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New intrinsic defect in as-grown thermal SiO_2 on (111)Si

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K-band electron-spin resonance (ESR) has revealed an isotropic signal of $g=2.00246\pm0.00003$ in as-prepared SiO_2 thermally grown on (111)Si in dry O_2 at 700–850 °C. The spectrum comprises a symmetric central signal of peak-to-peak width $\Delta B_{pp}=1.0$ G amid a ^{29}Si hyperfine doublet of splitting $a_{hf}=16.1$ G. The salient ESR features point to an intrinsic defect in SiO_2 characterized by an unpaired spin occupying an effectively nearly pure *s* state, which is not primarily localized at a Si site while exchanging a ^{29}Si superhyperfine interaction with three equivalent neighboring Si sites.

The intrinsic defects so far observed by electron-spin resonance (ESR) in *as-grown* thermal Si/SiO_2 are interface defects,[1,2] generally referred to as P_b centers,[3] which are considered as the natural result of lattice mismatch. But, of course, other spin-active centers do appear upon damaging of the Si/SiO_2 entity in some sense, e.g., as a result of postoxidation irradiation by energetic photons or particles.[2,4] A typical example is the widely studied E' center[5] in SiO_2 (generically referred to as the $O_3\equiv Si^{\cdot}$ defect), which has been demonstrated to account for the dominant deep hole trap in SiO_2.

The present work reports on the observation of a "new" intrinsic defect in as-grown (111)Si/SiO_2. The generation of this center, at least in its ESR-active state, has been noticed during a detailed investigation of the P_b properties as a function of oxidation conditions; it is observed after thermal oxidation of (111)Si at a temperature $T_{ox}=700$–850 °C, and appears to reside in the a-SiO_2 layer. There is high interest, from both applied and fundamental viewpoints, in the identification of any such defect in the a-SiO_2 layer. This is strongly driven by the vital impact the quality of SiO_2 has on Si-based devices. Indeed, defects in SiO_2 are potential charge traps. And if present in a substantial amount (e.g., $\approx 10^{12}$ cm^{-2}), such a charged layer will have a pronounced impact on the operation of, for example, the metal-oxide-semiconductor (MOS) device through its band bending effect on the crucial conducting Si channel. Worse even is that the trapping nature of such defects may alter during device operation, e.g., as a result of thermal cycling or environment radiation, which will result in early device failure. Defects in the Si/SiO_2 structure are a main issue in radiation hardness of Si-based devices.

Slices measuring $2\times9\times0.12$ mm^3 were fabricated from a commercially available Czochralski-grown (111)Si wafer (*p* type, ≈ 10 Ω cm) polished to optical quality at both sides. Each slice was oriented such that its 9-mm edge was a $[11\bar{2}]$ direction. They were generally submitted to three types of thermal treatments alternated with ESR observations: (1) Oxidation in dry O_2 (99.999% pure) at a pressure of 20–110 kPa at $T_{ox}=700$–850 °C for times in the range 120–200 min; (2) degassing ("dehydrogenation") at 750–800 °C in vacuum (pressure $<3\times10^{-5}$ Pa) for times in the range 60–160 min; (3) hydrogenation in 99.9999% pure H_2 at 110 kPa for about 20 min at 360 °C.

The pre-thermal-treatment "cleaning" of the samples implied two steps: After an initial "training" oxidation along the lines described above, the samples had their oxide layer removed (etch rate ≈ 0.5 nm/s) in a 4% HF aqueous solution. This etching was kept short (typically 20–30 s), that is, not any longer than needed for turning the sample surfaces hydrophobic. This indicated that pristine Si surfaces were created that are protectively covered essentially by monohydride.[6] Then the various thermal steps were initiated, starting with oxidation.

ESR spectra were recorded with a *K*-band (≈ 20.1 GHz) reflection spectrometer in the absorption mode in the temperature range $T=4.3$–30 K. First-derivative spectra $dP_{\mu a}/dB$ were obtained using sinusoidal modulation of the applied magnetic induction **B** at about 110 kHz. The modulation amplitude B_m was constrained to the range where the peak-to-peak signal amplitude $2A_{pp}\propto B_m$. The microwave power P_μ incident on the TE_{011} cavity, of loaded $Q\approx 10000$, was varied in the range 0.5–100 nW to monitor eventual saturation effects.

Figure 1 shows a typical *K*-band signal of the newly observed defect, denoted for convenience as *EX* center. It

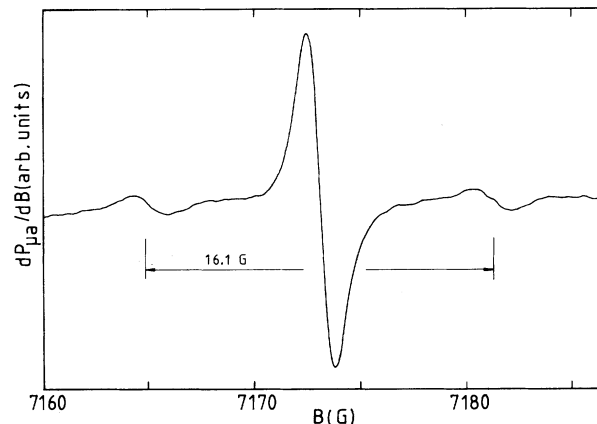

FIG. 1. First derivative ESR spectrum (20.105 GHz) of the observed defect measured at 4.3 K using $P_\mu=-50$ dBm on (111)Si/SiO_2 for $\mathbf{B}\perp[111]$. The structure was grown at 800 °C for 105 min in 110-kPa O_2 and subsequently vacuum treated for 70 min.

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has been measured at 4.3 K for $\mathbf{B}\perp[111]$ direction[7] [$\mathbf{B}$ parallel with the (111)Si/SiO_2 interface] on a Si/SiO_2 structure thermally oxidized at 800±10 °C for 105 min in a 110-kPa O_2 ambient, which was subsequently treated in vacuum for 70 min. The spectrum is characterized by a narrow, symmetric central line of peak-to-peak width $\Delta B_{pp}=1.0\pm0.05$ G and $g=2.00246\pm0.00003$, which is found to be *isotropic*. It has a Voigt line shape of line-shape factor $\kappa\equiv I_c/(A_{pp}(\Delta B_{pp}))^2=1.8\pm0.1$, where I_c represents the signal intensity (area under absorption curve). The remarkable isotropy of its g tensor is also reflected in the absence of any "glass-powder" effect[8] in its line shape. No T dependence has been observed.

Also observed is a symmetric hyperfine (hf) doublet of splitting $a_\parallel=a_\perp\equiv a_{hf}=16.1\pm0.1$ G, the width of each hf line being ≈1.2 G, i.e., comparable to the central signal width. As is well known in ESR spectrometry, a key quantity for identification of observed hf structure is the intensity ratio $R\equiv I_{hf}/I_c$ of the hf spectrum to the central signal, for which the average value 0.142 ± 0.022 is found. The same ratio in terms of spectral heights is 0.09 ± 0.01 indicating that the hf signals are indeed slightly broadened ($\approx23\%$) compared to the central signal. No other hf signals could be traced.

Sequential etch back experiments in diluted HF acid on a sample which had grown on a (11.4±1.2)-nm-thick oxide showed that the signal disappeared entirely after etching off ≈6 nm of the oxide layer.

As mentioned, the signal is only observed when oxidizing in the range 700–850 °C, as shown in Fig. 2. This figure illustrates the areal spin density N_s after exhaustive (for ≈60 min) postoxidation vacuum treatment versus oxidation temperature, showing that a maximum value of $N_s=(1.20\pm0.05)\times10^{12}$ cm^{-2} is found for $T_{ox}\approx800$ °C. No signal could be observed for T_{ox} outside this temperature window, where T_{ox} has been varied from 25 up to 1200 K. The overall weak signal intensity together with the fact that the signal-generating T_{ox} window is out of the favored range (≈900–950 °C) for applied Si processing probably explain why the EX signal has so far escaped detection.

An important factor in the signal's observability is the postoxidation vacuum treatment (dehydrogenation). Although the signal is well observed on (111)Si/SiO_2 structures as-oxidized within the appropriate T_{ox} window, the ESR intensity is profoundly enhanced by such an anneal. It was noticed, for example, that the EX signal in a sample oxidized at 775 °C for 124 min grew to its maximum value of 4 times stronger after vacuum annealing at 775 °C for 65 min. Subsequent treatment in 110-kPa H_2 at 361 °C for 21 min, however, totally wiped out the signal. A remarkable observation, then, is that this hydrogenation-degassing procedure is fully *reproducible*; that is, after complete quenching as a result of hydrogenation, the signal fully reappears after appropriate dehydrogenation. This indicates that the originating defect's thermochemical properties are dominated by interaction with hydrogen; it is interesting to note that in this respect, EX behaves much like P_b.[9]

The saturability of the central signal has been compared to that of the copresent P_b signal and an E' signal. The latter has been obtained by crushing a small piece of HSQ200-type fused quartz[10] ([OH] < 30 ppm, [other impurities] ≤ 20 ppm). This powder was inserted into the cavity next to the (111)Si/SiO_2 structure described in Fig. 1, with the results shown in Fig. 3. The normalized continuous-wave saturation curves in this figure, where B_1 is the microwave field amplitude at the sample site, were measured at 4.3 K for $\mathbf{B}\perp[111]$. Here, it is clear that, while exhibiting a saturability intermediate between that of E' and P_b, the relaxation behavior of the EX defect as incorporated in its saturation characteristics matches neither that of E' nor P_b. This indicates that EX does not belong to either type of defect.

The crucial question then remains as to the nature of

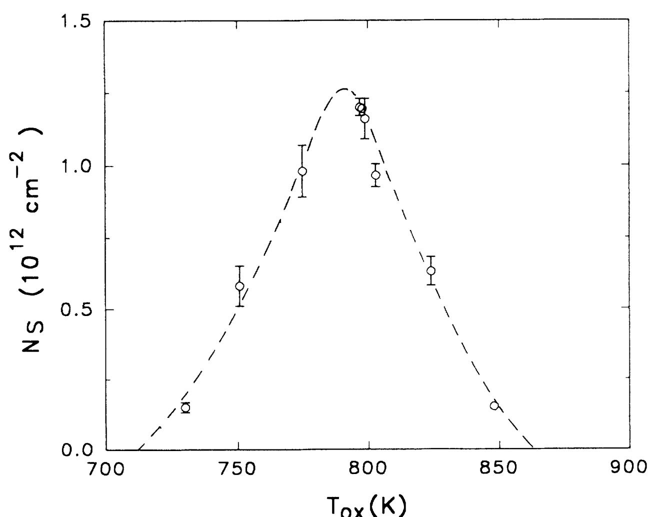

FIG. 2. Dependence of the maximum areal spin density of the EX center on T_{ox} for (111)Si/SiO_2 structures grown in 110-kPa O_2 for ≈130 min. The maximum spin density at each T_{ox} is observed after postoxidation exhaustive dehydrogenation in vacuum for ≈1 h. The dashed curve is a guide to the eye.

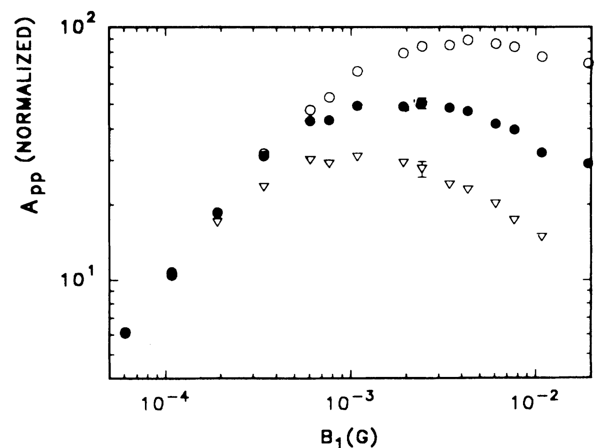

FIG. 3. Continuous-wave saturation curves measured at 4.3 K for E' (▽), EX (●), and P_b (○). The data were normalized in the nonsaturation regime. The EX and P_b signals were observed on the structure described in Fig. 1, while the E' signal stems from crushed fused quartz.

the EX defect. A first, very informative step in this direction is tracing the center's location. It is clear that, dealing with a Si/SiO_2 structure, there are three main possibilities: the Si substrate, the SiO_2 layer, or at the Si/SiO_2 interface. The first possibility, i.e., EX centers in bulk Si, has to be discarded for various reasons. A main one comes from the etch back experiment with the result that the EX signal is entirely obliterated upon removing half of the oxide layer. More convincing evidence follows from the defect's markedly isotropic g value and symmetric line shape. Second, there is the possibility of location at the Si/SiO_2 interface. One could feel tempted to rule out this possibility right away also on the basis of the etch back results. But this demands somewhat more caution as etching off only half of the SiO_2 cover does not necessarily imply that eventual defects in the remaining half remain unaffected. Indeed, when referring to the H_2-dominated thermochemical properties of the EX center, these defects, if residing at the Si/SiO_2 interface, for example might well be reached by hydrogen liberated at the etch front in diluted HF, even during the limited etching times applied: The diffusion lengths after 10 s of H^0 and H_2 in a-SiO_2 at 300 K are ≈ 20000 and 250 nm, respectively.[11] Much, of course, will depend on the reaction energies involved in the EX passivation kinetics.

While the etching results might thus not be decisive, the reason then why we disfavor the possibility that the EX defects reside right at the Si/SiO_2 interface plane (location in *near* interfacial SiO_2 layers, of course, remains possible) is based on the signal's isotropy and symmetry: Such salient ESR features are hard to envisage for a defect bordering c-Si, at least not within the conventional conception of unpaired orbitals at the Si/SiO_2 interface. Thus we draw the conclusion that EX centers reside in the top a-SiO_2 layer.

The question then is raised whether the observed defect is intrinsic to a-SiO_2, or, instead, impurity related. The impurity origin, however, cannot be retained: This follows from the fact that of all known common impurity isotopes with nuclear spin $I=\frac{1}{2}$ in Si (SiO_2) and taking into account their natural abundance, there is not one that would fit the observed R ratio. This is further corroborated by the fact that there is no known impurity-related defect in SiO_2 for which the ESR features would match the EX properties.[8]

We are thus led to an intrinsic defect in a-SiO_2. But, again, also within the class of intrinsic defects, in whatever form of SiO_2, the author is unaware of an account of an EX-like signal. The one, perhaps, that comes closest is the E'_δ defect,[12] a variant of E', introduced in synthetic silica (plasma oxidation of $SiCl_4$) of low OH content (≤ 10 ppm) and ~ 3000 ppm Cl impurities after 100-keV x-ray irradiation. It is characterized by a narrow line of $\Delta B_{pp} \approx 0.6$ G, principal g tensor values $g_1 = 2.0018$ and $g_2 = g_3 = 2.0021$, and a ^{29}Si HF doublet of $a_{hf} \approx 100$ G. But this cannot be the EX center.

Actually, the observed g_{EX} value, i.e., $g_{EX} > g_0$ ($\equiv 2.002319$, the free-electron g value) *vis-à-vis* the known E' variants mean values $g_{E'} < g_0$, together with the saturation data presented in Fig. 3, is counter to an E'-type origin of EX, at least not in the sense of the conventional $O_3{\equiv}Si^{\cdot}$ model. The value $g_{EX} > g_0$ would point to a hole center. The fully isotropic g tensor of the EX defect refers to a highly s-like state, or perhaps better to an unpaired defect orbital of which the p contribution is spatially averaged out over various lattice sites, e.g., in the sense as suggested for the E'_δ center.[12] Alternatively, the EX unpaired spin could reside in an sp^3-type unpaired hybrid that is fully relaxed over various, e.g., four, tetrahedral bonds as a result of the dynamic Jahn-Teller effect,[13] even at 4.3 K.

We now turn to the EX defect's salient ESR features for possible hints for its identification. As usual in ESR studies of defects, such information almost exclusively results from in-depth analysis of observed hf structure.[8]

The hf doublet in the EX spectrum, EX being an intrinsic defect in SiO_2, must stem from ^{29}Si nuclei of 4.7% natural abundance and nuclear spin $I=\frac{1}{2}$ (^{17}O, of only 0.037% natural abundance and $I=\frac{5}{2}$, is excluded). Then there are two important hf parameters, i.e., R and a_{hf}. The R value may provide specific information regarding the number of equivalent Si sites the unpaired electron interacts with to give rise to the observed hf signals. It is easily derived that the theoretical R ratios are 0.0493, 0.0986, 0.147, and 0.197 for interaction with one, two, three, or four equivalent Si sites, respectively. The experimental value of 0.142 ± 0.022 would thus refer to three equivalent sites.

The measured a_{hf} ($=16.1$ G) in relation with the latter result provides information on the unpaired orbital's localization. Since a pure $3s$ Si orbital would give rise to a hf splitting[14] of ≈ 1220 G, we conclude that the unpaired orbital is not primarily localized on the three equivalent Si sites, that is, these three sites are not the defect's central core sites, but second- or higher-order nearest neighbors; analysis indicates that only $\sim 1\%$ of the supposed $3s$-like orbital is localized on each of the three equivalent Si sites.

We thus arrive at the following preliminary model of the EX center: It implies an effective highly s-like (hole) state not localized into first order on a Si site and which has a superhyperfine interaction with three equivalent neighboring Si sites. A further tentative suggestion is that the unpaired orbital consists of an average over various sp^3 hybrids.

In summary, the low-temperature ESR observation of a new intrinsic defect, likely residing in the top half of thermal SiO_2, grown at 700–850 °C, has been reported. While a conclusive identification of the defect's atomic structure is still lacking, much is expected from the reported ESR properties in combination with proper theoretical analysis of holelike defects in a-SiO_2. Needless to say, it is important to understand any occurring charge traps, especially intrinsic ones, for the fundamental understanding of a-SiO_2 and the related basic Si/SiO_2 structure.

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[1]See, e.g., E. H. Poindexter and P. J. Caplan, Prog. Surf. Sci. **14**, 211 (1983).

[2]B. Henderson [Appl. Phys. Lett. **44**, 228 (1984)] has measured a low number of E' defects on an apparently undamaged (111)Si/SiO_2 structure using the sensitive spin-dependent recombination technique. The signal, however, was observed under strong optical excitation.

[3]Y. Nishi, Jpn. J. Appl. Phys. **10**, 52 (1971).

[4]C. L. Marquardt and G. H. Siegel, Jr., IEEE Trans. Nucl. Sci. **NS-22**, 2234 (1975); K. L. Brower, P. M. Lenahan, and P. V. Dressendorfer, Appl. Phys. Lett. **41**, 251 (1982).

[5]R. A. Weeks, J. Appl. Phys. **27**, 1376 (1956).

[6]M. Grundner, D. Graf, P. O. Hahn, and A. Schnegg, Solid State Technol. **34**, 69 (1991).

[7]The coobservation of the [111]P_b signal ($g_{\parallel} \approx 2.0013$, $g_{\perp} \approx 2.0087$), which will generally badly interfere with the EX signal ($g_{\parallel} = g_{\perp} = 2.00246$), is almost unavoidable whenever studying in an as-prepared (111)Si/SiO_2 interface. Thus the $\mathbf{B}_{\perp}$[111] measurement configuration is preferred as the field distance between both resonances is then maximum.

[8]For a recent review on spin centra in silica, see, e.g., D. L. Griscom, Glass Sci. Technol. **4B**, 151 (1990).

[9]K. L. Brower, Appl. Phys. Lett. **53**, 508 (1988); A. Stesmans and G. Van Gorp, Phys. Rev. B **42**, 3765 (1990).

[10]Trade name of Heraeus, Inc.

[11]See, e.g., D. L. Griscom, J. Appl. Phys. **58**, 2524 (1985).

[12]D. L. Griscom and E. J. Friebele, Phys. Rev. B **34**, 7524 (1986).

[13]F. S. Ham, Phys. Rev. **138**, A1727 (1965).

[14]P. W. Atkins and M. C. R. Symons, *The Structure of Inorganic Radicals* (Elsevier, Amsterdam, 1967).