RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 40, NUMBER 6 15 AUGUST 1989-II

Self-trapped holes in amorphous silicon dioxide

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(Received 27 March 1989)

Electron-spin-resonance spectra tentatively attributed to self-trapped holes (STH's) in amorphous silicon dioxide are reported and analyzed. Two types of STH's were found in a numerical ratio ~1:1 in all silica samples investigated (including high-OH flame hydrolytic, low-OH O_2-plasma fused, sol-gel, and less pure isotopically enriched materials) following either 100-keV x-ray irradiation or 6.4-eV excimer-laser illumination at 77 K: STH_1, stable below ~180 K, is suggested to comprise a hole trapped on a "normal" bridging oxygen in the glass network. STH_2, stable below ~140 K, is provisionally ascribed to a hole trapped on *two* normal oxygens, in analogy with the V_K center in alkali halides.

While radiation damage processes in ionic crystals are now relatively well understood, the degree to which this knowledge can be transferred to partially covalent materials such as SiO_2 has remained in doubt. Only recently has strong evidence been given that the principal ionizing radiation damage mechanism in amorphous silica (a-SiO_2) is radiolytic.[1,2] That is, permanent atomic displacements are created primarily in the course of nonradiative decay of self-trapped excitons (STE's), rather than by elastic collisions of the bombarding particles (or Compton electrons) with lattice nuclei. In general, the mechanism(s) of exciton localization may be hole-lattice, electron-lattice, or exciton-lattice coupling.[3] In the alkali halides it is well known from electron-spin-resonance (ESR) experimentation that holes self-trap, forming V_K centers (halogen molecular ions X_2^-). Recombination of a conduction electron with a V_K center has been shown[4] by ESR to result in the formation of a stable Frenkel pair consisting of a halogen vacancy (F center) and a halogen interstitial (H center). The structure of the STE in alkali halides has been determined to comprise an F-H pair on adjacent sites.[5,6] But despite the availability of excellent optically detected magnetic resonance data,[7] the structure of the STE in SiO_2 has remained a matter of conjecture for lack of critical ground-state ESR characterizations of V_K- and/or H-type species.

Very recently, Hayes and Jenkin[8] have elucidated a defect center in germanium-doped α quartz which consists of a hole trapped on an oxygen bridging between a lattice silicon and a substitutional germanium impurity. With the absence of the impurity Ge, such a defect would be considered a self-trapped hole (STH). Hayes and Jenkin's negative results for *undoped* quartz indicate that for temperatures above ~4 K the hopping rate for holes is too fast to permit ESR observation.[8] This is not surprising, given the pairwise equivalence of oxygens in α quartz. By contrast, in *amorphous* SiO_2 any two oxygens are likely inequivalent due to the randomness in the vitreous state, presumably leading to greatly reduced hole-hopping rates and easier ESR observation. Many "oxygen-associated hole centers" (OHC's) have indeed been detected by ESR in irradiated a-SiO_2, but previous attention has focused on two *room-temperature stable* species, the nonbridging-oxygen hole centers (NBOHC's, $\equiv Si-O\cdot$) (Refs. 9 and 10), and a class of peroxy radicals (PR's, $\equiv Si-O-O\cdot$).[10,11] Here I describe the deconvolution of a universally observed, but heretofore unanalyzed, ESR spectrum recorded only after irradiation below ~200 K. I tentatively attribute the major components of this spectrum to STH's.

Samples included 4-mm-diam rods of high-purity Suprasil 1 (flame hydrolysis, 1200 ppm wt% OH) and Suprasil W1 (O_2 plasma, < 5 ppm OH), as well as sol-gel silicas and small beads of flame-fused SiO_2 isotopically enriched in ^{28}Si and ^{29}Si. ESR spectra were recorded at temperatures ≤ 110 K following 77-K irradiation by 100-keV x rays or 6.4-eV (ArF) excimer-laser light. Spectral components herein attributed to STH's were clearly discernable in *all* samples despite varying degrees of overlap with the spectra of NBOHC's and/or PR's. Minimum interference by NBOHC's was encountered in the spectrum of x-ray-irradiated Suprasil W1 [fully drawn curve in Fig. 1(a)]. However, Suprasil W1 was always found to display one or more radiation-induced components ascribable to PR's [e.g., peaks P_1, P_2, and P_3 in Fig. 1(a)], presumably due to the well-known high content of dissolved O_2 molecules in this material (e.g., Ref. 12). The use of low microwave power (0.4 mW) and field modulation (0.05 mT), not common in earlier studies, was crucial to resolving the spectral features of the putative STH's from those of the PR's. Another fundamental defect, the well-known E' center ($\equiv Si\cdot$), was observed in all samples under x-ray irradiation but was not detectable in any sample subjected at 77 K to 6.4-eV photon fluences sufficient to produce an equally intense STH spectrum [see dotted curve in Fig. 1(a)].

Figure 2 illustrates the isochronal annealing behaviors of certain designated peaks in Fig. 1(a). The features ascribed to PR's (peaks P_i) are clearly more stable thermally than are peaks A, B, and C, which will be attributed to STH's. Peaks A and B appeared in approximately the same initial amplitude ratio in all silica samples studied, regardless of dose or whether x-ray or uv irradiated, strongly suggesting that the defect(s) responsible are both interrelated and fundamental to a-SiO_2. Nevertheless, there is no obvious way that peaks A and B can be com-

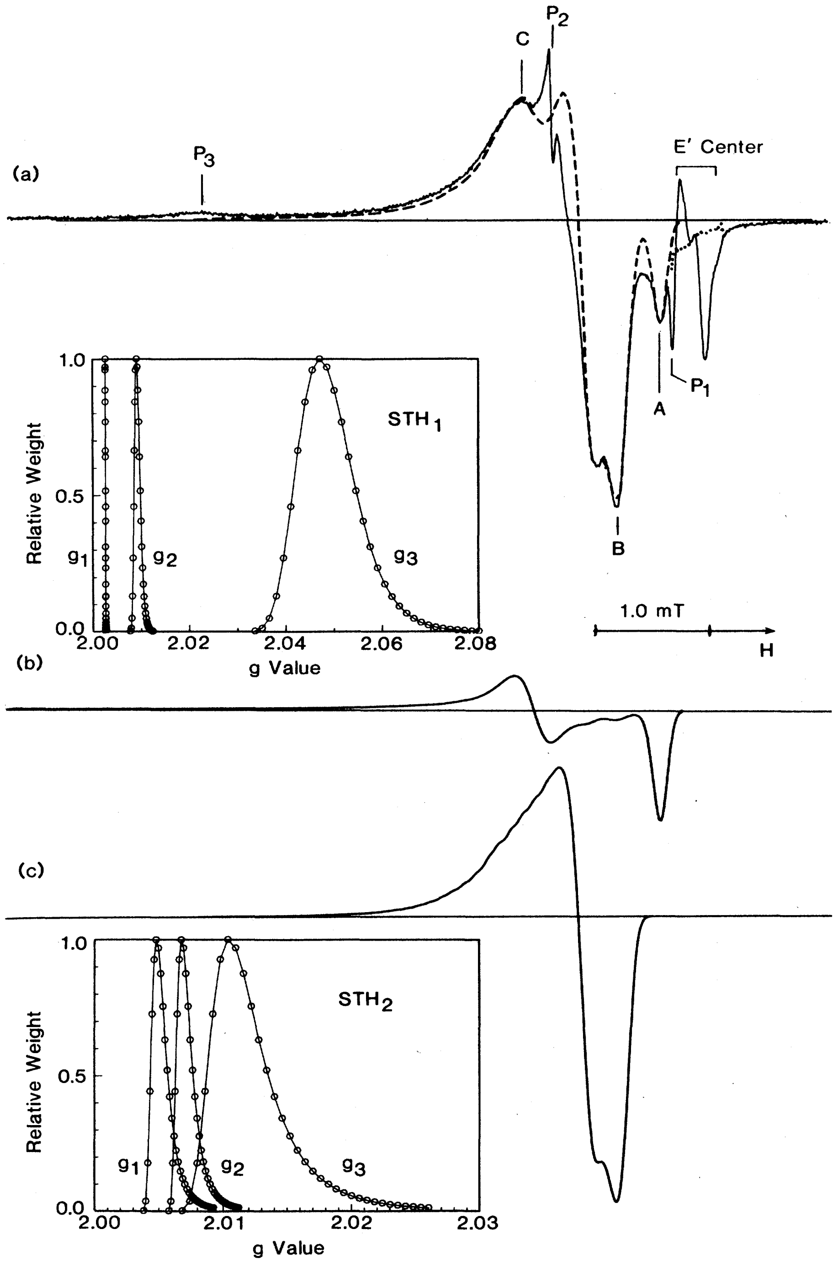

FIG. 1. (a) X-band (9.42 GHz) ESR spectra recorded at 110 K for Suprasil W1 subjected at 77 K to a 6-Mrad dose of 100-keV x rays (fully drawn curve) or a 10^7 mJ/cm^2 fluence of 6.4-eV photons (dotted curve drawn only in region marked "E' center"). Bold dashed curve in (a) is a computer simulation comprising a linear combination of synthetic spectra (b) and (c) based in turn on the illustrated g-value distributions. Features marked P_1, P_2, and P_3 arise from peroxy radicals (not simulated). The total STH spin density by numerical integration is $\sim 10^{16}/g$.

puter simulated[13] as features of a single spectrum. Moreover, the distinctly different anneal curves of peaks A and B confirm that these two features arise from separate centers. From inspection of the line shapes, peaks A and B must then each represent a powder-pattern feature corresponding to the smallest principal-axis g value of a defect with an anisotropic g matrix. Any reasonable analysis of the overall spectrum must assume that component spectra A and B overlap at field values equal to or less than the field position of peak B. In Fig. 2, the anneal curve for feature C is intermediate in temperature dependence between those for features A and B, thus suggesting that field position C is a region of substantial overlap of the A and B components. Constrained by these observa-

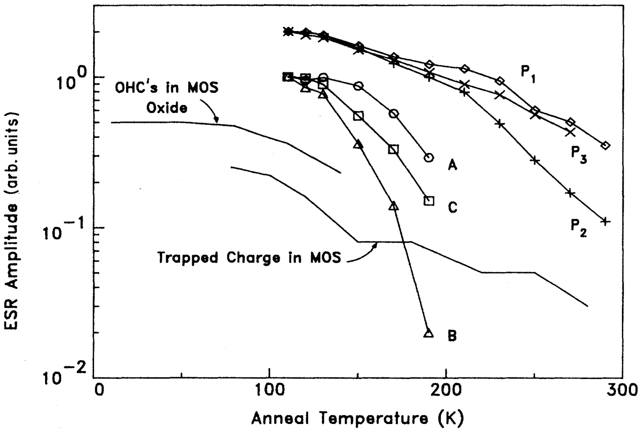

FIG. 2. Isochronal anneal curves (5 min at temperature) for x-ray-induced defect centers in Suprasil W1 (data points). Arbitrarily normalized ESR spectral amplitudes due to STH's (*A*, *B*, and *C*) or PR's (P_1, P_2, and P_3) are keyed to Fig. 1(a). Curves without data points are isochronal data (20 min at temperature) for OHC's (Ref. 20) and trapped positive charge (Ref. 19) in γ-irradiated MOS structures.

tions, the dashed computer simulation of Fig. 1(a) was obtained by a protracted cut-and-try procedure (~50 trials) as a linear combination of two simulated spectra denoted by STH_1 [Fig. 1(b)] and STH_2 [Fig. 1(c)]. The illustrated fit[14] corresponds to a concentration ratio $[STH_1]:[STH_2] = 1.15$. Following theoretical expectation and successful practice for vitreous-state ESR spectra,[15] the *g*-value distributions used in simulating the component spectra (insets in Fig. 1) were further constrained to be derived from the formula $g_i = g_0 - \lambda C_i/\Delta$ by introducing Gaussian distributions in the energy denominator Δ (here, g_0 is the free-electron *g* value $\equiv 2.0023$, λ is the spin-orbit coupling constant, and C_i are fitting parameters).

The mean principal-axis *g* values for STH_1 are superficially similar to those for various NBOHC's and PR's (Table I), except that g_1 for STH_1 is notably larger than for the other species. (PR_1 was previously identified by its ^{17}O hyperfine structure,[11] while PR_2 is tentatively assigned by successfully fitting its *g* matrix to the theoretical formulas of Känzig and Cohen.[16]) STH_1 is further distinguished from the NBOHC's and PR's by its relative thermal instability (Fig. 2, curve *A*). Finally, I point out that the *g* values for STH_1 correspond rather well to those of the Ge trapped-hole center in crystalline α quartz. The latter defect comprises a hole trapped on an oxygen bridging between a silicon and a substitutional germanium and owes its stability (up to 35 K) (Ref. 8) to the presence of the Ge. By analogy, I suggest that STH_1 is a hole trapped on a "normal" bridging oxygen in the glass network, and I attribute its stability to ~180 K to the intrinsic randomness of the vitreous state.

The principal *g* values for STH_2 differ sharply from those of any known NBOHC's or PR's (Table I), and its production efficiency and thermal instability (Fig. 2, curve *B*) clearly ally it with STH_1. As seen in Table I, the *g* matrix of STH_2 bears a particular similarity to that of the HC_2 defect center in irradiated alkali silicate glasses,[15] namely, in each case all three *g* shifts, $\delta g_i \equiv g_i - g_0$, are of roughly the same magnitude (whereas for the other OHC's $\delta g_1 \simeq 0$). I have argued elsewhere[15] that a likely explanation of this phenomenon is that the wave function of the unpaired spin is delocalized over two *noncolinear* 2*p* orbitals of two separate oxygens. If the analogy between HC_2 and STH_2 should prove decisive, STH_2 would be a V_K-type center (O_2^{3-})—as distinguished from a PR-type defect (O_2^-).

Additional evidence that STH_1 and STH_2 are holes trapped on oxygens includes preliminary spectra (not shown) for x-ray-irradiated silica samples enriched in ^{29}Si exhibiting hyperfine splittings ~0.9 mT. This value is virtually identical to that determined for the Ge trapped-hole centers in quartz (~0.8 mT) (Ref. 8) and shows the degree of wave-function overlap with silicon nuclei to be no more than ~1%. My tentative interpretation of the observed ^{29}Si hyperfine spectra is that the unpaired spin of STH_2 interacts with two nearly equivalent silicon nuclei, but this assessment remains to be tested by computer simulation.

Evidence associating STH_1 and STH_2 with trapped *positive charge* derives from a comparison of their isochronal anneal curves with those of holes trapped in the oxide layers of silicon-based metal-oxide-semiconductor

TABLE I. Principal *g* values of several oxygen-associated hole centers in silica, quartz, and silicate glass.

Defect	g_1	g_2	g_3
NBOHC in silica[a]	1.9999	2.0095	2.078
PR_1 in silica (γ rays at room temperature)[b]	2.0018	2.0078	2.067
PR_2 in silica (x rays at 77 K)[c]	2.0020	2.0085	2.027
Ge trapped hole in quartz[d]	2.003	2.008	2.046
STH_1 in silica[c]	2.0026	2.0093	2.049
STH_2 in silica[c]	2.0054	2.0073	2.012
HC_2 in alkali silicate glass[e]	2.012	2.013	2.016

[a] References 9 and 10.

[b] References 10 and 11.

[c] This work.

[d] Reference 8.

[e] Reference 15.

(MOS) structures (Fig. 2). While ESR electrical correlations[17] have established that much of the radiation-induced positive charge in MOS oxides is due to E' centers, recent studies[18] involving charge generation by high-field stressing have resulted in trapped hole densities greatly exceeding the E'-center densities. Griscom, Brown, and Saks[19] have proposed that much of this "excess" positive charge may be in the form of STH's. Support for this suggestion is found in the ESR observation by Brower, Lenahan, and Dressendorfer[20] of OHC's, but not E' centers, in an MOS structure subjected to γ irradiation at 4 K. Although Brower's signals were too weak to resolve the kinds of spectral detail revealed in Fig. 1(a), it seems reasonable to suggest that his OHC's were in fact STH's. Indeed, the isochronal anneal curve of Brower's OHC's (Fig. 2) closely parallels those of STH_1 and STH_2 of the present study (a relative shift of ~ 20 K is attributable to the difference in anneal times). Note that the cause of this anneal stage cannot be reaction of STH's with radiolytic hydrogen,[21] since I determined the initial concentration of H^0 in irradiated Suprasil W1 to be $\sim 10^2$ times less than the initial STH population. (Of course, trapped charges in an MOS structure cannot be removed by reaction with a neutral species.) Thus, the data of Fig. 2 prompt the suggestion that the defects which I denote STH's are in fact identical with the positive charges which thermally detrap in the temperature range ~ 100–200 K.

In summary, I report a detailed deconvolution of two dominant ESR spectral components observed when a-SiO_2 is irradiated at cryogenic temperatures, and I present several arguments for ascribing these components to self-trapped holes. Such defects may be responsible for much of the positive charge trapping in MOS oxides, and careful study of their spectroscopic properties may ultimately permit informed modeling of the self-trapped exciton in silicon dioxide. A more detailed report of this work is in preparation.

I thank E. J. Friebele for adding several time-saving improvements to his indispensible line-shape simulation program.

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