Spin dependent recombination in Pt-doped silicon $p$-$n$ junctions

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Electrically detected magnetic resonance experiments showing spin dependent recombination in commercial $p$-$n$ diodes are presented. The observed anisotropy in the $g$ values along with the marked shift from the free electron $g$-value point to a metal-vacancy complex. Deep level transient spectroscopy reveals the presence of the Pt acceptor level ($0/ -$) at $E_C - 0.23$ eV and the donor level ($+/0$) at $E_V + 0.32$ eV in the same device. Calculations of the recombination rates support that spin dependent recombination occurs at the Pt ($+/0$) donor level.

The detailed knowledge about the microscopic structure of deep and shallow impurities in Si has mainly been supported by conventional electron paramagnetic resonance (EPR). EPR allowed conclusions about site (interstitial, substitutional) and symmetry (isolated, complexed, Jahn–Teller distorted) of the point defects. While EPR is best suited for large-volume samples, it is often limited for applications in thin, epitaxial samples and especially in active devices. Detection of electrically active defects by EPR in a space charge region of a Si diode could bring together two important characterization techniques, i.e., the space-charge techniques like deep level transient spectroscopy (DLTS) and EPR. DLTS gives the information about the number of defects, their capture cross sections and positions of the levels in gap, information not always so easily obtained by EPR, but more serious, not obtainable on the same device. Electrically detected magnetic resonance in Si $p$-$n$ diodes has been reported first in 1977; the resonance observed was attributed to dangling bond centers ($P_b$) at the Si/SiO$_2$ interface.

Here we report on electrically detected magnetic resonance (EDMR) and DLTS experiments in a commercial Si $p$-$n$ diode deliberately doped with Pt. The results, supported by numerical calculations, show the presence of a metal-related deep impurity in the spin dependent recombination current. This confirms recent EDMR investigations, where EDMR signals, based on the very low $g$ values, were tentatively assigned to metallic impurities.

The EDMR experiments were performed at room temperature on a commercially available Si $p$-$n$ diode (BY 448). The diode was forward biased with a current flow in the range from 1 nA up to 1 mA. Synchronous changes in the voltage under constant current (Keithley 225 Current Source) were detected by on/off modulation of the micro-waves. The sample was placed in a cylindrical TE$_{101}$ resonator with a loaded $Q$ of 12 000. The microwave system operates in the 9 GHz region ($X$ band). A maximum power of 200 mW was delivered by a frequency stabilized klystron (Varian V-262). DPPH was used as a $g$ marker. Narrow bandwidth lock-in detection (PAR 124A) was essential.

Figure 1 shows the EDMR signal at a magnetic field position corresponding to $g = 2.02$ obtained as microwave induced change in the voltage (the negative signal is due to the $g$ marker DPPH). The best signal to noise ratio is observed for a modulation frequency of 900 Hz: up to the maximum microwave power available no saturation effects could be found. The signal is first detectable for a current of 1 nA, showing a maximum signal strength at 500 nA and is decreasing again for higher currents (see Fig. 2). This strong variation of the resonance signal with the diode current was observed also in the first experiments of that kind and attributed to the recombination limited current $I_R$, i.e., recombination of the injected carriers in the space charge region of the diode. In the following we will calculate the EDMR signal dependence on the applied current. The diode current $I$ has two contributions, one due to the diffusion current $I_D$ and one due to the recombination current $I_R$.

$$I = I_D(e^U - 1) + I_R(e^{U/2} - 1).$$

For clarity we take $e/kT = 1$. When resonance occurs, the recombination current increases by an amount $\delta I_{SR}$ but causes a decrease in voltage $\delta U$ by $\delta U$, since the total current $I$ remains the same. It thus follows

![Figure 1. Electrically detected magnetic resonance (EDMR) signal in a Si $p$-$n$ diode (BY 448), microwave frequency 9.51 GHz, room temperature. The negative signal is due to the $g$ marker, DPPH.](image-url)
The change in voltage can hence be calculated setting both currents \( I = I_D(e^{U/2} - U/2 - 1) + (I_R + \delta I_{SR})(e^{U/2} - U/2 - 1) \). (2)

Figure 2 shows the fit to the experimental data (the current applied was converted to voltage from the measured \( I-U \) curve of the diode). Values for \( I_R \) and \( I_D \) were also taken from the \( I-U \) curve: \( I_R = 4 \times 10^{-3} \) A, \( I_D = 4 \times 10^{-14} \) A. \( \delta I_R \) was varied as the only fit parameter. The best fit is obtained for \( \delta I_R = 8 \times 10^{-16} \) A. We find close agreement between experiment and calculation, by assuming that only the recombination current, but not the diffusion current is spin dependent. For the diffusion current to be spin dependent, the EDMR signal should continue to increase for currents above 500 nA.

EDMR results reported quite recently were performed on \( N_{4007} \) \( p-n \) diodes and found isotropic resonances at 1.965 and 1.984. It was argued that they might originate from metallic ions, a point we want to substantiate in the following. The EDMR resonance in the diode BY 448 is not isotropic: We observe the resonant increase in current for \( B_0 || (111) \) at \( g = 1.97 \pm 0.01 \) and for \( B_0 \perp (111) \) at \( g = 2.04 \pm 0.01 \), where \( || \) and \( \perp \) mean parallel and perpendicular to the \( (111) \) crystallographic plane of the Si diode. The measured angular dependence is periodic in 180 degrees and resolves the axial symmetry of the defect (see Fig. 3). From the large anisotropy and the considerable deviation of the \( g \) values from the free electron value (\( g = 2.0023 \)), especially to values below \( g = 2 \), it is immediately apparent that we are not dealing with the \( P_b \) centers (dangling bond center) so far the most common defects as assigned by EDMR.

The EDMR detects the spin resonance of the defects in the space charge region of the \( p-n \) diode. This gives the possibility to use the same device for capacitance spectroscopy, DLTS. Figure 4 shows the temperature scan for the same diode under reverse bias. The DLTS experiments revealed the presence of only one dominating majority carrier trap at \( E_c = 0.23 \pm 0.005 \) eV with an electron capture cross section \( (\sigma_{Pt}) \) of \( 5 \times 10^{-14} \) cm\(^{-2}\) and a concentration of approximately \( 6 \times 10^{13} \) cm\(^{-3}\). These results identify the center as being due to the Pt \((0/+\) - ) acceptor level in Si. DLTS also revealed the presence of two additional traps at \( E_c = 0.55 \) eV and \( E_c = 0.3 \) eV but in concentrations \( 10^{-4} \) below the background doping. There, definite assignment to defects in Si is not immediately possible: the level at \( E_c = 0.55 \) eV is sometimes attributed to a Pt-Pt pair defect. Under forward bias the Pt related donor level at \( E_v = 0.32 \) eV \( (\sigma_D = 1 \times 10^{-14} \) cm\(^2\)\) was observed as a minority carrier trap. Both levels belong to the same center, the isolated substitutional Pt impurity. Our DLTS observations are in line with information obtained from the manufacturer of the diodes. Pt was introduced into the diodes as a lifetime killer resulting in faster switching times.

The question is, which charge state of Pt is involved in the spin dependent recombination: we examine the relative contributions of the two different levels in the Shockley–Read–Hall recombination of the diode. We use the numerical 1D solution of the stationary semiconductor equation (Poisson equation, continuity equation for electron and holes). The doping concentrations on both sides of the \( p-n \) junction were obtained from \( C-V \) measurements to be \( N_a - N_d = 5 \times 10^{14} \) cm\(^{-3}\). The applied voltage is \( U_D = 0.1 \) V. In the numerical simulation the recombination rate \( R_\text{e} \) through midgap centers with concentration
dependent electron and hole lifetimes is compared with the recombination rate \( R_{Pt} \) through the Pt acceptor and Pt donor level both with equal concentrations of \( 7.5 \times 10^{13} \text{ cm}^{-3} \). The parameters for the Pt centers, i.e., binding energies and cross sections are taken from the DLTS experiments. The electron and hole lifetimes are taken to be equal: their respective values for the acceptor and donor centers were estimated to be \( t_\gamma = 6 \times 10^{-7} \text{ s} \) and \( t_\delta = 1 \times 10^{-7} \text{ s} \). The result of the simulation is shown in Fig. 5. The Pt related recombination \( R_{Pt} \) is higher than the typical Si recombination \( R_S \). This difference, which is about one order of magnitude for \( U_D = 0.1 \text{ V} \) (the corresponding current is 65 nA), increases further with increasing applied voltage. One further important aspect is that the contribution of the Pt acceptor level to the total recombination rate \( R_{tot} \) is negligible compared to the contribution of the donor level. Its recombination rate does not differ from \( R_{tot} \) shown in Fig. 5. This calculation would rule out the Pt\(^-\) center being responsible for the EDMR resonance signal.

The singly ionized donor and acceptor charge states of Pt, Pt\(^+\) and Pt\(^-\) are expected to be paramagnetic. In conventional EPR, Pt\(^-\) shows orthorhombic symmetry and a resolved hyperfine (hf) interaction with 34\% abundant isotope \(^{195}\text{Pt} \) with \( I = 1/2 \) (all other isotopes have \( I = 0 \)).\(^{1,6,12}\) The measured resonance data for Pt\(^-\) obviously do not agree with our experimental findings.

Also Pt\(^+\) is expected to be paramagnetic and our calculations of the recombination current indicate the donor level is dominating. Pt\(^+\) could in analogy to Pt\(^-\) produce an anisotropic spectrum.\(^{13}\) However, no hf interactions with the Pt nucleus were observed. So far for Pt\(^+\) neither EPR results, nor theoretical calculations on the electronic structure were reported to compare with Ref. 14. Further experiments, especially extending the measurements to low temperatures are needed to clarify this point.

In summary we report on electrically detected magnetic resonance investigations in Si p-n diodes where the spin dependent recombination with a Pt-related deep center is observed. The spin dependent effects as a function of applied voltage are shown to be due to the recombination current. Although more information about the precise defect structure of the center observed are needed, the measured g values, the DLTS experiments and the calculation of the recombination rates give evidence that the singly ionized Pt donor state is involved.

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7. In contrast in Ref. 3, the spin dependent effects were calculated in terms of saturation current \( I_s \), its respective change due to resonance and an additional fitting parameter \( V_0 \), the voltage where \( I_p \) equals \( I_R \).
10. J. Van Tiggelen, Philips, Eindhoven (private communication).
14. Reorientation effects (motionally averaging) at higher temperatures might significantly alter the hf splitting.