

LOW-TEMPERATURE ESR STUDY OF P_{b0} DEFECTS RESIDING IN THE (111) Si/NATIVE OXIDE INTERFACE

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A K-band electron spin resonance (ESR) study of the (111) Si/native SiO_2 structure has been carried out in the temperature range $2.4 \leq T \leq 30$ K. The ESR signal of the interfacial [111] P_{b0} center was observed, exhibiting in general similar properties to the well-documented [111] P_{b0} signal observed on firmly thermally-oxidized (TO) Si. However, many details in the P_{b0} spectrum differ like, e.g., the strain-induced inhomogeneous (g -spread) part (ΔB_{pp}^G) of the linewidth. For $\mathbf{B} \parallel [111]$ (\mathbf{B} being the externally applied magnetic field), the ^{29}Si hyperfine structure of the [111] P_{b0} center has been observed which is characterized by the hyperfine splitting $a^{\text{hf}} = 159 \pm 2$ G and the hf signal width $\Delta B_{pp}^{\text{hf}} = 14.8 \pm 0.5$ G. Both the observed ΔB_{pp}^G and $\Delta B_{pp}^{\text{hf}}$ reveal the existence of a significantly larger strain-induced g distribution in Si/native SiO_2 . Apart from the [111] P_{b0} center, also the signals of the P_{b0} defects with their dangling orbital parallel to $[1\bar{1}\bar{1}]$, $[1\bar{1}1]$ or $[\bar{1}11]$ have been observed; as yet, these signals have not been observed on TO structures. The saturation behaviour has been examined showing the P_{b0} Si/native oxide interface center to be much less saturable than the P_{b0} in TO structures. The observations are related to the particular physico-chemical interface structure.

1. Introduction

For many years already, the Si/ SiO_2 interface has been known to contain defects which may act both as recombination and trapping centers, thus significantly influencing the properties of Si-based semiconductor devices. In view of the profound technological interest, this has caused the basic Si/ SiO_2 structure to be subjected to numerous investigations by a wealth of methods [1], among which the electron spin resonance (ESR) technique has been particularly successful.

Till now, two ESR-active interface defects have been observed, labelled as P_{b0} and P_{b1} centers respectively, and commonly referred to as P_{b0} centers, a symbol introduced by Nishi [2], who was the first to observe this anisotropic defect. The final identification, however, was done by Caplan and coworkers [3], leading to the atomic models, namely $\text{'Si} \equiv \text{Si}_3$ and $\text{'Si} \equiv \text{Si}_2\text{O}$ for the P_{b0} and

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P_{b1} defects respectively. The conclusive proof for the P_{b0} model, that is, an unpaired electron in a dangling Si hybrid orbital on an interfacial Si atom pyramidally backbonded to three Si atoms in the bulk was considered to be given by the observation [4] of the ^{29}Si (nuclear spin $I = 1/2$; 4.7% natural abundance) hyperfine structure (hfs) on P_{b0} . The model proposed for P_{b1} still remains somewhat less convincing. However, regarding the P_{b0} model, the formerly accepted conclusive proofs are at present interpreted somewhat more reserved [5]. Instead of the *undercoordinated* Si model, i.e., ' $\text{Si} \equiv \text{Si}_3$ ', an *overcoordinated* defect, referred to as a floating bond, has been proposed. This suggestion has caused renewed interest in the correct atomic modelling of the P_{b0} signal.

As it stands today, most of the ESR work on P_{b0} has been carried out on state-of-the-art high-quality thermally-oxidized (TO) c-Si (i.e., oxidized at $\sim 1000^\circ\text{C}$ in 1 atm O_2 ambient), whereby the [111] Si/SiO₂ interface has been most extensively analysed, mainly for practical spectroscopical reasons [6]; the sensitivity [7] of the defects to various types of irradiation and electrical bias has been well analysed. However, one might expect to gain some relevant additional information by expanding the measurements to differently-oxidized Si-SiO₂ structures and do some comparative analysis. The present work has to be put in the light of this goal: It reports on the study of the P_{b0} defect located in the (111) Si/native interface. Related to this, it is interesting to note that recently a first observation of P_{b0} in a somewhat different structure, namely, the crystalline Si/buried SiO₂/crystalline SiO₂ (SIMOX) structure, has been reported [8].

2. Experimental details

2.1. Sample preparation

The samples studied were taken from p-type (B-doped) Czochralski-grown 3 inch diameter Si plates ($10 \pm 2 \Omega \text{ cm}$). These (111)-main-face oriented wafers were two-sided polished to optical finish using the cupric-ion chem-mechanical polishing method, resulting for the two wafers treated in thicknesses of $d_{\text{Si}} = 140 \pm 20$ and $89 \pm 9 \mu\text{m}$ respectively. Via scribing and breaking, ESR samples having either a $1 \times 9 \text{ mm}^2$ or a $2 \times 9 \text{ mm}^2$ (111) face were obtained. A schematic presentation of the sample shape relative to the crystallographic orientation is given in fig. 1. In order to eliminate interference from a cracking-induced dangling-bond (DB) line, the slices were first treated in planar etch at room temperature (RT) for 20 s. Subsequently, they were submitted to a chemical cleaning procedure after which they were allowed to grow a native oxide in air at RT for several days. In stacking several slices together to form an ESR sample, identical crystallographic positioning of the platelets regarding the [112] direction pointing "left" or "right" in the bundle, was taken care off.

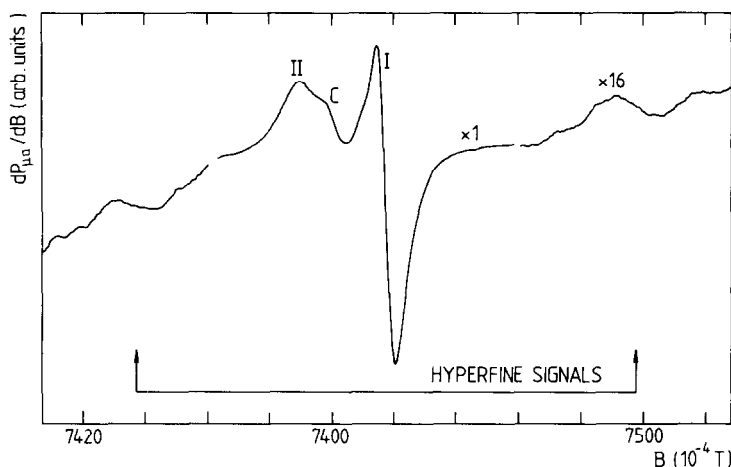


Fig. 2. K-band (20.775 GHz) ESR P_{b0} spectrum observed from a (111) Si/native SiO_2 sample at 4.7 K for $B \parallel [111]$. The sample thickness is $89 \pm 9 \mu\text{m}$ and microwave power in the cavity = -13 dBm. Signal I together with the hf signals correspond to the $[111]$ P_{b0} center, while signal II is the sum of the $[\bar{1}\bar{1}1]$, $[1\bar{1}\bar{1}]$ and $[1\bar{1}\bar{1}]$ P_{b0} centers; for $B \parallel [111]$, all three 19° centers coincide.

the $[111]$ P_{b0} defect, i.e., with the $\text{'Si}\equiv\text{Si}_3$ unsaturated bond perpendicular to the sample surface. This may be inferred from the generally similar ESR properties observed for $[111]$ P_{b0} centers in TO structures.

For $B \parallel [111]$, the linewidth has its minimum value given as $\Delta B_{pp} = 3.6 \pm 0.1$ G (equally for both samples), which increases to 9.0 ± 0.6 G for $|\phi_B| \rightarrow 90^\circ$. Concomitantly, the line shape, which is a mixture of Lorentzian and Gaussian shapes (Voigt profile) at $\phi_B = 0^\circ$, changes to an almost Gaussian profile for $|\phi_B| \rightarrow 90^\circ$. X-band (8.99 GHz) measurements at 4.7 K gave $\Delta B_{pp}(X) = 2.31 \pm 0.05$ G for $B \parallel [111]$; this reveals the presence of a significant inhomogeneous line broadening part, thus accounting for the observed Voigt profile.

The g value of the $140 \mu\text{m}$ slices varies from $g_{\parallel} = 2.00186 \pm 0.00004$ to $g_{\perp} = 2.0087 \pm 0.0001$ for B parallel with and perpendicular to $[111]$ respectively; the g tensor is found to be axially-symmetric and T -independent. The observed $g(\phi_B)$ behaviour is perfectly in agreement with the "theoretical" g versus ϕ_B limb calculated for the position $DB \parallel [111]$ from an axially-symmetric g tensor using $g_{\parallel} = 2.00186$ and $g_{\perp} = 2.0088$. However, it has to be remarked that while about equal g_{\perp} values have been found at 4.3 K for both sample types, a somewhat different g_{\parallel} value, i.e., $g_{\parallel} = 2.00144 \pm 0.00004$, is observed for the thinner sample; the latter value is more in agreement with the data of TO samples [3]. This difference in g_{\parallel} between both sample types could not be ascribed to misorientations in sample mounting; apparently, the results show that slight variations in g may occur between various Si/native oxide samples.

Apart from the well-known [111] P_{b0} defect, the signals due to the other possible out-of-(111) plane pointing DB orientations, i.e., $[\bar{1}11]$, $[1\bar{1}1]$ and $[11\bar{1}]$ P_{b0} centers ($\approx 19^\circ$ P_{b0} centers, cf. fig. 1), have been observed too. In fig. 2, it is signal II which is due to these centers; because of the symmetry (namely, $\mathbf{B} \parallel [111]$; cf. fig. 1), all three signals are identical and coincide; for other ϕ_B values, however, the signal splits up. The inferred values of g and ΔB_{pp} and the variations of g , ΔB_{pp} and line shape with ϕ_B (ϕ_B now being the angle between \mathbf{B} and the symmetry axis of the particular center concerned) are very similar to the [111] P_{b0} behaviour, from where the observation of the 19° P_{b0} centers has been concluded.

For the [111] P_{b0} center a spin concentration $N_S = (1.2-1.3) \times 10^{12}$ ($\pm 30\%$) has been found, which value comes out rather low compared with the typical TO value, i.e., $N_S(\text{TO}) \approx 5 \times 10^{12} \text{ cm}^{-2}$.

The observed K-band line shape of the [111] P_{b0} centers for $\mathbf{B} \parallel$ could be computer fitted with a Voigt profile characterized by the ratio $a_c \equiv (3/2)^{1/2} \Delta B_{pp}^L / \Delta B_{pp}^G = 0.86 \pm 0.05$ and $L = 1.7 \pm 0.1$; ΔB_{pp}^L and ΔB_{pp}^G represent the widths of the "natural" constituent spin-packet line and the Gaussian broadening function arising from a strain-induced [9,10] g distribution (i.e., "glass effect"; predominantly a distribution on g_\perp) respectively. The ΔB_{pp} data obtained at both frequencies (f) for $\phi_B = 0^\circ$ could be self-consistently computer deconvoluted, resulting in $\Delta B_{pp}^G = 1.10$ and 2.56 G at X and K band respectively, together with the ϕ_B and f independent value $\Delta B_{pp}^L = 1.8$ G.

As described above, the observed properties of the [111] P_{b0} Si/native SiO_2 signal are in general agreement with the similar defect prevailing in TO (111) Si/ SiO_2 structures [3,9,10]. However, there are several differences, two of which are considered of special importance, as they clearly pertain to the particular physico-chemical interfacial structure. Firstly, there is a significantly larger ΔB_{pp}^G value for [111] P_{b0} Si/native SiO_2 centers, which reveals a substantially increased g distribution compared to TO samples and which indicates an enhanced strain-induced degree of local distortions of the P_{b0} structure. Secondly, the 19° P_{b0} centers have been clearly observed on Si/native oxide interfaces which so far has not been the case for TO structures; however, they have previously also been observed [11] on thermally-treated (TT) samples (i.e., oxidized at $T \approx 1000^\circ\text{C}$ in reduced O_2 pressure; $p_{\text{O}_2} \lesssim 10^{-5}$ Torr).

3.2. Saturation behaviour; measurement of T_1

The saturation of the [111] P_{b0} defect has been analysed for various T 's by measuring the variation of V_D with B_1 , the latter varying in the range $0.007 \leq B_1 \leq 0.16$ G, where $2B_1$ represents the amplitude of the linearly-polarized hf field at the sample site. From this data, values of the spin-lattice relaxation time T_1 have been deduced using the saturation theory [12] for

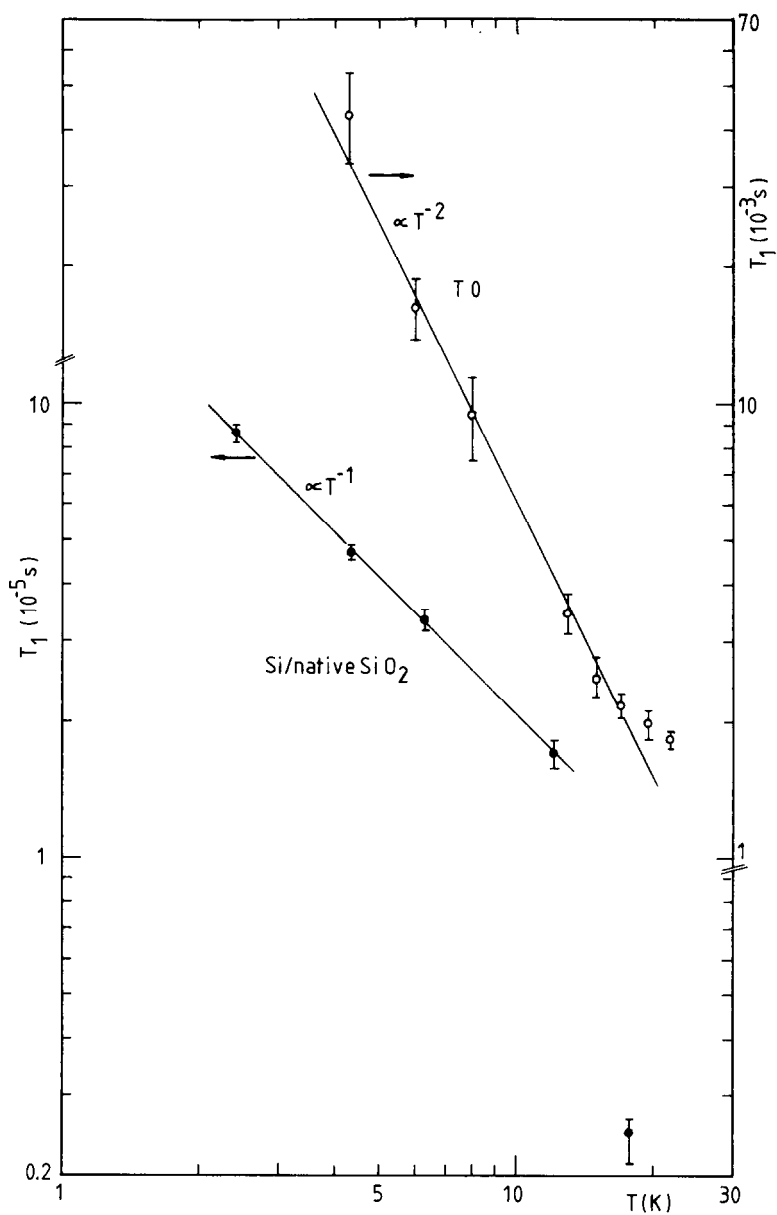


Fig. 3. Plot of measured spin-lattice relaxation time versus T of the $[111] P_{b0}$ center. Solid and open symbols represent the situation of $[111] P_{b0}$ residing at the interfaces of (111) Si/native SiO_2 and thermally-oxidized (111) Si/ SiO_2 structures respectively.

inhomogeneously-broadened lines and using the T -independent transverse relaxation time T_2 derived from the previously determined ΔB_{pp}^L , giving $T_2 = 2/\sqrt{3} \gamma \Delta B_{pp}^L = 3.6 \times 10^{-8}$ s. The T_1 results thus obtained are shown in fig. 3. As may be seen, for $T \leq 12$ K, a $T_1 \propto T^{-1}$ relation is found, T_1 decreasing much faster for higher T 's. For reasons of comparison, previously obtained T_1 data [13] on TO samples is also included in fig. 3.

Clearly, there are two remarkable differences between the two interface types. Firstly, the [111] P_{b0} center appears much less saturable (about a factor of 1000 at 4.2 K) when prevailing at the Si/native SiO_2 interface than when placed in a TO structure. Secondly, a significantly different T dependence for both interface types emerges, indicating two different spin-relaxation mechanisms to be operative. Likely, the behaviour of the [111] P_{b0} defect located at the Si/native SiO_2 interface is to be explained by the interaction of the [111] P_{b0} unpaired electron spin with an at the interface accumulated conduction electron (CE) layer, i.e., a kind of Korringa relaxation. The CE layer may arise as a result of the action of positive fixed oxide charge N_{ox} residing close to the Si/ SiO_2 interface in a nonstoichiometric thin " SiO_2 layer" and which does not exchange charge with the Si; the presence of the latter N_{ox} is generally agreed upon [14]. The N_{ox} is known to be strongly dependent on the oxidation process (anneal temperature) and to be relatively more expressed in Si/native oxide structures, which may explain the difference in spin-lattice relaxation between the two interface types. In view of the "short" T_1 values observed for the [111] P_{b0} Si/native SiO_2 center, another possible explanation, i.e., the direct-phonon relaxation mechanism [15], is held improbable.

3.3. ^{29}Si hyperfine interaction

An interesting detail in the P_{b0} spectrum is the ^{29}Si hyperfine structure, which observation supplies valuable information on the character and extension of the wavefunction. As shown in fig. 2, these signals could be observed at K band, in spite of their low amplitude (each signal is expected to contain only 2.35% of the main signal's intensity). The observed hyperfine splitting, i.e., $a^{hf} = 159 \pm 2$ G, is in good agreement with previous observations on TO samples [4], and also with observations on thermally treated [11] samples. However, the hf linewidth observed for $\mathbf{B} \parallel [111]$, namely $\Delta B_{pp}^{hf} = 14.8 \pm 0.5$ G is significantly broader than the TO one [4] (~ 8 –9 G). As the hyperfine interaction is known to be highly sensitive to fluctuations in local environments, this result bears out the presence of a broader variation of distortions on the local configuration of P_{b0} in the Si/native oxide structure compared to the TO situation. This affirms the previous conclusion drawn from the observed broader ΔB_{pp}^G for the Si/native SiO_2 structure. The ratio in spectra intensities of the hf signals to the Zeeman resonance is found to be 0.03, in fair agreement with expectations.

4. Conclusive remarks

As clearly shown, the P_{b0} signal exhibits well-resolved differences in its ESR spectrum between the various "types" of Si/SiO₂ interfaces studied. This, in fact, is as expected since the ESR features are extremely sensitive to local structural alterations; it is known that the Si/SiO₂ interfacial regions do not come out identical over the various preparations techniques and one can hardly imagine a probe more sensitive to the particular interface morphology than the P_{b0} center.

Various differences in the ESR spectra of the P_{b0} center when residing in either TO or Si/native SiO₂ structures are noticed like, e.g., spectra composition, line shape and width, g tensor and T dependence. However, regarding the comparison of different oxidation methods, two main items are striking. The first one concerns the markedly differing spin-relaxation behaviour of the unpaired P_{b0} electron for the two interface types compared. Secondly, the Si/native SiO₂ interface contains a higher degree of strain-induced local disorder. This clearly relates to the differing physico-chemical structure of the particular interfaces compared; the chemical composition of the interface has previously been found to be Si₂O and SiO for the Si/native SiO₂ and TO interfaces respectively [16].

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