_2 + J \mathbf{S}_1 \mathbf{S}_2 + \mathbf{S}_1 \mathbf{D} \mathbf{S}_2, \qquad (1)$$

taking into account the Zeeman interaction between the applied magnetic field **B** and the electrons spins S_1 and S_2 (μ_B is the Bohr magneton, g_1 and g_2 are g-tensors of the

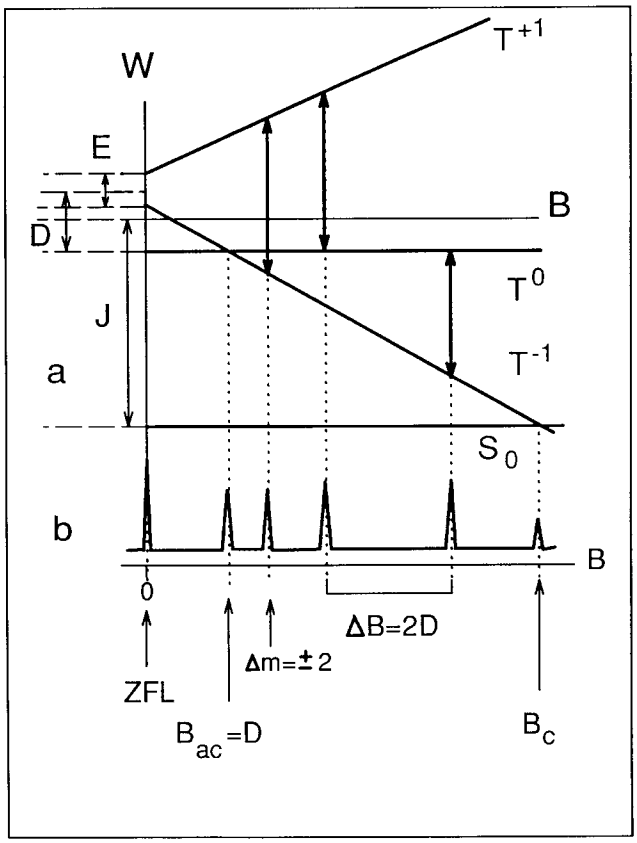

Figure 1. Energy levels of a system of two electrons in a magnetic field B (a) and the expected positions of the SDR detected lines of the change of the microwave photoconductivity (b).

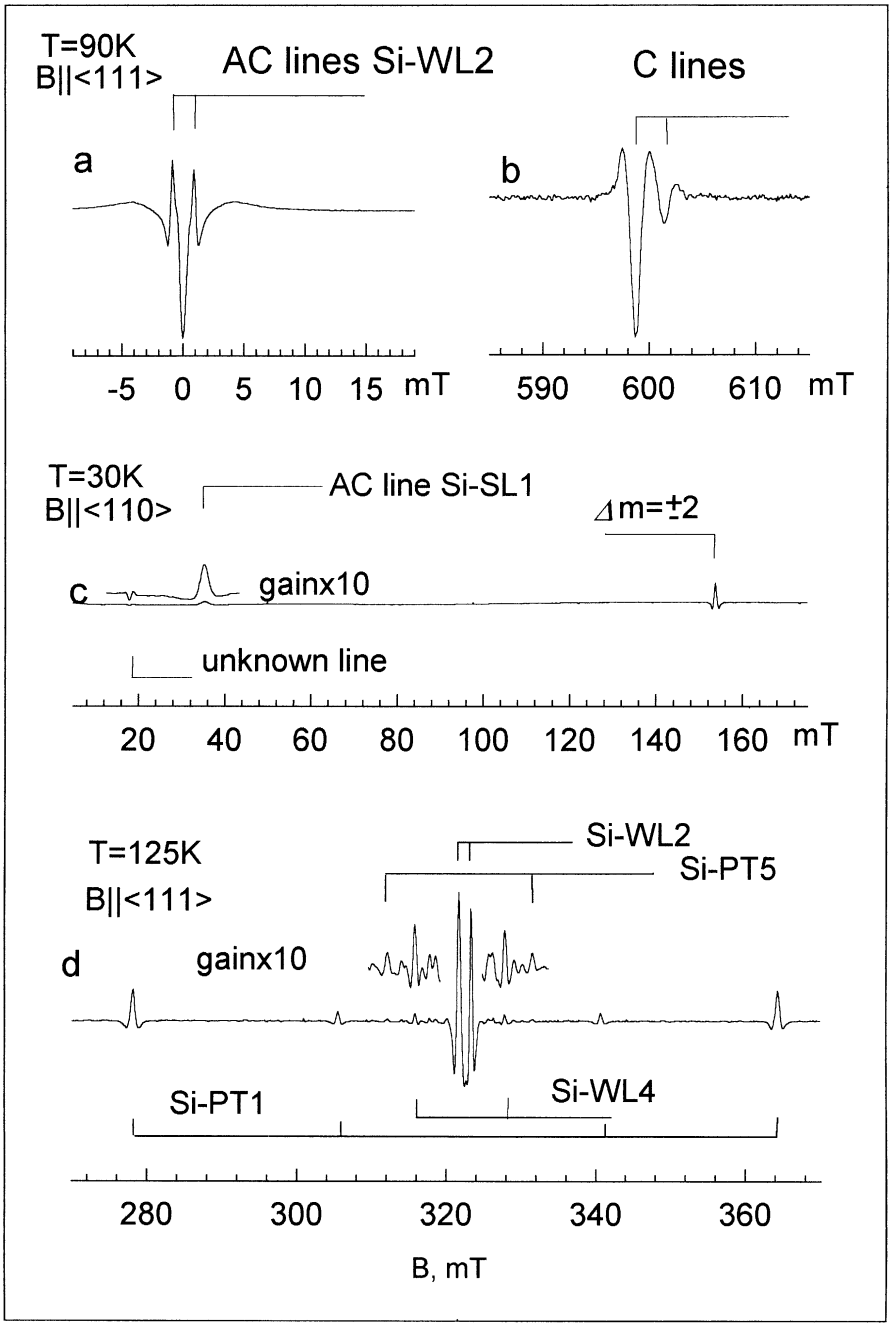

Figure 2. SDR detected lines of microwave photoconductivity in irradiated silicon, observed in different ranges of magnetic field B for various defects. Zero field line and anticrossing (a) and crossing (b) lines correspond to the Si–$WL2$ center. Anticrossing line and line of the forbidden transition (c) are related to the excited triplet state of the oxygen + vacancy complex (Si–$SL1$ spectrum). SDR–EPR spectra of the defects with different D-constant are presented in (d).

first and second electrons), the isotropic exchange interaction $J\mathbf{S}_1\mathbf{S}_2$, and the anisotropic magnetic dipole-dipole interaction $\mathbf{S}_1\mathbf{D}\mathbf{S}_2$, where $\mathbf{D}$ is a symmetric traceless tensor determined by two parameters, D and E, in the principal coordinate frame corresponding to the symmetry of the defects. The energy levels obtained from the Hamiltonian (1) for the case of two identical electrons ($\mathbf{g}_1 = \mathbf{g}_2$ and $S_1 = S_2 = 1/2$) are shown in Fig. 1, a.

The exchange interaction between two unpaired electrons leads to formation of a ground singlet S_0 state with spin $S = 0$ and an excited metastable triplet state T ($S = 1$). In zero magnetic field these states are separated by the energy $J \cong W(T) - W(S_0)$ where J is the exchange interaction constant. An additional zero field splitting between T^{+1}, T^{-1}, and T^0 states is due to the magnetic dipole-dipole interaction $\mathbf{S}_1\mathbf{D}\mathbf{S}_2$. The expected spectrum of

the change of photoconductivity of the sample containing defects in the excited triplet state is shown in Fig. 1, *b*.

The formation of the excited triplet states of defects under illumination and the change of the recombination rate of the photoexcited carriers under saturation of the EPR transitions between magnetic sublevels T^{+1}, T^0, and T^{-1} as well as the change of photoconductivity at the magnetic field $B = B_{ac}$ corresponding to the anticrossing of the sublevels T^{-1} and T^0 without magnetic resonance (see Fig.1, *b*) was considered in detail in Refs. [5,6]. In addition, the spin dependent change of photoconductivity can be observed at zero magnetic field (ZFLine), at the magnetic field $B = B_c$ corresponding to the crossing of excited T^{-1} state and ground S_0 state, and under magnetic resonance between T^{+1} and T^{-1} sublevels (forbidden $\Delta = \pm 2$ transitions). The examples of the experimentally detected lines of the SDR related change of photoconductivity are shown in Fig. 2. The angular and temperature dependences of intensity and position of these lines allow us to get additional information about the parameters of the Hamiltonian (1).

2. Parameters of the Spectra and Models of the Defects

The components of the **g**- and **D**-tensors determined from the experimentally observed angular dependences of the EPR spectra bear an information on the symmetry of point defects. The exchange interaction constant J and the component D of the **D**-tensor depend of the distance r between interacting electrons, which is important for consideration the models of defects.

The value of J depends exponentially on the distance r and is usually many orders of magnitude higher than the Zeeman energy. For such defects the crossing (C) lines cannot be detected at reasonable strength of the magnetic field. The defects having the value of J comparable with the Zeeman energy were found recently [9,10]. The positions and angular dependences of the anticrossing and crossing lines for such defects (see Fig. 2, *a, b*) are described by the same parameters of Hamiltonian (1) as the new SDR detected Si–*WL*2 [10] spectrum shown in Fig. 2, *d*.

The value of parameter D is proportional to the $1/r^3$ averaged over the electron wave function. It can be determined experimentally from the fine structure splitting of the Zeeman lines separated by $\Delta B \cong 2D$ as well as from the position of the anticrossing line (AC) (see Fig. 1, *b*).

The knowledge of D values allows us to estimate the average distance between two unpaired electrons forming the total spin $S = 1$ of the defects and to suggest the models of the investigated defects. The comparison of the ΔB values for Si–*WL*2 and for other SDR–EPR spectra with the theoretical dependence of ΔB on the distance r calculated in Ref. [11] is shown in Fig. 3. The models of some carbon related defects derived from the SDR–EPR spectroscopic data are shown in Fig. 4.

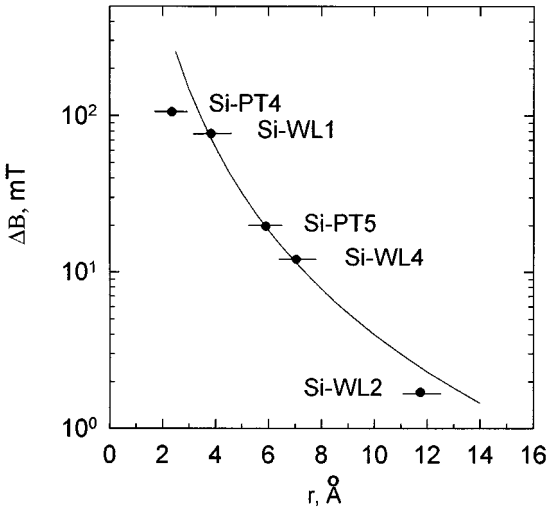

Figure 3. Dependence of the fine structure splitting ΔB on the distance r between two interacting electrons.

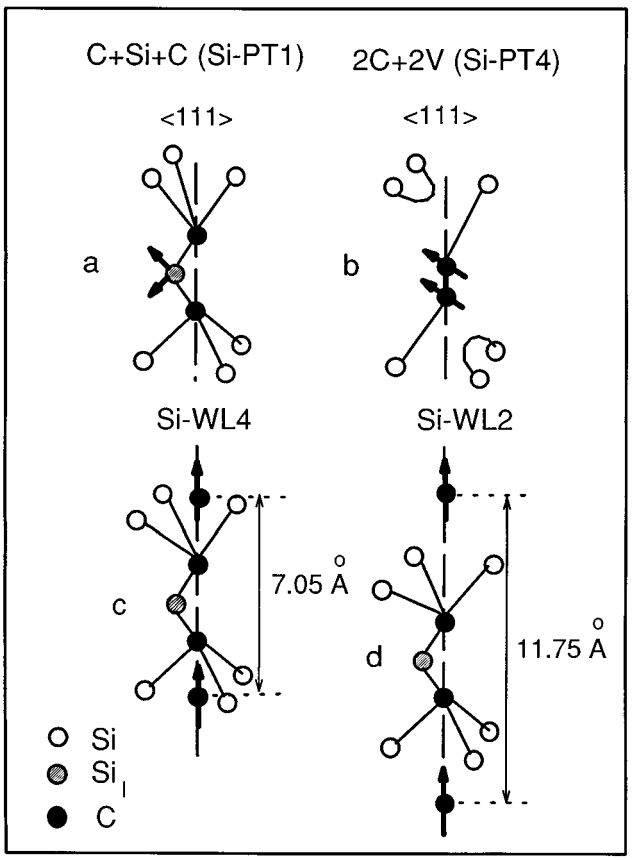

Figure 4. The models of the carbon related defects corresponding to the SDR–EPR spectra Si–*PT*1 (*a*), Si–*PT*4 (*b*), Si–*WL*1 (*c*), and Si–*WL*2 (*d*).

Carbon impurities play an important role in the formation of the radiation defects in silicon. One of the main defects in the irradiated pure float–zone grown silicon is the (C_I–Si_S–C_I) complex (Fig. 4, *a*) giving the

SDR–EPR spectrum labeled Si–$PT1$. Under isochronal thermal annealing in the temperature range of 200–300°C the spectrum Si–$PT1$ decreases and new spectrum Si–$PT4$ appears simultaneously. It was found that this spectrum has the symmetry similar to the symmetry of divacancy and shows the hyperfine structure due to the interaction with two equivalent carbon atoms. The model of the defects responsible for the Si–$PT4$ spectrum is shown in Fig. 4, *b*. This defects can be considered as a complex of two carbon atoms + divacancy.

Two weak spectra Si–$WL2$ and Si–$WL4$ [10] shown in Fig. 2, *d* are observed in the unannealed samples. The models of the defects giving these spectra are shown in Fig. 4, *c, d*. These models were derived from the trigonal symmetry of the spectra and from the values of the fine structure splitting $\Delta B = 2D$ determined by the distance between two electrons forming the total spin of defects $S = 1$. These electrons can be localized at the carbon atoms occupying the tetrahedral interstitial positions along $\langle 111 \rangle$ directions of silicon lattice near the $(C_I–Si_S–C_I)$ complex.

In summary, the spin-dependent effects and detection of the EPR spectra by the change of microwave photoconductivity of samples allow us to observe the spectra of the excited triplet state of defects at their low concentration, which cannot be detected by traditional EPR spectroscopy. The nonresonat crossing and anticrossing change of photoconductivity allows us to obtain additional information about the parameters of the triplet centers and to suggest their models.

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