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Time-resolved EPR of spin-polarized mobile H atoms in amorphous silica: The involvement of small polarons

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Time-resolved pulsed electron paramagnetic resonance (EPR) was used to study the formation and decay kinetics of spin-polarized mobile H atoms in ''wet'' fused silica containing ~1200 ppm of SiOH groups. The H atoms were produced using 5–100 ns pulses of 3 MeV electrons. The EPR polarization pattern of these H atoms indicates the occurrence of chemically induced dynamic electron polarization in spin-selective reactions of H atoms with other paramagnetic species. The EPR kinetics observed from 180 to 530 K are independent of the dose absorbed per pulse and exhibit fast exponential growth and slow exponential decay. The slow component with activation energy of 15–18 kJ/mol corresponds to diffusion-controlled scavenging of H atoms by metastable paramagnetic centers ($\sim 3\times 10^{17}$ cm^{-3}) generated by electron irradiation. At room temperature, the diffusion coefficient is 10^{-7}–10^{-6} cm^2/s. The fast component with activation energy of 6–8 kJ/mol corresponds to the decay of a mobile radical (ion) partner of the H atom. It is argued that this partner is a small polaron (intrinsic hole) in amorphous silica. [S0163-1829(96)07845-9]

I. INTRODUCTION

Annealing of metastable radiation-induced paramagnetic centers by freely-diffusing H atoms in ''wet'' fused silica is the prime cause of the remarkable ability of this material to withstand continuous exposure to penetrating radiation without deterioration of its optical and mechanical properties.[1] Little is known about these annealing reactions at temperatures above 150 K. The EPR studies on H atoms trapped at 77–120 K showed that (1) the decay kinetics of H atoms are dose independent (the H atoms are reacting with stable defects rather than each other), (2) these kinetics can be fit by stretched exponential dependences, $[H]_t = [H]_{t=0}\exp(-[kt]^{\beta})$, typical for dispersive diffusive transport, with $\beta \approx 0.37$, (3) the activation energy Q_H of diffusion is the same in any time regime and is ≈15–16 kJ/mol, both for H and D atoms.[2–7] This activation energy is close to the estimate obtained using Frenkel's formula,[8] $Q_H = \pi G d(d_H - d)^2$ where $G = 3\times 10^{10}$ N/m^2 is the elastic modulus of amorphous SiO$_2$ (a-SiO$_2$), d_H is the van der Waals diameter of the H atom (0.32–0.36 nm),[9,10] and $d \approx 0.3$ nm is the diameter of the site-connecting channels (estimated from the data on solubility and diffusion of atomic gases).[8] Using his low-temperature EPR data,[4] Griscom estimated that the diffusion coefficient D_H of H atoms is given by $D_H = D_0 \exp(-Q_H/kT)$, where $Q_H \approx 17.4$ kJ/mol and $D_0 = 10^{-4}$ cm^2/s, which gives an estimate of $D_H = 8\times 10^{-8}$ cm^2/s at 300 K.

We have previously reported the observation of spin-polarized short-lived H atoms generated in the room-temperature radiolysis of a-SiO$_2$ with ns electron pulses.[11] At 300 K, the formation of polarization was complete in 5 μs. Using the estimates of radiolytic yield of H atoms from the data on trapped H atoms[5] we explained the observed rate of the formation kinetics assuming that the H atoms decay by cross recombination (as suggested by Griscom)[2–4] with D_H in excess of 10^{-4} cm^2/s. This estimate is inconsistent with the low-temperature data; it also implies that the H atoms move through the channels in a-SiO$_2$ without interaction with the network. The activation energy of such diffusion must be considerably lower than the observed Q_H.

In this work, we revisit this problem and demonstrate that the diffusion of H atoms is not much faster than was estimated by Griscom.[4] At 180–530 K, the activation energy of this diffusion is close to that observed at 77–120 K. The decay of mobile H atoms is mainly due to reactions with metastable spin centers, as at low temperatures. The fast component in the spin polarization kinetics of H atoms observed in Ref. 11 cannot be due to these slow reactions. It comes from spin-selective reactions of H atoms with a short-lived paramagnetic species, whose diffusion has three times lower activation energy. We speculate that these mobile species are the small polarons observed in the dc conductivity experiments, by Hughes.[12]

II. CIDEP IN RADICAL REACTIONS

In this work, mobile H atoms were observed by time-resolved pulsed EPR within 10^{-8}-to-10^{-3} s after their generation in a radiolytic pulse. These H atoms exhibit nonthermal population of their electron spin states caused by chemically induced dynamic electron polarization (CIDEP).[13] Briefly, there are two causes of CIDEP: (i) transfer of polarization from a short-lived triplet precursor to the product radicals (triplet mechanism) and (ii) polarization due to spin correlation in a radical pair formed on dissociation of a precursor or in a random encounter [radical pair mechanism (RPM)].

In the high magnetic field of the EPR spectrometer, only one of the triplet states of the radical pair, T_0, is close to the singlet state, S. Hyperfine interactions (hfi) of electrons with nuclei induce rapid spin transitions between these two states. In close pairs, the electron spin exchange (J) between the radical partners enlarges the energy gap between the S and T_0 states and slows the hfi-induced transitions down. The so-called ST_0 RPM originates in the interplay of hfi and spin exchange driven by modulation of J by diffusion.[14] In the ST_0 RPM polarized radicals, the high and low-field halves of the EPR spectra have opposite polarization, either E/A (here E is for emission and A is for absorption) or A/E, depending on the sign of J and the initial spin state of the pair. In the singlet-born pairs the polarization is A/E if $J<0$ and E/A otherwise; in the triplet-born pairs the polarization is opposite in phase. The ST_0 RPM polarization in pairs formed in random encounters of radicals depends on the spin sorting: if the singlet pairs recombine faster, as is usually the case, then the polarization is E/A (for $J<0$).

In encounters of H atoms with other radicals, the ST_0 RPM results in the EPR spectrum of H atoms in which the $M_s=+1/2$ line is in emission and the $M_s=-1/2$ line is in absorption. According to the ST_0 RPM theory, these two lines should have approximately equal intensity.[13] The asymmetry $\sim\Delta g\mu_B B_0/A_H$ results from the difference Δg in the g factors of the H atoms and their partners,[14] where $A_H\approx 51$ mT is the hfi constant of the H atom, μ_B is the Bohr's magneton, and $B_0\approx 0.3$ T is the magnetic field of the spectrometer.

Additional spin polarization of H atoms via RPM is caused by hfi-driven transitions in the region of avoided crossing between the singlet (S) and the lowest triplet state (T_-) in radical pairs (ST_- RPM, $J<0$).[15] The ST_- mechanism yields the $M_s=+1/2$ line in emission ($E+E/A$). In the continuous diffusion model, the ST_0 RPM polarization $\rho_{ST_0}\propto[A_H\tau_D]^{1/2}$ and the ST_- RPM polarization $\rho_{ST_-}\propto(A_H 2/B_0)\tau_D$, where $\tau_D=R_H{}^2/D_H$ is the lifetime of the contact radical pair and R_H is the radius of the closest approach.[14,15] From these formulas, the ratio ρ_{ST_-}/ρ_{ST_0} should *decrease* with temperature (that is, D_H). This was observed in many radical pair systems.[13]

In a-SiO$_2$, however, the relative weight of the ST_- polarization in H atoms *increases* with temperature (see below). This peculiar behavior can be qualitatively explained in terms of the site-to-site migration of the H atoms in glasses. The ST_- transitions are effective only within ± 0.05 nm from the point where the S and T_- terms cross. In low-temperature glass, these sites may not be accessible for H atoms. By contrast, the ST_0 polarization is formed in the region where the spin exchange J between the H atoms and their partners is less than A_H,[14] which is a large sphere ca. 2 nm in diameter. Since a typical diameter of the void in a-SiO$_2$ is $d\approx 0.3$ nm,[8] there are many sites inside this sphere that are accessible to H atoms and, therefore, the ST_0 RPM is always efficient. As the temperature increases, the network starts to breathe, and the ''ST_- crossing'' sites become more accessible to the H atoms. Since the diffusion of H atoms at these higher temperatures is still rather slow, the hfi-induced transitions occur before the H atoms leave the active sites, and the ST_- RPM is efficient.

In a-SiO$_2$, the most likely precursor of the H atoms is the ≡SiOH group interacting with free triplet excitons:[17]

$$\equiv\mathrm{SiOH}\ +\ {}^3\mathrm{exciton}\rightarrow{}^3\{\equiv\mathrm{SiOH}\}\rightarrow\equiv\mathrm{SiO}\cdot\ +\ \mathrm{H}. \quad (1)$$

If the spin-lattice relaxation in the triplet occurs prior to its dissociation, the polarization in the radicals is 4/3 of the Boltzmann polarization.[16] If the relaxation is slower than the dissociation, the non-Boltzmann polarization of the triplet can be passed to the radicals (triplet mechanism). The corresponding polarization in the fragment radicals can be emissive (E) or absorptive (A), depending on the initial polarization of the triplet and the sign of its zero-field splitting parameter.[13] We expect that the triplet precursor in reaction (1) is not spin-polarized, i.e., the initial absorptive polarization in the H atoms is close to thermal.

III. EXPERIMENT

The EPR spectra were obtained at 9 GHz using a pulsed microwave (μw) bridge described elsewhere [e.g., Ref. 18], 5–100 ns pulses from a 3 MeV Van de Graaff electron accelerator were used to radiolyze tubes (OD 6 mm) or rods (4 mm) made of Suprasil I (3×10^{19} cm^{-3} SiOH groups). The repetition rate of the electron pulses was varied from 60 Hz to 720 Hz to keep the average current of 3 μA. The time resolution in our experiment was $\sim$10 ns: the ring down time of the EPR spectrometer was 0.4–1 μs. The suprasil samples were inserted in a sapphire jacket; compressed dry air was passed at the rate of 1–3 dm^3/min through the sample assembly to regulate the temperature from 90 K to 550 K. On radiolysis, sapphire does not yield EPR signals with $g\sim 2$, so the EPR signals were observed from the Suprasil sample only. To observe the EPR signals from H atoms we either used 90°-τ-180°-τ spin echo (where τ is the delay time between 90° and 180° microwave pulses) or integrated a part of the free induction decay (FID) detected after the excitation with a single 90° pulse.

A typical experiment was performed with 20 nC electron pulses at the repetition rate of 120 Hz. Using the stopping power of 1.64 MeV cm^2/g and linear energy transfer $\sim$3.8 MeV/cm/electron,[19] the sample-averaged dose rate is 0.8 kGy/pulse. This strong flux of electrons results in the formation of stable paramagnetic centers, such as E'_γ centers ($\equiv$Si$\cdot{}^+$Si$\equiv$) (Ref. 20) and oxygen hole centers ($\equiv$SiO$\cdot$),[17] whose g factors are close to 2. Their EPR signal reaches the steady-state level after a cumulative dose of $(1–5)\times 10^7$ Gy. The total concentration of stable paramagnetic centers was determined by correlation of b, the decay parameter of θ-τ-2θ-τ spin echo from the E'_γ centers, $E(\tau)=\exp(-2b\tau)$, with the flip angle θ.[21] For instantaneous spin diffusion caused by dipole-dipole interactions of paramagnetic centers

$$b=\mathrm{const}+4\pi^2/9\sqrt{3}(g\mu_B)^2N_s\sin^2(\theta/2), \quad (2)$$

where N_s is the number density of spin centers. From this formula we found that $N_s\approx 3\times 10^{17}$ cm^{-3}. A comparison between the ESR signals from metastable spin centers and H atoms indicates that the maximum magnetization of H atoms is $\sim 1.5\times 10^{15}$ cm^{-3} Boltzmann units (for the 20 nC pulse). Using the reported G value of 0.02 trapped H atoms per 100 eV[5] the initial concentration of H atoms is estimated as $\sim 2\times 10^{15}$ cm^{-3}. Taking into account the uncertainty of these estimates (which can be $\sim$2–3 times), we can only conclude that the spin polarization due to RPM is not greater than several Boltzmann units.

In Ref. 11 we reported that the EPR kinetics were dependent on the dose absorbed per radiolytic pulse. This result was interpreted in terms of the cross recombination of H atoms. In this study it has been determined that the kinetics are actually dose independent at any temperature, but in some samples the kinetics are dependent on the *average dose rate*. Apparently, in those samples there is a relatively long-lived metastable spin center reacting with H atoms; the steady- state concentration of this center depends on the dose rate but not the dose *per se*. In most of the samples, the kinetics are independent both of the dose per pulse and the dose rate (providing that the cooling of the sample is adequate).

To measure the time T_1 of spin-lattice relaxation for H atoms, an inversion-recovery experiment was performed.[22] A short 180° μw pulse was applied at a delay time t_{180} after the radiolytic pulse in order to invert the longitudinal magnetization $M(t)$ of the H atoms. Due to the spin-lattice relaxation, this magnetization quickly recovers. This recovery was measured by integration of the FID detected after excitation with a 90° μw pulse (applied at a delay time t after radiolytic pulse). The curves obtained with and without the 180° μw pulse were subtracted, and the difference traces $M_{\text{rec}}(t)$ were fit by

$$M_{\text{rec}}(t)=2M(t)\exp[-(t-t_{180})/T_1]. \tag{3}$$

In these experiments, the 180° pulse was applied at the falling part of the kinetics (as shown in Fig. 5), so that $M(t)$ was approximately exponential (see below).

IV. RESULTS

The EPR signals of H atoms indicate the occurrence of CIDEP (Fig. 1). The EPR spectra obtained below 220 K immediately after the radiolytic pulse exhibit the E/A+A pattern (Fig. 1 bottom). The E/A contribution is certainly due to ST_0 RPM, which suggests that the H atoms have a triplet precursor to account for the excess absorption. This absorption cannot be due to ST_0 or ST_- RPM. No known spin center has a g factor sufficiently different from that of the H atoms to provide for the asymmetry more than 5%, whereas the asymmetry observed at 190 K is ca. 15%. Thus we believe that the absorption is due to a transfer of thermal polarization in dissociation of triplet $\equiv$SiOH groups [reaction (1)]. At higher temperatures the pattern gradually changes from $E/A+A$ to $E/A+E$ (Fig. 1, from the bottom to the top); at 400 K the asymmetry is ca. 35%. The most likely explanation of the emissive polarization is that at these higher temperatures the ST_- mechanism becomes operative. Indeed, the net emission can be observed many microseconds after the radiolytic pulse which suggests that this polarization is formed in random encounters of H atoms with spin centers, similarly to the long-term ST_0 polarization. The latter contribution can be extracted by subtracting the intensity of $M_s=+1/2$ line from the intensity of the $M_s=-1/2$ line. Only these multiplet $S_-(t)$ kinetics will be considered in the following.

The spin echo $S_-(t)$ kinetics do not evolve in the τ domain; the normalized $S_-(t)$ kinetics obtained by integration of different parts of the FID are also the same. The phase relaxation in H atoms does not depend on their concentration and is determined by magnetic interactions with metastable spin centers. Following the 90° μw pulse excitation, FID $\propto$ $\sin(\Omega t)\exp(-b_F t)$. Below 350 K, b_F decreases from 3.5×10^6 s^{-1} at 230 K to the minimum value of 1.2×10^6 s^{-1}. Above 350 K, b_F increases from 1.2×10^6 s^{-1} to 2×10^6 s^{-1} at 500 K (Fig. 2). The decay parameter b of spin echo in the τ domain exhibits the same behavior.

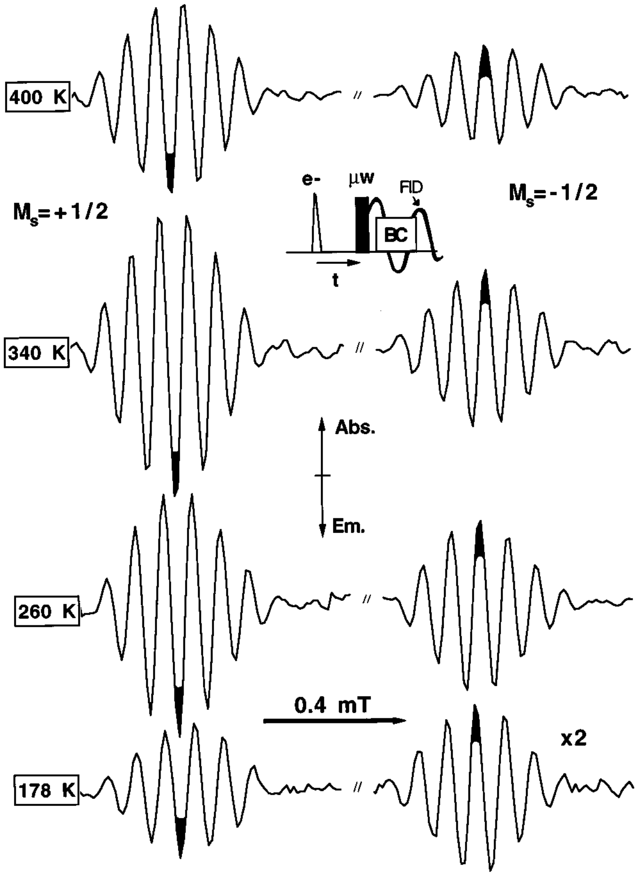

FIG. 1. EPR spectra (9 GHz) of mobile H atoms in ''wet'' a-SiO$_2$ observed at $t=50$ ns after the end of the 100 ns electron beam pulse (178 K to 400 K). The spectra are obtained by boxcar integration (BC) of free induction decay (FID) following the excitation of H atoms with 90° microwave pulses ($\approx$30 ns wide). The oscillations in the field domain are due to transient nutation of the magnetization. The splitting between the $M_s=+1/2$ (low-field) and $M_s=-1/2$ (high-field) lines is 51.4 mT (these two lines were scanned individually). The exact field positions of the $M_s=\pm1/2$ resonances are shown by shadows; these signals were used to acquire the EPR kinetics. As the temperature increases, the $E/A+A$ polarization pattern transforms to the $E/A+E$ pattern.

This dependence can be understood in terms of two contributions to the phase relaxation in H atoms caused by magnetic interactions with metastable spin centers. For dipole-dipole interaction, the rate constant of phase relaxation is

$$T_{2d}{}^{-1}\propto[(g\mu_B)^2\hbar]^2N_sR_H{}^{-2}D_H{}^{-1} \tag{4}$$

(the proportionality coefficient depends on the model of diffusion).[23] For exchange interaction,[23]

$$T_{2e}{}^{-1}\approx2\pi R_HD_HN_s. \tag{5}$$

Thus $T_{2d}{}^{-1}$ decreases and $T_{2e}{}^{-1}$ increases with D_H (that is, temperature). From Eqs. (4) and (5), we estimate that the diffusion coefficient D_H at 350 K must be $\sim10^{-6}$ cm^2/s.

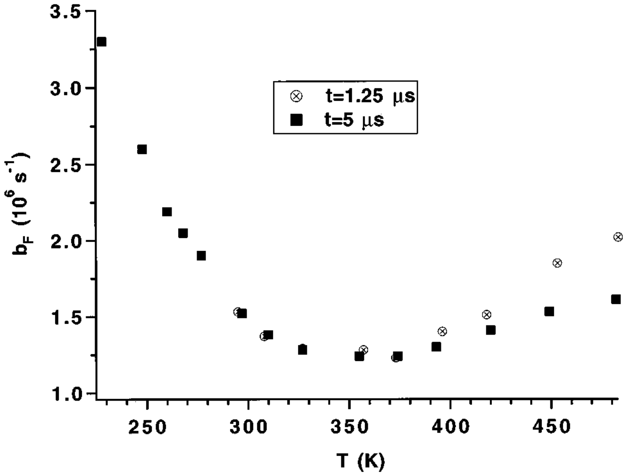

FIG. 2. Temperature dependence of the decay factor b_F of FID (the rate of phase relaxation) for H atoms in "wet" a-SiO$_2$, measured at $t=1.25$ μs and $t=5$ μs after radiolytic pulse. At lower temperatures, the phase relaxation is dominated by dipole-dipole interactions with metastable centers and b_F decreases with D_H. At higher temperatures, the electron spin exchange is faster, and b_F increases with D_H. The difference in the b_F for different delay times t of the 90° μw pulse (at $T>350$ K) is due to attenuation of FID by the decay of H atoms. Immediately after the radiolytic pulse, the H atoms decay faster than later in time, due to reactions with short-lived polarons (see the text).

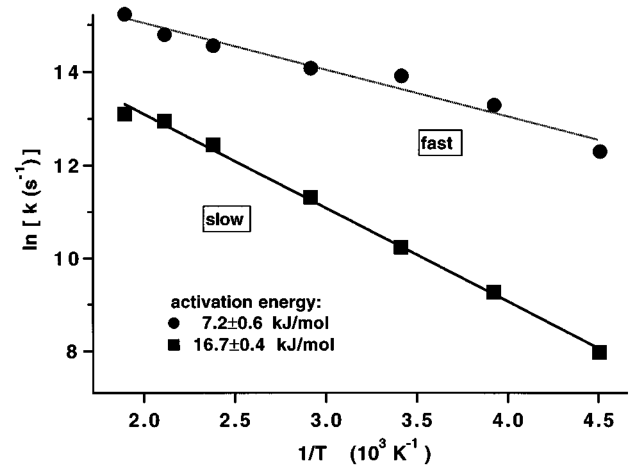

FIG. 4. Arrhenius plot for the fast and slow components of biexponential fits to the $S_-(t)$ kinetics (the same sample as in Fig. 2).

The signal from polarized H atoms grows linearly with the radiolytic dose absorbed per pulse. At any temperature, the kinetics can be fit by two exponential functions stretching over 2–4 decades in time (Fig. 3). Figure 4 shows the Arrhenius plot for the fast and slow components (with pseudo first-order rate constants k_s and k_f). The activation energy of the slow component is 15–18 kJ/mol (the uncertainty is mainly due to the sample-to-sample variations) which is close to the activation energy of H atom diffusion as determined by low-temperature EPR.[4–6] The inversion-recovery EPR experiments (Fig. 5) indicate that $T_1^{-1} \approx 2k_s$ over the entire temperature range. Apparently, the T_1 relaxation of H atoms is due to electron spin exchange with metastable centers whose polarization is thermal. The factor of 2 is expected since recombination occurs only in singlet encounters (1/4 of encounters are reactive), whereas the spin exchange occurs in every $\alpha\beta$ and $\beta\alpha$ encounter (that is, in 1/2 of encounters). Our observations indicate that the slow component in the kinetics is due to diffusion-controlled reactions of H atoms with scattered metastable spin centers. Using the equation $k_s = \pi R_H D_H N_s$, where $R_H = 0.2$–0.5 nm, we obtained D_H which are ~10 times greater than estimates given in Ref. 4.

The fast formation component with the activation energy of 6–8 kJ/mol cannot be explained in terms of geminate

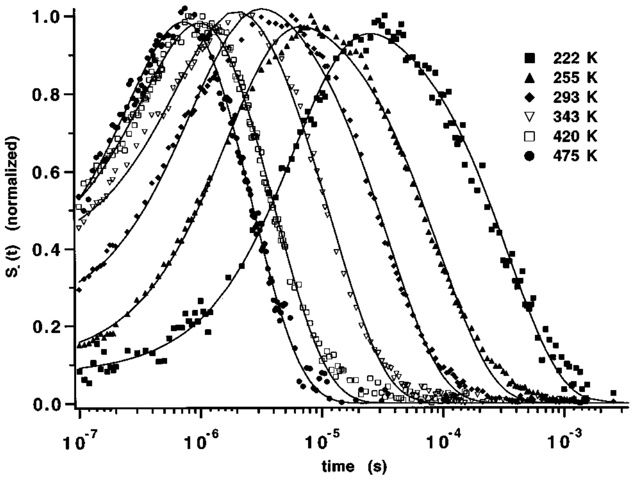

FIG. 3. Normalized $S_-(t)$ kinetics as a function of temperature (55 ns electron pulse, FID detection). A pseudologarithmic sweep of delay time t was used to obtain these kinetics. The solid lines drawn through the points are biexponential fits, $S_-(t) = \exp(-[k_s t]^\beta)\{A - B\exp(-[k_f t]^\beta)\}$ with $\beta=1$. Using stretched exponential functions with $\beta \approx 0.8$–0.9 and corrections for the T_1 relaxation further improve the fit quality.

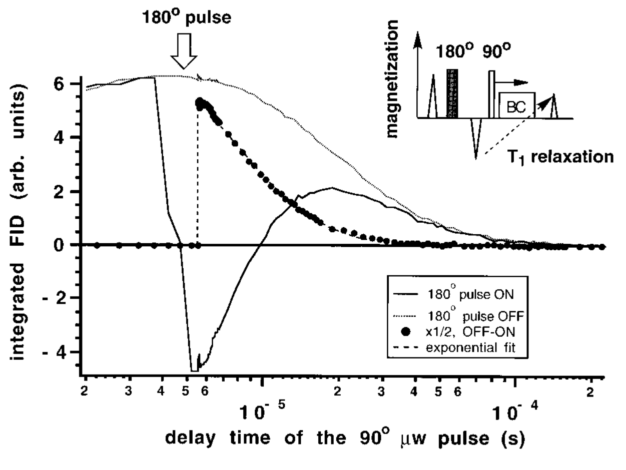

FIG. 5. Inversion-recovery EPR experiment with the $M_s=-1/2$ line of H atoms in "wet" a-SiO$_2$ at 300 K. The inverting 180° μw pulse is applied at $t_{180}=5$ μs after a 20 nC radiolytic pulse. The recovery of magnetization $M_{\rm rec}(t)$ due to spin-lattice relaxation (the difference trace, broken line) was observed by scanning the 90° μw pulse and integration of FID using a boxcar averager. The recovery is exponential, $M_{\rm rec}(t) = M(t)\exp[-(t-t_{180})/T_1]$, with $1/T_1 \approx 2k_s$.

recombination of H atoms with $\equiv$SiO$\cdot$ centers and must involve some short-lived paramagnetic species. This species (P) need not have very high mobility in order for the formation kinetics of polarization to be fast, or the activation energy to be low, as long as the concentration of P is high and its lifetime is short. Since the elimination of radicals P competes with their (relatively slow) reaction with H atoms, the latter are polarized with the rate equal to that of the decay of their partners in a side reaction. Assuming that the decay of H atoms and their partners is pseudo-first order and the formation of ST_0 polarization is second order, one obtains

$$dM_H/dt = k_{HP}\rho_{HP}[P] + k_s\rho_{HC} - T_1^{-1}(M_H - 1), \quad (6)$$

$$d[P]/dt \approx -k_f[P], \quad (7)$$

$$d[H]/dt \approx -k_s[H] = -k_{HC}N_s[H], \quad (8)$$

where M_H is the polarization per H atom (in the units of thermal polarization), k_{HP} and k_{HC} are the rate constants of encounters of H atoms with P and metastable centers (C), ρ_{HP} and ρ_{HC} are the ST_0 polarizations per encounter. The EPR signal $M(t) \propto M_H[H]$. Equations (6)–(8) account for the observed bi exponential kinetics in the t domain.

The ''tails'' of the EPR kinetics in Fig. 3 can be simulated with better accuracy if the exponential functions are replaced by $\exp(-[k_{s,f}t]^{\beta})$ with β increasing as T/T_R, $T_R \approx 300$ K, at $T < T_R$. In hydrogenated amorphous silicon the dispersion parameter β was also found to increase as T/T_R, with $T_R = 600$ K.[24]

V. DISCUSSION

The thermal activation energy of 6–8 kJ/mol corresponds to the energy of a single phonon. The only paramagnetic species which are relatively long-lived, mobile, and have low activation energies of diffusion are hopping charges. Since electrons in a-SiO$_2$ are rapidly trapped in deep wells,[25,26] the only candidate is the intrinsic hole, i.e., a small polaron. Only polarons can have the initial concentration comparable to that of the metastable centers, which explains why the formation of ST_0 polarization in the $H+P$ encounters is predominant. Our supposition is corroborated by the following observations.

(1) The onset for the observation of polarized H atoms is 170–180 K, though the EPR signals from trapped H atoms appear only below 150 K. According to Griscom,[27] self-trapped holes ($\equiv$Si-O$\cdot^+$Si$\equiv$) in EPR spectra of X-irradiated a-SiO$_2$ and the holes trapped in the oxide layers of Si-based metal-oxide-semiconductor (MOS) structures anneal at 180 K. No other spin centers in γ-irradiated a-SiO$_2$ have annealing temperatures below 300 K.[17,20]

(2) Hughes studied the mobility of small polarons in MOS structures and determined that this mobility $\mu_P = 2\times10^{-5}$ cm^2/V s($D_P \sim 5\times10^{-7}$ cm^2/s) at 300 K while the lifetime of small polarons is $\sim$70 ns (increasing to 6μs at 175 K).[12] This lifetime is controlled by impurity and defects; in the bulk of fused silica the concentration of traps is much less than in the ''steam'' oxide layers studied by Hughes.[12] The mobility of small polarons abruptly changes at 180 K (ca. 1/3 of the Debye temperature for a-SiO$_2$) in full accordance to the theory of Emin.[28] Hughes gives a preferred value of 13.5 kJ/mol for the activation energy of hopping. However, his data can be fit using the estimate of 8.2 kJ/mol obtained from the studies on dielectric relaxation in ''smoky'' quartz, in which the hole hops between the bridging oxygens at the aluminum center.[29] The latter estimate is close to our result. Our estimate is also close to 7.7 kJ/mol obtained for diffusive migration of short-lived relaxed excitons in crystalline and vitreous SiO$_2$.[30]

McLean has proposed that the reaction of small polarons with H atoms in the oxide layer of MOS structures[31]

$$\text{H} + \equiv\text{Si—O}\cdot^{+}\text{Si}\equiv \;\rightarrow\; \equiv\text{Si}-\text{OH}^{+}\text{—Si}\equiv \quad (9)$$

yields slowly-hopping protons whose accumulation in the Si/SiO$_2$ interface compromises the performance of electronic devices.[32–34] If our assignment of the partner of H atoms is correct, spin-sorting reaction (9) also polarizes the H atoms. Assuming that the scavenging radius of small polarons by neutral defects is 0.2 nm and using the mobilities given by Hughes[12] we estimate that the concentration of polaron-trapping defects is ca. 10^{19} cm^{-3}, which is close to the concentration of $\equiv$SiOH groups.

It has been suggested that in radiolysis of ''wet'' silica the H atoms and oxygen hole centers are produced mainly in reaction (1).[17] In this case one needs to assume that only paired $\equiv$SiOH groups can fragment, since in ''wet'' silica every oxygen hole center includes a neighboring proton. The alternative mechanism considered by several authors is the reaction of $\equiv$SiOH with mobile holes (e.g., Robertson[35]):

$$\begin{aligned}&\equiv\text{Si—O}\cdot^{+}\text{Si}\equiv \;+\; \equiv\text{Si—OH}\\ &\rightarrow\; \equiv\text{Si—OH}^{+}-\text{Si}\equiv \;+\; \equiv\text{Si—O}\cdot \end{aligned} \quad (10)$$

Our results indicate that reaction (10) may indeed occur in a-SiO$_2$.

VI. CONCLUSION

At 180–530 K the H atoms in a-SiO$_2$ are not particularly mobile. At 300 K, the diffusion coefficient of H atoms is on the order of 10^{-7}–10^{-6} cm^2/s, and the activation energy of this diffusion is 15–18 kJ/mol. The slow decay of H atoms observed on the time scale of 10^{-6}-to-10^{-3} s is due to diffusion-controlled reactions with dispersed metastable spin centers. The paramagnetic relaxation in mobile H atoms (both spin-spin and spin-lattice) is due to magnetic interactions with these centers.

Rapid formation of spin polarization in H atoms must be due to their encounters with some abundant short-lived paramagnetic species. The decay reactions of these species exhibit rather low activation energy of 6–8 kJ/mol. We present several arguments that the radical partner of the H atoms is a small polaron and that the nonthermal polarization is gained in spin-selective reaction (9). The fast decay of small polarons can be explained in terms of their trapping by $\equiv$Si-OH defects via reaction (10).

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