Observation of the localized Si dangling-bond P_b defect at the Si/Si$_3$N$_4$ interface

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(Received 25 July 1988)

Low-temperature electron-spin resonance (ESR) reveals the presence of the P_b defect (identified with $\cdot$Si$\equiv$Si$_3$) at the thermally grown (111)Si/Si$_3$N$_4$ interface. This constitutes the first observation of this defect (called P_{bN}) at a natural Si/solid interface other than the Si/SiO$_2$ one. It is argued that ESR analysis of the P_{bN} center is a powerful tool for characterizing the Si/Si$_3$N$_4$ interface on an atomic scale. This observation again confirms P_b as a prototype dangling-bond center, its main properties being determined by the backside Si matrix.

The full characterization of defects prevailing at interfaces, particularly Si/SiO$_2$, remains of high interest both for practical and fundamental reasons. As regards the (100)Si/SiO$_2$ interface, so far two types of defects[1] have been reported, labeled as P_{b0} and P_{b1}. On (111)Si/SiO$_2$ only the P_{b0} equivalent is observed[2]—referred to[3] as P_b. The latter defect has been most intensively studied,[2,4–7] and mainly by the electron-spin resonance (ESR) technique it has convincingly been modeled on an atomic scale as $\cdot$Si$\equiv$Si$_3$ (the dot represents an unpaired electron), i.e., a dangling sp^3 bond (DB) located on an interfacial Si atom which is backbonded to three Si atoms in the bulk, the center thus having C_{3v} symmetry. A schematic of this model is shown in Fig. 1. The most convincing evidence for the $\cdot$Si$\equiv$Si$_3$ model came from observation of the ^{29}Si hyperfine (hf) structure in the P_b spectrum.[8] The direct influence this center has on the transport properties has been demonstrated by the observation of a spin-dependent recombination current[9] and of optically detected magnetic resonance.[10] As observed on the (111)Si/SiO$_2$ structure, P_b is characterized[1,5,7,11] by an axially symmetric g tensor with $g_\parallel = 2.0013 \pm 0.0001$ and $g_\perp = 2.0086 \pm 0.0003$, and peak-to-peak X-band ESR linewidth $\Delta B_{PP}(X) = 2$–3 G.

FIG. 1. Schematic view of the atomic configuration at the (111)Si/SiO$_2$ interface together with applied sample geometry. Entity a represents a P_b defect.

Much information has already been assembled about the fundamental properties of these centers. Yet, some important items remain unclear, such as the way these centers get rid of excess energy after resonant excitation (spin-lattice relaxation processes), which seems to vary among differently oxidized Si/SiO$_2$ structures.[11] Further, there is the build up of the low-temperature (T) line shape (linewidth), particularly regarding the origin of the non-g-distribution-induced (natural) linewidth[7] and the observed line narrowing[11] with increasing T in the range 4.2–18 K. Additionally, the previously well-accepted P_b model, $\cdot$Si$\equiv$Si$_3$, has recently been questioned in general.[12,13] A new model has been advanced for the dominant defect found in amorphous Si (a-Si), i.e., the D center of $g \approx 2.0055$. Previously, this defect was universally identified with a threefold *under*coordinated DB defect, namely, $\cdot$Si$\equiv$Si$_3$—the equivalent of the P_b defect, but now placed in the *bulk* of a-Si. Instead, an *over*coordinated defect (fivefold coordinated Si) is now proposed (labeled as a floating-bond defect) which, *a fortiori*, would affect the P_b model too. Hence, the revived interest for the DB modeling.[13–15] However, the latter idea seems to be largely abandoned for P_b by now, while it appears to gain support for the a-Si case.[13,14]

While one could hope to assemble further fundamental information from more measurements on P_b in state-of-the-art high-quality thermally oxidized Si/SiO$_2$ structures, more success is likely to be achieved by studying the center in somewhat different circumstances. For instance, one could compare the defect appearance among differently oxidized structures,[11] samples treated with isotopic substitution,[16] and buried oxide layers.[17] Of particular interest would be the observation of P_b at *natural* Si/solid interfaces[18] other than Si/SiO$_2$, in the view of the unequal Si-solid interactions—the solid having a lattice parameter and/or crystal structure different from SiO$_2$. The present work deals with such observation. It reports the first observation of the P_b center at the thermally-grown (111)Si/Si$_3$N$_4$ interface.[18] It will be shown that the P_b center shows up as remarkably similar to the one in (111)Si/SiO$_2$, thus identifying it as a P_b defect. Yet, in some significant details it bears out the differences between both interfaces, thus further highlighting this center as an excellent interface probe.

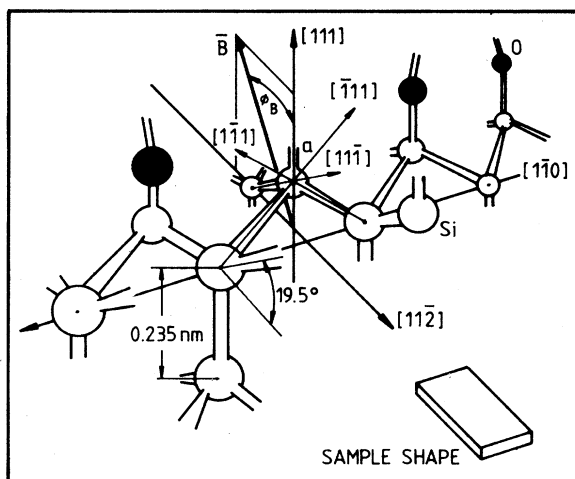Samples were prepared from Czochralski-grown p-type

(B-doped) (111)Si wafers (10 Ω cm) of 3-in diam which were polished on two sides to optical finish. ESR-sized slices of 1×9-mm^2 main face and thickness d_{Si} $=153\pm19$ μm were obtained by scribing and breaking; their 9-mm edge was along [11$\bar{2}$] (see Fig. 1). The slices were thermally treated in a double-walled quartz tube placed in an conventional oven which has exclusively been used for high-purity Si processing. Typical preanneal cleanings have been described elsewhere.[19] The slices were thermally nitrided at $T_N=1120\pm20$°C for times $t_N=123$-206 min in a flow of high-purity ($>99.999\%$) NH$_3$ (flow rate ≈40 sccm) at a pressure $p_{NH_3}=1.3$ atm. A typical treatment resulted in a Si$_3$N$_4$ layer of thickness ≈25 Å in agreement with former results.[20] The nitridation was preceded by a treatment at the same T in a flow of 99.9999% pure H$_2$ (sent through a liquid-N$_2$ trap) at $p_{H_2}\approx1.2$ atm to eliminate efficiently the native Si oxide film. The nitridation, generally, was followed by a treatment in a flow of 99.9999% pure N$_2$ at $T=T_N$ for a time $t_p=17$-98 min after which the sample cooled down slowly to room temperature in about 15 min.

ESR observations were carried out in the range $4.2<T<40$ K at both X (8.99 GHz) and K (20.95 GHz) bands using homodyne reflection spectrometers driven in the absorption mode. Sinusoidal modulation of the externally applied magnetic induction **B** at ~150 kHz resulted in the detection of absorption-derivative (dP$_\mu$/dB) spectra. In view of the easy saturability[7] of the P_b signal, particularly at low T, care was taken to record traces at nonsaturating microwave power (P_μ) levels; at $T=4.3$ K, P_μ never exceeded -16 dBm in the K-band TE$_{011}$ cavity of loaded $Q\approx3000$.

The Si/Si$_3$N$_4$ composition has been analyzed by Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). Detailed XPS data (Al $K\alpha$ excitation; energy $h\nu=1486$ eV) were obtained within a window opened in the region of the Si $2p$ peak for different exit angles θ_i between the photoelectrons and the (111) plane. Only two clearly resolved symmetric (Voigt profiles) peaks are observed; a first one, at $E_{b1}=98.6$ eV, represents the $2p$ binding energy[21] of Si atoms in the bulk Si substrate and is observed since the XPS probing depth exceeds the thin (≈25 Å) top Si$_3$N$_4$ layer. The second peak, at $E_{b2}=E_{b1}+3.15\pm0.1$ eV is characteristic[22] for Si bound in stoichiometric Si$_3$N$_4$; no other Si compounds are observed. With decreasing θ_i one notices the relative decrease of the bulk Si peak as a result of decreasing effective probing depth without any noticeable shift in the "Si$_3$N$_4$" peak. This shows that the Si substrate is covered with a homogeneous thin stoichiometric Si$_3$N$_4$ layer. The measurements at various θ_i also indicated the presence of a thin O- and C-rich surface layer, in agreement with AES results. Such contamination occurs at the Si$_3$N$_4$ surface if exposed to air.[20] No impurities were found at the Si/Si$_3$N$_4$ interface above the 1 at.% level.

Figure 2 shows characteristic ESR spectra observed at 4.3 K of a sample nitrided for 123 min. Signal I in these spectra is the one ascribed to P_b centers at the (111)Si/Si$_3$N$_4$ interface, based on the various striking similarities with the (111)Si/SiO$_2$ P_b defect. The center exhibits axial symmetry, i.e., g stays constant for **B** varying in the
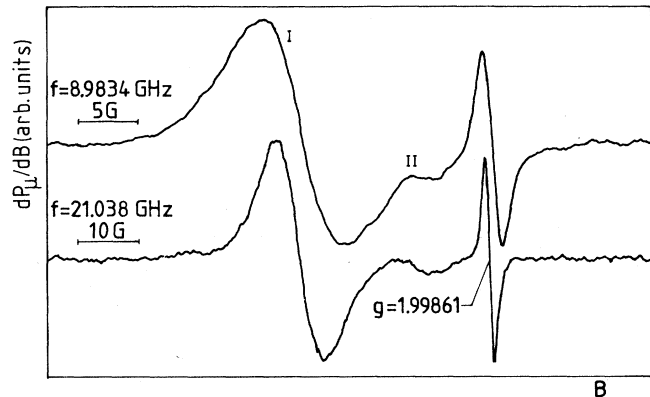

FIG. 2. Representative ESR spectra for **B**∥ [11$\bar{2}$] observed at 4.3 K ($P_\mu=-16$ dBm) on (111)Si/Si$_3$N$_4$ grown by thermal nitridation in NH$_3$ for 123 min at 1000 ± 20°C followed by an anneal in N$_2$ for 24 min. The signal with $g=1.99861$ is due to a Si:P reference sample. Signals I and II are ascribed to interfacial P_b defects (i.e., ˙Si≡Si$_3$) and bulk Si$_3$N$_4$ dangling Si bonds, respectively.

(111) plane given as $g_\perp=2.0086\pm0.0001$. However, for **B** varying in the (1$\bar{1}$0) plane it exhibits strong anisotropy as appears from the $g(\phi_B)$ map shown in Fig. 3(a), ϕ_B being the angle between **B** and [111] (see Fig. 1). The data is nicely computer-fitted with

$$g=[g_\parallel^2\cos^2\phi_B+g_\perp^2\sin^2\phi_B]^{1/2}, \qquad (1)$$

resulting in $g_\parallel=2.00150\pm0.00004$ and $g_\perp=2.00859\pm0.0001$ as extremal $\tilde{g}$ dyadic values. These results refer to C_{3v} symmetry and are remarkably close to the (111)Si/SiO$_2$ P_b data.

Chemical etchback sequences in diluted HF (5 vol%) located the signal-I centers near the Si/Si$_3$N$_4$ interface. The removal of the Si$_3$N$_4$ layer entirely eliminated the sig-
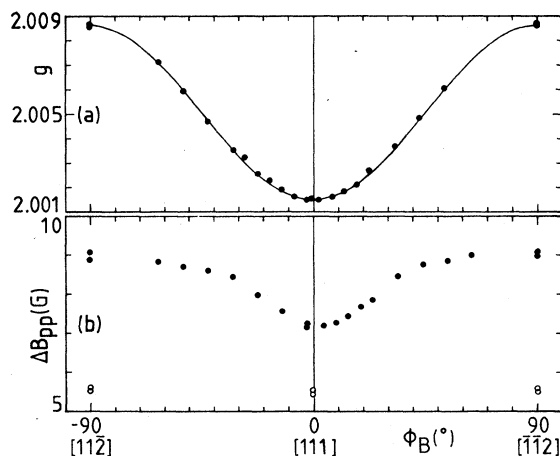

FIG. 3. (a) g values and (b) linewidths observed at 4.3 K of the P_{bN} center located at the (111)Si/Si$_3$N$_4$ interface for various directions of **B** in the (1$\bar{1}$0) plane (cf. Fig. 1). The sample has been thermally nitrided in 99.999% pure NH$_3$ at 1120 ± 20°C for 206 min. Open and solid symbols represent X- and K-band data, respectively.

nal showing it not to originate from the Si substrate. Thus, like the $(111)\text{Si/SiO}_2$ P_b defect this signal also concerns an interfacial center keeping strong correlation to the monocrystalline-Si substrate.

The linewidth is anisotropic too as pictured in Fig. 3(b). From Fig. 2 it is clear that ΔB_{PP} also depends on the microwave frequency f. This shows that like the $(111)\text{Si/SiO}_2$ P_b center, the signal comprises a substantial inhomogeneous broadening due to a g distribution induced by interfacial strain which is mainly reflected[7,11] in $g_\perp$. Hence, the increase in ΔB_{PP} for increasing ϕ_B and the generally Voigt profile (i.e., a Lorentzian convoluted with a Gaussian) line shape. At sufficiently low $f (\lesssim x$ band) and $B\|[111]$, the line shape is almost Lorentzian, i.e., $\Delta B_{PP}^G \ll \Delta B_{PP}^L$, and becomes almost perfectly Gaussian as $\phi_B \rightarrow 90°$ at K-band f, i.e., $\Delta B_{PP}^G \gg \Delta B_{PP}^L$, as expected for such inhomogeneous broadening; ΔB_{PP}^G and ΔB_{PP}^L represent the width of the g distribution function (assumed to be Gaussian) and the natural Lorentzian line shape, respectively.

These ESR results clearly reveal the common origin of signal I and the $(111)\text{Si/SiO}_2$ P_b signal. Hence, the $\cdot\text{Si}\equiv\text{Si}_3$ defect is shown to be a main defect at the $\text{Si/Si}_3\text{N}_4$ interface too, built in to relieve stress; at the $(111)\text{Si/Si}_3\text{N}_4$ interface we will refer to it as the P_{bN} center. However, while the primary ESR signatures come out identical, secondary—though significant—details should differ. Indeed, one cannot expect the natural interfaces that Si forms with two different solids (Si compounds) to be identical in all respects. For instance, the Si_3N_4 structure, missing the Si-O-Si bond angle flexibility, is known to be much more rigid[23] than the SiO_2 structure which somehow should show in the P_b (P_{bN}) characteristics. The study of these differences should allow a thorough (ESR) characterization of the $\text{Si/Si}_3\text{N}_4$ interface and simultaneously add to our fundamental insight into the P_b defect. That this center is almost identical at both interfaces just shows that its properties are primarily set by the Si substrate.

Many differences show up; a first one concerns the linewidth which, while showing a similar anisotropy, is generally much broader[7,11] for P_{bN}. This is a characteristic for all six samples studied so far. In light of the strain-induced g distribution broadening, this would suggest a more strained (disorderly) $\text{Si/Si}_3\text{N}_4$ interface as compared to the Si/SiO_2 one, as expected for the rigid Si_3N_4 structure. Perhaps this also refers to a distinctly rougher and/or broader interface region. Similar to the $(111)\text{Si/SiO}_2$ P_b Zeeman resonance, the P_{bN} signal is also sensitive to saturation, but not as much so. It is situated somewhere between the behavior[24] of P_b in Si/native oxide and state-of-the-art thermal Si/SiO_2, closer to the latter. Likely, this means that its spin-lattice relaxation time T_1 is shorter than that of P_b situated at good-quality Si/SiO_2, indicating that another or more effective relaxation mechanism is operative. Further, it has been observed that in all samples, albeit not to an equal extent, the linewidth narrows for T increasing from 4.3 to ≈ 30 K; e.g., for the sample of Fig. 3 ΔB_{PP} narrows from 7.14 ± 0.25 at 4.3 K to 4.8 ± 0.25 G at 34 K for $B\|[111]$. Such an effect has been observed on some $(111)\text{Si/SiO}_2$

interfaces too,[11] though much weaker. Additionally, for particular ϕ_B values the line shape shows distinct asymmetries, previously for $(111)\text{Si/SiO}_2$ P_b ascribed to particular DB orientation deviations from those ideally prescribed by the (111) substrate.[11] A full analysis of these details will likely lead to a fundamental disentangling of the line-shape (width) buildup of the $\cdot\text{Si}\equiv\text{Si}_3$ defect, i.e., the relaxation and broadening mechanisms operative.

Surface densities of P_{bN} centers (N_s) have been determined using double-numerical integration (estimated accuracy $\approx 20\%$) relative to a calibrated $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ standard via a Si:P marker. N_s varies in the range $(7-32) \times 10^{12}$ cm^{-2}. These values are somewhat larger than the $(111)\text{Si/SiO}_2$ case[11,16] (i.e., a few times 10^{12}) as expected. This variation of N_s over various samples within, apparently, an identical preparation method and set up may be understood. It starts from the important observation that in whatever thermally nitrided sample no ESR is observed if omitting the post-nitridation treatment in N_2; the signals only appear after such treatment. This is as expected since hydrogen, of which plenty is available during nitridation, is known to be an effective passivator of P_b (DB) defects. It is only after the post-nitridation anneal in N_2—*dehydrogenation*—that the signal(s) shows up, to an extent somewhat dependent on t_p. Hence, likely, much of the passivation-generation kinetics of defects in $\text{Si/Si}_3\text{N}_4$ will be related to H, as is true for the Si/SiO_2 structure.[25]

Apart from P_{bN} a second signal (designated as signal II in Fig. 3) of $g = 2.0028 \pm 0.00014$ and $N_s \approx 7 \times 10^{10}$ cm^{-2} for $B\|[111]$ is generally observed. It is inhomogeneously broadened, scaling linearly with f; $\Delta B_{PP} = 2.4 \pm 0.3$ and 6.3 ± 0.8 G at X and K band, respectively. Like the P_{bN} signal it only shows up after dehydrogenation and totally disappears after etching off the Si_3N_4 layer. It originates from defects—ascribed to dangling Si bonds[26]— distributed throughout the Si_3N_4 layer and is considered to be the characteristic signature of (dehydrogenated) a-Si_3N_4.

In summary, the ESR observation at the $(111)\text{Si/Si}_3\text{N}_4$ interface of a defect (P_{bN}) configurationally identical to the well-documented interfacial $(111)\text{Si/SiO}_2$ P_b center is reported. While the basic identifying properties are the same, finer details unveil various differences between the two interfaces concerned, as expected. Like the P_b defect[11] P_{bN} is an excellent probe of the $\text{Si/Si}_3\text{N}_4$ interface, suggesting its possible use for that aim. Analysis of its properties, compared to the Si/SiO_2 P_b ones will add substantially to our fundamental understanding of the $P_b (P_{bN})$ defect.

Regarding the recent controversy about the atomic modeling of Si DB defects, of which the P_b center is considered to be a subclass, the present observation of P_{bN} adds—if still needed[27]—to the belief that P_b is a prototype DB defect with the unpaired orbital highly localized on one atom—*not* a floating bond. This has been the conviction ever since the ^{29}Si hf structure observation, which has recently firmly been restated from the floating-bond–DB controversy.[13] In the interfacial floating-bond Si/SiO_2 P_b picture, an O atom is suggested likely to be an essential part[12] of the four-atom structure. Should a N

atom be involved similarly for Si/Si$_3$N$_4$, one could hardly expect the two defects, i.e., P_b and P_{bN}, to be identical to first order. Instead, it demonstrates that the main configuration of these centers is set by the Si matrix underneath, pointing out their DB nature.

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