JOURNAL OF APPLIED PHYSICS **97**, 056101 (2005)

Triplet recombination at P_b centers and its implications for capture cross sections

Felice Friedrich, Christoph Boehme,[a] and Klaus Lips
Hahn–Meitner Institut Berlin, Kekuléstrasse 5, D-12489 Berlin, Germany

(Received 3 May 2004; accepted 30 November 2004; published online 10 February 2005)

Pulsed electrically detected magnetic resonance measurements are presented showing that P_b centers at the crystalline silicon (c-Si) (111) to silicon dioxide ($\mathrm{SiO_2}$) interface can cause recombination of strongly coupled spin pairs in singlet and triplet configurations. The implication of these findings is that two different electron capture cross sections can exist at a single defect. This shows that the previously observed two capture cross sections at the c-Si/$\mathrm{SiO_2}$ interface do not necessarily imply the existence of additional non-P_b-like centers such as oxygen-backbonded silicon dangling bonds. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1851593]

P_b centers are trivalent silicon (Si) atoms at the crystalline silicon (c-Si)/silicon dioxide ($\mathrm{SiO_2}$) interface, which is of great importance for semiconductor device technology.[1] Since P_b centers dominate the c-Si/$\mathrm{SiO_2}$ interface trapping and recombination, their microscopic understanding has been investigated extensively since their discovery in 1971.[2] P_b centers are paramagnetic when uncharged[3] and therefore suited for microscopic studies with electron-spin resonance[4–6] (ESR). They are localized, singly occupied anisotropic electronic states with much p and little s content.[7,8] Since P_b centers point into a defined direction that only depends on the surface orientation, their microscopic anisotropy is reflected by macroscopic ESR spectra.[9] Hyperfine coupling studies have shown that ESR signatures of P_b centers are only due to unpaired electrons of Si atoms without oxygen backbonds.[7,10]

Parallel to the microscopic ESR studies, c-Si/$\mathrm{SiO_2}$ interface defects have been characterized by macroscopic methods such as capacitance–voltage (CV) measurements which quantify capture cross sections but do not distinguish qualitatively different defects. Modulated CV (MCV) experiments[11] showed that (111)-oriented c-Si/$\mathrm{SiO_2}$ interface states exhibit two clearly distinguishable capture cross sections σ_{n1} and σ_{n2} over large energy ranges deep within the band gap. This observation is remarkable since broken Si bonds are the only defect types that can account for the observed deep states. Albohn *et al.*[11] suggested that the previously proposed oxygen backbonds of the Si radical, the so-called P_L centers[12] are the origin of the shifted capture behavior. However, this idea fails to explain why these centers have not been observed by ESR. Moreover, it is not clear how the backbond-related distortion of unpaired electrons can shift the capture cross section by almost three orders of magnitude ($\sigma_{\mathrm{n1}}/\sigma_{\mathrm{n2}} \approx 10-10^3$) and why this fraction between the two observed cross sections is almost independent of the defect energy even though the magnitudes of the cross sections change strongly throughout large energy ranges of the band gap.

In the following, a pulsed electrically detected magnetic resonance (p-EDMR) study of P_b recombination is presented. EDMR connects the microscopic sensitivity and selectivity of ESR with the detection of electronic transport and recombination processes. It is based on the measurement of small photocurrent (PC) changes when recombination or transport currents through paramagnetic defects are changed by means of ESR. EDMR has traditionally been carried out as an adiabatic field sweep experiment, the so-called cw-EDMR. cw-EDMR is much more sensitive than ESR especially with regard to defects at two-dimensional systems such as interfaces. Because of this, many cw-EDMR studies have been carried out on the c-Si/$\mathrm{SiO_2}$ interface[1,6,13–15] in the past which showed that the P_b anisotropy of the ESR spectrum is also reflected by the EDMR spectrum. This was the proof for the existence of spin-dependent recombination through P_b centers. In a sense, the measurement of the P_b signature in the PC is a selective observation of recombination rates through P_b centers only. Since cw-EDMR is an adiabatic or quasiadiabatic experiment (low modulation frequencies), it is unable to reveal quantitative information about the dynamics of the observed processes such as recombination rates. In order to overcome this drawback, p-EDMR has been developed in recent years, which is the transient measurement of small current changes from a steady state due to the pulsed ESR-induced manipulation of spin-dependent transport or recombination rates. The theoretical and experimental foundations of p-EDMR are described elsewhere.[16–18] It has to be emphasized that p-EDMR is not a conventional, microwave-chopped, and lock-in detected cw-EDMR; it is the transient detection of coherent, pulsed ESR-induced spin motion by means of current measurements. The motivation of the p-EDMR study presented here is to resolve the contradictive pictures about c-Si/$\mathrm{SiO_2}$ interface defects that arise from ESR and electronic measurements.

Experimentally, a native oxide was grown between interdigited lateral contact grids with the following procedure: First, a 300-nm-thick Al layer was deposited with electron-beam evaporation on top of a (111)-oriented surface of a slightly n-doped ($[P] \approx 4 \times 10^{13}\ \mathrm{cm^{-3}}$) Czochralski-Si wafer

---

[a] Electronic mail: boehme@hmi.de

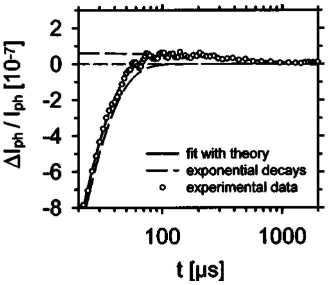

FIG. 1. The PC transient after a short coherent mw pulse ($\tau=64$ ns, $P=24$ W) under application of a B_0 field which was perpendicular to the (111) direction. The mw frequency was in paramagnetic resonance with the Landé-factor $g\approx 2.009$ that corresponds to the P_b center for the given magnetic-field orientation. The PC transient consists of negative and positive contributions which could be fitted with a biexponential decay function (solid line). The dashed lines represent the single exponential components of the fit function.

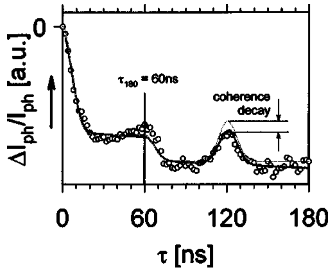

FIG. 2. PC response of the P_b center as a function of the pulse length τ during a recombination echo experiment. At $\tau=\tau_{180}$, a sudden 180° change of the mw radiation is introduced. The mw power is $P=64$ W. The black line is a fit of the data with a theoretical function predicted for strongly coupled spin pairs, as given in Ref. 16. The gray line represents the same transient function plotted with the fit parameters obtained from the black function but under negligence of the coherence decay.

that had been cleaned with a standard RCA procedure and then subjected to a 1% HF dip for 1 min right before the metal deposition. The Al layer was then structured with standard photolithography into the contact system. After the contacts were made, the bare Si surface between the contact grids was then exposed to dry air at room temperature for 24 h, causing the growth of a thin native oxide layer. Note that the room-temperature growth of the oxide has the advantage that (i) a contact system can be deposited first without causing Al contamination due to diffusion during the oxidation process and (ii) due to the slow interface relaxation of chemical bonds, high interface defect densities will occur yielding high intensities of the EDMR signals that are to be investigated. Note that we have chosen the (111)-oriented Si surface in order to ensure the greatest possible comparability of the experimental systems investigated to those used by Albohn *et al.*[11]

For the experiments presented here, a steady-state PC was induced by irradiation with infrared and ultraviolet-filtered white light of a halogen lamp. A constant voltage of $U=4$ V was applied. All experiments were carried out at $T=15$ K in order to keep spin-lattice relaxation slow. The pulsed ESR excitation was induced by an X-band (9.7 GHz) Bruker E580 spectrometer. The PC transients were recorded as a function of the magnetic field B_0, different angles between the orientations of the B_0 field, and the sample surface as well as different pulse lengths τ. All data displayed in the following are solely due to recombination at P_b centers recorded at $g\approx 2.009$, with a B_0 field applied perpendicularly to the (111) direction. The data has been corrected by underground currents due to microwave (mw)-induced conductivity, with a procedure outlined in Ref. 19. The identification of the signals discussed in the following with the P_b center was tested by means of angular dependence measurements between the B_0 field and the sample surface (not shown here) which exhibited the P_b anisotropy described in the literature.[14]

Figure 1 shows the PC response caused by a short and intensive mw pulse that ended at $t=0$. The transient exhibits positive and negative contributions that show an identical dependence on the B_0 field (line shape). It is therefore assumable that both the positive and the negative signals stem from P_b recombination. This double decay has been predicted theoretically for the response of spin-dependent recombination channels with non-negligible triplet recombination.[16,19] In accordance with the nomenclature of Ref. 16, we assign the decay constants of a double exponential fit with $r_2=6.9(2)\times 10^4$ s^{-1} and $r_T=1.9(1)\times 10^3$ s^{-1} corresponding to the fast and slow decay of the data shown in Fig. 1, respectively. Note that Ref. 16 also predicts the existence of a third, much faster decay constant r_3 which limits the coherence of electron-defect pairs (in the following referred to as e-P_b spin pairs).

In order to determine the coherence time of the e-P_b spin pairs, the dynamics of the P_b recombination has to be measured on a nanosecond time scale. The latter can be done with a recombination echo experiment which is the detection of a fast dephasing Rabi oscillation by means of pulse length dependence measurements of the PC changes. After the dephasing of the e-P_b spin pairs, a sudden 180° microwave phase change, introduced at a time τ_{180}, causes a short recombination rate spike at the time $(2\tau_{180})$ which is a spin rotary echo, reflected by the recombination rate. By measuring the decay of this rotary echo, the coherence time of the e-P_b spin pairs can be determined. Details about the theoretical and experimental foundations of this experiment are outlined in Refs. 18 and 16.

Figure 2 shows a recombination echo transient measured for $\tau_{180}=60$ ns. One can recognize a brief (≈ 30 ns) PC increase at $2\tau_{180}$. The experimental data displayed in Fig. 2 was fitted with the characteristic steplike-shaped echo function for strongly coupled electron defect spin pairs described in Ref. 16. This fit (black line) was carried out with three fit parameters; (1) A vertical scaling factor which is proportional to the arbitrary sample resistance; (2) The echo width that reflects the inverse of the width of the Rabi frequency distribution induced by the sample contacts which damp away all macroscopic oscillations, and (3) the echo decay constant r_3. The gray line is a calculation for a PC transient when incoherence is negligible. The difference in the two echo intensities is due to incoherence induced by recombination. Under the given experimental conditions we find $r_3=1.6(2)\times 10^6$ s^{-1}. This result was confirmed by additional echo decay measurements (not shown here) carried out with

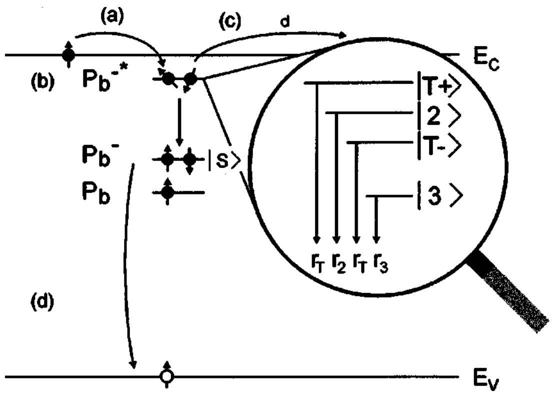

FIG. 3. Model of the microscopic P_b recombination mechanism. When an electron is captured into a charged P_b^- state, it is localized first in an energetically high P_b^{-*} state (a). From there, a spin-dependent readjustment transition may take place either into the ground state with probability r_i, as indicated in the inset (b), or a reemission of one electron into the conduction band with probability d (c). Recombination is concluded by hole capture into the P_b^- ground state (d).

larger phase change times τ_{180} that caused smaller echoes at rephasing times $2\tau_{180}$.

The experimental data are discussed in the following according to the model presented in Ref. 16. Both the slow relaxation of the PC after the pulsed ESR excitation as well as the echo effect recorded are in agreement with the theoretical predictions. Note that the functions used to fit the data are valid only for spin pairs that (i) are strongly coupled, which means the exchange coupling within an e-P_b pair exceeds the Larmor separation $\Delta\omega$ (this corresponds to the difference of the Landé factors), that (ii) have small Larmor separation,[20] and (iii) have non-negligible triplet recombination. Hence, due to the agreement between theory and experiment, we conclude that properties (i)–(iii) apply for e-P_b recombination. The theoretically predicted three decay constants r_T, r_2, and r_3 could be determined. The process behind r_T is recombination out of pure triplet states $|T+\rangle$ and $|T-\rangle$. The other two constants r_2 and r_3 can be associated with recombination from spin eigenstates with mixed symmetry: $|2\rangle$ and $|3\rangle$ correspond to $|T_0\rangle$ and $|S\rangle$ states with B_0-field-induced small singlet and triplet mixture, respectively. Figure 3 is a sketch of the P_b recombination model that we propose from these insights. This picture corresponds to the description of spin-dependent Shockley-Read recombination developed by Rong *et al.*:[21] Therein, the capture of delocalized electrons into deep level states takes place by a two-step process where electrons first localize in intermediate charged excited states P_b^{-*} before they undergo spin-dependent transitions into the charged ground-state P_b^-. The exact nature of the P_b^{-*} is not discussed further in the following; however, we note that with a procedure described elsewhere,[22] the dissociation probability d that the electron leaves the P_b^{-*} state without recombination can be estimated to be $d < 8 \times 10^2\ \mathrm{s}^{-1}$ at $T = 15$ K. Assuming a simple thermal escape model with an attempt frequency of $\nu_0 = 10^{12}\ \mathrm{s}^{-1}$, the P_b^{-*} is estimated to lie more than 30 meV below the c-Si conduction band.

For the recombination mechanism described above, the electron capture cross section σ correlates linearly to the fraction $\sigma \propto r_i/d$ of the readjustment probability and the dissociation probability d.[21] When the intermediate state can exist in four spin eigenstates $|i\rangle$ and the readjustment transition r_i is different for three different i (see Fig. 3), then in the presence of an external magnetic field, three different capture cross sections σ_i exist at one P_b defect. Note that this requires that triplet recombination is non-negligible, which is the case as shown above [see property (iii)]. The σ_i that applies when an electron passes the defect is random and only depends on the mutual spin orientation of both the electron and the defect, before the encounter. In the absence of magnetic fields, the eigenbase of the four spin eigenstates of the intermediate spin pairs tilts back to a pure singlet/triplet base and the three cross sections collapse into only two cross sections, $\sigma_S \propto r_S = r_3$ and $\sigma_T \propto r_T = r_2$.

The picture described above is able to reconcile the hyperfine studies made by Brower *et al.*[7] as well as by Stesmans and Vanheusden,[10] which did not indicate a significant number of oxygen-backbonded Si radicals and the findings of Albohn *et al.*[11] drawn from MCV. The observation of two different capture cross sections σ_{n1} and σ_{n2}, as reported by Albohn *et al.*, has a natural explanation in our model without the need of two microscopically different defects. Since the data presented by Albohn *et al.* were recorded in the absence of magnetic fields, the two different capture cross sections $\sigma_{n1} = \sigma_S$ and $\sigma_{n2} = \sigma_T$ exist at a single, nonoxygen-backbonded P_b center.

[1] J. T. Krick, P. M. Lenehan, and G. J. Dunn, Appl. Phys. Lett. **59**, 3437 (1991).
[2] Y. Nishi, Jpn. J. Appl. Phys. **10**, 52 (1971).
[3] Y. Nishi, T. Tanaka, and A. Ohwada, Jpn. J. Appl. Phys. **11**, 85 (1972).
[4] P. J. Caplan, E. H. Poindexter, B. E. Deal, and R. R. Razouk, J. Appl. Phys. **50**, 5847 (1979).
[5] E. H. Poindexter, Z. Phys. Chem., Neue Folge **151**, 165 (1987).
[6] J. H. Stathis, Appl. Phys. Lett. **68**, 1669 (1996).
[7] K. L. Brower, Appl. Phys. Lett. **43**, 1111 (1983).
[8] M. Cook and C. T. White, Phys. Rev. B **38**, 9674 (1988).
[9] P. M. Lenahan and J. F. Conley, J. Vac. Sci. Technol. B **16**, 2134 (1998).
[10] A. Stesmans and K. Vanheusden, Phys. Rev. B **44**, 11353 (1991).
[11] J. Albohn, W. Füssel, N. D. Sinh, K. Kliefoth, and W. Fuhs, J. Appl. Phys. **88**, 842 (2000).
[12] H. Flietner, Surf. Sci. **200**, 463 (1988).
[13] R. L. Vranch, B. Henderson, and M. Pepper, Appl. Phys. Lett. **52**, 1161 (1988).
[14] B. Henderson, M. Pepper, and R. L. Vranch, Semicond. Sci. Technol. **4**, 1045 (1989).
[15] D. Vuillaume, D. Deresmes, and D. Stivenard, Appl. Phys. Lett. **64**, 1690 (1994).
[16] C. Boehme and K. Lips, Phys. Rev. B **68**, 245105 (2003).
[17] C. Boehme and K. Lips, Appl. Phys. Lett. **79**, 4363 (2001).
[18] C. Boehme and K. Lips, Phys. Rev. Lett. **91**, 246603 (2003).
[19] Christoph Böhme, *Dynamics of Spin-Dependent Charge-Carrier Recombination* (Cuvillier, Göttingen, 2003).
[20] Small Larmor separation means $\hbar\Delta\omega/g\mu_B < B_1 < 0.1$ mT whereas $g \approx 2$, μ_B is Bohr's magneton, and B_1 is the microwave field strength.
[21] F. C. Rong, W. R. Buchwald, E. H. Poindexter, W. L. Warren, and D. J. Keeble, Solid-State Electron. **34**, 835 (1991).
[22] C. Boehme and K. Lips, Phys. Status Solidi C **1**, 1255 (2004).