Electron-paramagnetic-resonance study of the microscopic structure of the Si(001)- SiO₂ interface

J. Cantin, M. Schoisswohl, J. von Bardeleben, N. Hadj Zoubir, M. Vergnat

► To cite this version:

J. Cantin, M. Schoisswohl, J. von Bardeleben, N. Hadj Zoubir, M. Vergnat. Electron-paramagnetic-resonance study of the microscopic structure of the Si(001)- SiO₂ interface. *Physical Review B: Condensed Matter and Materials Physics* (1998-2015), 1995, 52 (16), pp.R11599-R11602. 10.1103/PhysRevB.52.R11599 . hal-02113426

HAL Id: hal-02113426

<https://hal.science/hal-02113426>

Submitted on 28 Apr 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Electron-paramagnetic-resonance study of the microscopic structure of the Si(001)-SiO₂ interface

J. L. Cantin,* M. Schoisswohl,* and H. J. von Bardeleben*

Groupe de Physique des Solides, Universités Paris 6&7, URA 17 au CNRS, 2 place Jussieu, 75251 Paris Cedex 05, France

N. Hadj Zoubir and M. Vergnat

Laboratoire de Métallurgie Physique et Sciences des Matériaux, Université de Nancy I, Boîte Postale 239, 54506 Vandoeuvre les Nancy, France

(Received 1 May 1995)

The defects of the Si(001)-SiO₂ interface have been studied by the electron-paramagnetic-resonance (EPR) technique taking advantage of the high specific surface area of porous silicon. This interface is characterized by the presence of two interface defects P_{b0} and P_{b1} . We report here a detailed study of the P_{b1} defect, which, in spite of being a dominant defect of this interface, had escaped any detailed EPR study up to now due to sensitivity limitations. The P_{b1} defect is characterized by spin $S = \frac{1}{2}$, a monoclinic I point symmetry and principal values of the g tensor $g_1 = 2.0058$, $g_2 = 2.0029$, $g_3 = 2.0069$. Unlike the P_b and P_{b0} defects, its linewidth of 4.5 G is isotropic and frequency independent, indicating an atomic configuration not influenced by stress distributions. The central ^{29}Si hyperfine interaction of the P_{b1} defect is at least a factor of 2 smaller than that of the P_b and P_{b0} defects, implying a delocalization of its electron wave function over more than one Si nucleus. The properties of the P_{b1} defect are compatible with a dangling-bond defect on a Si dimer as previously proposed by Edwards.

INTRODUCTION

The microscopic structure of the Si-SiO₂ interface is still a major research subject in semiconductor physics with implications both for the fundamental understanding of the interface formation during the oxidation process and for the improvement of metal-oxide semiconductor (MOS) devices. In spite of the use of many experimental techniques, the structure of the Si(001)-SiO₂ interface is still a matter of debate.^{1,2} Two types of experimental results are generally available: those concerning the global properties of the interface, such as those obtained by x-ray photoemission spectroscopy (XPS) measurements for the oxidation states on the Si interface atoms or those which concern its local properties as investigated via defect structures. As a consequence of the mismatch between the Si and the SiO₂ crystal structures, the Si-SiO₂ interfaces contain intrinsic point defects in the 10^{12} cm^{-2} concentration range.³ These defects have been called P_b centers, a generic name for different Si dangling-bond defects. Some of their properties such as their point symmetry, g -tensor, central, and superhyperfine interactions, can be used as local probes of the microscopic structure of the interface. Due to their electrical activity, their concentration is also a prime parameter in MOS devices.

The electron-paramagnetic-resonance (EPR) technique is particularly suited for the study of P_b centers and has been used in the past with high success for the Si(111)-SiO₂ interfaces.³⁻⁵ At (111) interfaces only one defect, the P_b center, is present; it has been convincingly modeled as a $[111]$ oriented $\cdot\text{Si}\equiv\text{Si}_3$ defect.^{6,7} The Si(001)-SiO₂ interface has equally been studied by the magnetic-resonance technique and two different intrinsic defects P_{b0} and P_{b1} have been evidenced. The P_{b0} center is equally a $[111]$ oriented Si dangling-bond center with properties very close to the P_b center at the (111) interface. However, due to experimental

difficulties no detailed study of the P_{b1} center had been possible up to now and, consequently, its microscopic structure is still unclear. We have recently shown that porous silicon is an excellent material for interface studies due to its high internal surface area.^{8,9} We report here the results obtained for the P_{b1} defect at thin native oxide interfaces on porous silicon.

EXPERIMENT

Porous Si layers of 1 μm thickness were prepared by stain etching of p -type (100 $\Omega \text{ cm}$) substrates. In the as-prepared state such layers have hydrogen-passivated surfaces with oxidized fractions smaller than 0.01, which give rise only to weak P_b center EPR spectra. To increase the spin concentration the samples were then vacuum annealed at $T \approx 650^\circ\text{C}$ for hydrogen desorption and reexposed to ambient conditions for the formation of a native-oxide layer. As confirmed by XPS measurements,¹⁰ this treatment leads to the formation of a $\approx 5\text{-}\text{\AA}$ thin oxide film, characterized by relative amounts of Si^{3+} , Si^{2+} , and Si^+ oxidation states 0.26:0.37:0.37, typical for (100) interfaces.¹¹ X-band EPR measurements were taken at this stage at temperatures between 4 and 300 K. The g factors were determined by a microwave-frequency measurement and a magnetic-field measurement with a proton nuclear magnetic resonance probe.

EXPERIMENTAL RESULTS

Figures 1 and 2 display typical EPR spectra obtained at room temperature for orientations of the magnetic field $B \parallel [001]$ and $B \parallel [111]$, respectively. They are composed of the trigonal P_{b0} center spectrum, characterized by g factors $g_{\parallel} = 2.0019$ and $g_{\perp} = 2.0089$ and a hyperfine interaction constant $A_{B \parallel [001]} = 108 \text{ G}$ and an additional spectrum of mono-

FIG. 1. (a) Experimental EPR spectrum for $B \parallel [001]$ at $T = 300$ K and its decomposition in two P_{b0} and three P_{b1} Lorentzian lines. (b) The resulting difference line between the spectrum and the fit.

clinic I symmetry, attributed to P_{b1} , which is the object of this study. The observation of the P_{b1} center in porous Si has been attempted previously, but the results are clearly inconsistent.¹² For a rotation of the magnetic field in the (110) plane the orientational degeneracy gives rise for an arbitrary orientation to three P_{b0} center lines and to seven lines for the P_{b1} defect. For the high-symmetry orientations $B \parallel [001]$, $[111]$, and $[110]$ the total EPR spectrum simplifies in (1+2), (2+3), and (2+4) P_{b0} and P_{b1} lines, respectively. As the concentration of the P_{b1} defect giving rise to the monoclinic EPR spectrum is four times higher than that of the P_{b0} defect in the samples studied in this work, a computer assisted decomposition for the total EPR spectrum is possible with high accuracy. Demonstrative examples of decompositions for the magnetic-field orientation $B \parallel [001]$ and $B \parallel [111]$ are given in Figs. 1 and 2, respectively. This decomposition with a fixed intensity ratio $[P_{b1}]/[P_{b0}] = 4$ and a statistical distribution of the four (111) and the six (001) equivalent interfaces can be coherently performed for the complete angular variation of the magnetic field in the (110) plane.

FIG. 2. (a) Experimental EPR spectrum for $B \parallel [111]$ at $T = 300$ K and its decomposition in two P_{b0} and three P_{b1} Lorentzian lines. (b) The resulting difference line between the spectrum and the fit.

FIG. 3. Angular variation of the P_{b1} center spectrum for a rotation of the magnetic field in the (110) plane, as measured in this work (solid lines) and as reported in Ref. 4 for only two (100) interfaces (dashed lines).

From the respective line positions (Fig. 3), we obtain the g -tensor elements and, by diagonalization, the principal values and orientations of the principal axes reported in Table I. The principal axes of the g tensor relative to the interface are the following: the g_1 component is oriented parallel to a $[0\bar{1}1]$ axis, the g_2 component parallel to a $[2\bar{1}\bar{1}]$ axis, and the g_3 component parallel to the $[111]$ axis. The agreement of our effective g values with those previously observed by Stesmans *et al.*⁴ for the $B \parallel [001]$ and $B \parallel [110]$ orientations, where the P_{b1} and P_{b0} lines are easy to separate, show that the P_{b1} center in our porous silicon samples has a negligible g -factor difference as compared to bulk samples. The difference in the g values for intermediate field orientations must be attributed to an insufficient fit of the P_{b0} defect⁴ due to a severe overlap of the P_{b0} and P_{b1} defect lines at K -band spectroscopy, further amplified by the lower $[P_{b1}]/[P_{b0}]$ concentration ratio experienced in the preceding studies.^{3,4}

The line shape of the P_{b1} center lines is Lorentzian with a peak-to-peak linewidth of (4.5 ± 0.2) G. In contrast to the case of the P_{b0} and P_b defects, where strain-induced g -factor distributions lead to an apparent orientation-dependent linewidth, the linewidth of the P_{b1} defect is not

TABLE I. Principal values and axes directions for the g tensor of the P_{b1} center. Also added, the effective g values for the two orientations $B \parallel [100]$ and $B \parallel [110]$. Due to the six equivalent (001) interfaces developed in our sample, we detect more lines as compared to bulk samples (Refs. 3 and 4).

	This work $\Delta g = \pm 0.0003$	Orientation	Ref. 4	Ref. 3
g_1	2.0058	$[0\bar{1}1]$	2.0058	2.0052
g_2	2.0029	$[2\bar{1}\bar{1}]$	2.0020	2.0012
g_3	2.0069	$[111]$	2.0084	2.0081
$g \parallel [001]$	2.0041 2.0058	$[001]$	2.0041	2.0035
$g \parallel [110]$	2.0055 2.0058 2.0064 2.0037	$[110]$	2.0063 2.0058	2.0058 2.0052

FIG. 4. Microscopic structure of the strained bond (SB1) defect as proposed by Edwards (Ref. 1). Full and empty circles represent silicon and oxygen atoms, respectively. The defect atom is bigger and gray.

angular dependent; in addition, it is also close to the one observed in the previous *K*-band EPR study for the particular orientation $B||[001]$. This indicates a negligible *g*-factor distribution for the P_{b1} defect and thus a relaxed, strain-independent defect configuration.

Following a proposition of Poindexter *et al.*³ for the microscopic structure of the P_{b1} defect as a neutral dangling-bond defect in a $\cdot\text{Si}\equiv\text{Si}_2\text{O}$ complex, Edwards¹ has calculated the electronic structure and hyperfine interaction of this defect configuration as well as of two further strained bond defects. The predicted level structure and correlation energy of the $\cdot\text{Si}\equiv\text{Si}_2\text{O}$ defect was found to be incompatible with the properties of the P_{b1} defect and this model was consequently rejected; on the other hand, a model of a dangling bond located on a silicon dimer (Fig. 4), called SB1 (strained bond), had the experimentally found electrical level positions; but as its predicted central hyperfine structure was a factor of 2 smaller than the one observed by Brower,¹³ this model was not considered as a valid candidate for P_b either.

We have equally investigated the central hyperfine structure of the P_{b1} defect. At low temperatures ($T \approx 20$ K) a sufficient signal-to-noise ratio of $\approx 100:1$ for the observation of the ^{29}Si hyperfine interaction is easily obtained; the experimental situation is further simplified by the fact that the P_{b1} defect can be observed at microwave powers of ≈ 0.3 mW without saturation, whereas the P_{b0} defect is already partially saturated under this condition. Under these conditions we observe one hyperfine doublet of splitting of 108 G, which can be clearly attributed to the ^{29}Si hyperfine spectrum of the P_{b0} defect (Fig. 5). We do not observe any resolved hyperfine spectrum associated with the P_{b1} center. Only one attempt to observe the ^{29}Si central hyperfine interaction of the Si(001)-SiO₂ interface has been reported previously.¹³ In that work a resolved hyperfine spectrum characterized by a splitting of 160 G for the orientation of the magnetic field $B||[001]$ had been detected and attributed to the P_{b1} center. However, in spite of the propitious conditions of our case, no ^{29}Si hyperfine spectrum of comparable

FIG. 5. Low-temperature ($T=20$ K) EPR spectrum for $B||[001]$ showing only resolved P_{b0} ^{29}Si central hyperfine structure.

or higher splitting is observed for the P_{b1} defect in disagreement with the previous study.¹³ Our results (Fig. 5) put, on the contrary, an upper limit on the hyperfine splitting of the P_{b1} center of 40 G for $B||[001]$. The actual observation of the P_{b1} hyperfine spectrum with a splitting of less than 40 G is rendered difficult by the overlapping central lines. According to our results the central hyperfine splitting of the P_{b1} defect is reduced by at least 50% as compared to that of the P_{b0} center, in agreement with the predictions of Edwards¹ for the SB1 model.

Our results on the P_{b1} center are in agreement with the SB1 model, which is essentially a silicon dangling-bond defect on a Si-Si dimer configuration. This interface reconstruction is one of the two currently considered configurations—dimer and oxygen bridging models²—which allow us to simulate the Si^+ and Si^{2+} oxidation state distributions, characteristic of (100) interfaces. The *g* factors of the P_{b1} center, which are typically for single dangling-bond centers according to the classification by Sieverts,¹⁴ give further evidence for the Si dimer model. Additional calculations of *g*-tensor and hyperfine interactions are necessary to quantitatively confirm this model.

In conclusion, we have presented a detailed EPR study of the P_{b1} center at the Si(001)-SiO₂ interface, the results of which are in agreement with a Si dangling bond on a Si dimer configuration. It opens the way for future correlated XPS-EPR studies relating the P_{b1} and P_{b0} centers with the silicon oxidation states.

ACKNOWLEDGMENTS

We acknowledge useful discussions with A. Stesmans and are grateful to F. Rochet for XPS measurements performed on the EPR samples.

*Fax: (33-1) 43.54.28.78.

¹A. H. Edwards, in *Physics and Chemistry of SiO₂ and the Si/SiO₂ Interface*, edited by C. R. Helms and B. E. Deal (Plenum, New York, 1988).

²A. Pasquarello, M. S. Hybertsen, and R. Car, *Phys. Rev. Lett.* **74**, 1024 (1995).

³E. H. Poindexter, P. J. Caplan, B. E. Deal, and R. Razouk, *J. Appl. Phys.* **52**, 879 (1981).

⁴A. Stesmans, J. Braet, J. Witters, and R. F. Dekeersmaecker, *Surf. Sci.* **141**, 255 (1984).

⁵K. L. Brower, *Semicond. Sci. Technol.* **4**, 970 (1989).

⁶M. Cook and C. T. White, *Phys. Rev. Lett.* **59**, 1741 (1987).

- ⁷A. Edwards, Phys. Rev. B **36**, 9638 (1987).
- ⁸H. J. von Bardeleben, D. Stievenard, A. Grosman, C. Ortega, and J. Siejka, Phys. Rev. B **47**, 10 899 (1993).
- ⁹H. J. von Bardeleben, C. Ortega, A. Grosman, V. Morazzani, and D. Stievenard, J. Lumin. **57**, 301 (1993).
- ¹⁰F. Rochet, G. Dufour, J. L. Cantin, M. Schoisswohl, and H. J. von Bardeleben (unpublished).
- ¹¹F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J. A. Yarmoff, and G. Hollinger, Phys. Rev. B **38**, 6084 (1988).
- ¹²Y. Xiao, T. J. McMahon, J. I. Pankove, and Y. S. Tsuo, J. Appl. Phys. **76**, 1759 (1994).
- ¹³K. L. Brower, Z. Phys. Chem. Neue Folge **151**, 177 (1987).
- ¹⁴E. G. Sieverts, Phys. Status Solidi B **120**, 11 (1983).