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Structural relaxation of E'_γ centers in amorphous silica

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We report experimental evidence of the existence of two variants of the E'_γ centers induced in silica by γ rays at room temperature. The two variants are distinguishable by the fine features of their line shapes in paramagnetic resonance spectra. These features suggest that the two E'_γ differ in their topology. We find a thermally induced interconversion between the centers with an activation energy of about 34 meV. Hints are also found for the existence of a structural configuration of minimum energy and of a metastable state.

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The importance of point defects in silicon dioxide (SiO_2) both in crystalline and amorphous (a-SiO_2) polymorphs has been shown in connection with the use of this material in various optical and electronic devices.[1,2] Among these point defects one of the most diffusely characterized and discussed is the E'_γ center in a-SiO_2, which is an intrinsic paramagnetic point defect, i.e., involves only Si and O atoms.[3–5] Despite the huge number of theoretical and experimental works, the structure and the spectroscopic properties of this defect are still widely debated.[1,2,6] Recently, a new model for the E'_γ center has been suggested by Uchino, Takahashi, and Yoko,[7,8] in which the defect originates from an ''edge sharing'' oxygen vacancy (triangular oxygen-deficiency center) by trapping a hole (bridged hole-trapping oxygen-deficiency center, BHODC): $=\mathrm{Si}^\bullet$—O—$^+\mathrm{Si}=$ (where $=$ represents bonds to two distinct O atoms, • is an unpaired electron, and + is the trapped hole). This model succeeds to account for the experimental value, 42 mT, of the strong ^{29}Si hyperfine splitting[5,9] and it is rather different from the ''historical'' one originally proposed by Feigl and co-workers[10,11] (FFY) for the E'_1 center[3] in α-quartz, consisting in a hole trapped by a neutral oxygen monovacancy: $\equiv\mathrm{Si}$—$\mathrm{Si}\equiv + h^+ \rightarrow \equiv\mathrm{Si}^\bullet + {}^+\mathrm{Si}\equiv$ (where $\equiv$ represents the bonds with three distinct O atoms). Also this model, refined up to the puckered configuration, gave good agreement both with the strong and the weak hyperfine splittings measured in α-quartz.[12] In the latter configuration, one assumes that the $^+\mathrm{Si}\equiv$ group relaxes backward away from the vacancy and the Si^+ is also bonded to a normal bridging O becoming again fourfold coordinated[12] (see Fig. 1 in Ref. 8). Even though the presence of suitably positioned bridging O in the disordered matrix is unknown, the FFY model has been extended also to the E'_γ center in a-SiO_2, on the basis of the close analogies of its electron paramagnetic resonance (EPR) features to those of the E'_1.[13] This FFY model has been supported by various theoretical calculations,[14–17] but Uchino, Takahashi, and Yoko did not find backward puckering for the positively charged monovacancy and that the unpaired electron becomes almost equally distributed over the two adjacent Si.[8]

It is worth noting that the main EPR features (g values and hyperfine constants) of the E' center are theoretically explained in terms of the $\equiv\mathrm{Si}^\bullet$ structure. However, Griscom evidenced various typologies of E' centers in a-SiO_2, distinguished by small variations of the EPR line shape that can be ascribed to different atomic compositions of the neighborhood of the unpaired electron.[1,18] Moreover, just for the E'_γ center, an evolution of the line shape following thermal treatments at the temperature of $T\sim500$ K was found,[18,19] so revealing the existence of unexplained degrees of structural freedom of the defect.

The above considerations indicate that the E'_γ center deserves further experimental investigation and, to better evidence its degrees of freedom, a fine study of the EPR line shape. We report here a detailed EPR study of the E'_γ centers induced by γ irradiation in a variety of commercial a-SiO_2 that can be grouped as follows:[20] *Natural dry* Infrasil 301 (I301), EQ 906 (EQ906), EQ 912 (EQ912), Puropsil A (QPA); *Natural wet*, Herasil 1 (H1), Herasil 3 (H3), Homosil (HM); *Synthetic dry*, Suprasil 300 (S300) (EQ906, EQ912, and QPA supplied by Quartz & Silice, all the others by Heraeus). Each sample is slab shaped with size $5\times5\times1$ mm^3. Different pieces of each material were exposed to γ rays at room temperature in a ^{60}Co source, accumulating doses D in the range from 10^{-1} to 10^4 kGy at the rate $\sim$7 kGy/hr. EPR measurements were carried out at room temperature with a Bruker EMX spectrometer working at frequency $\nu\approx9.8$ GHz in the first derivative mode. E'_γ centers spectra were taken at a modulation magnetic-field frequency of 100 kHz, modulation amplitude of 0.01 mT, and at microwave power of 800 nW; the latter two conditions avoid line-shape distortions. The main spectroscopic g values were determined by accurate frequency measurements allowing us to find the differences between the g's with a maximum error of $\pm0.000\,01$. The spin concentration C_s of one sample of each material was determined, with absolute accuracy of 20%, using the instantaneous diffusion method in spin-echo decay measurements carried out in a pulsed spectrometer.[21] For the other samples, C_s was evaluated, with an accuracy of 10%, by comparing the double integral of the EPR spectrum with that of the reference sample. Our C_s detection limit (signal/noise$\geqslant$2) is estimated to be $\sim10^{15}$ spins/cm^3.

γ irradiation induces the E'_γ centers in all the investigated materials. They begin to be detectable at doses that strongly depend on the material. A typical dose dependence is re-

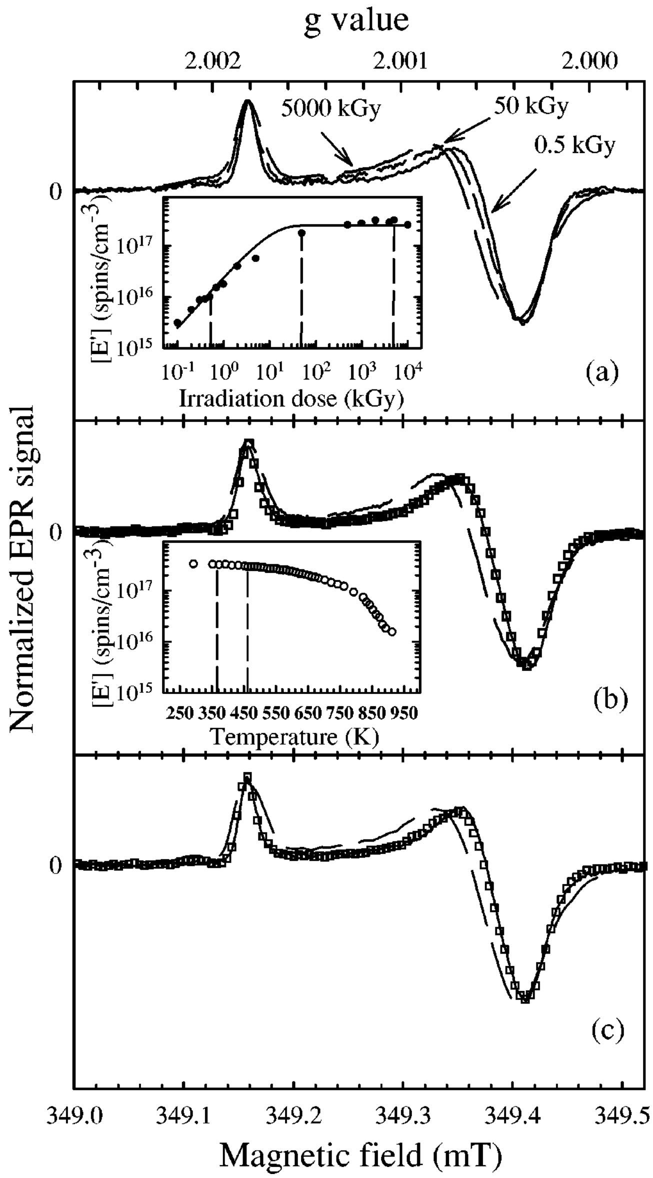

FIG. 1. EPR spectra of the E'_γ centers normalized to the peak to peak amplitude and horizontally shifted to overlap at the first maximum. (a) I301 samples irradiated at doses 0.5 (solid line), 50 (short-dashed), and 5000 kGy (long-dashed); in the inset the E'_γ concentration is reported as a function of the dose (the solid line is a guide to the eye). (b) I301 sample after irradiation at 4000 kGy (dashed) and after isochronal thermal treatments up to $T=460$ K (solid), the squares refer to the reference sample I301 irradiated at 0.5 kGy; in the inset the E'_γ concentration is reported as a function of the temperature in the isochronal thermal treatments. (c) S300 sample irradiated at 10^4 kGy (dashed) and after 9 hr of thermal treatment at $T=500$ K (solid), the squares refer to the reference sample I301 irradiated at 0.5 kGy.

ported in the inset of Fig. 1(a) for I301:[22,23] C_s initially grows and then reaches a constant value maintained up to the highest doses. This feature is evidence of a generation process from precursors.[24] A direct activation of the matrix has been observed at doses higher then those considered here.[23,24] Together with the variation of C_s, we observed a modification of the EPR line shape of the E'_γ centers on increasing the dose D. In Fig. 1(a), we report the line shapes as detected in the I301 material after γ doses of 0.5, 50, and 5000 kGy. We note a gradual shift of the zero-crossing point towards smaller resonance fields and an overall broadening of the line shape, on increasing the dose from 0.5 kGy upwards. A quantitative analysis can be carried out looking at the principal g values, g_1, g_2, and g_3, approximately determined from the field values at which the first maximum (g_1), the zero-crossing point (g_2), and the minimum of the EPR spectra (g_3) occur.[25] The difference $\Delta g_{1,2}=g_1-g_2$ varies from 0.001 24 at $D=0.5$ kGy (low-dose limit) up to 0.001 15 at $D=5000$ kGy (high-dose limit). The variation of $\Delta g_{1,3}=g_1-g_3$ is less pronounced on increasing the dose, $\Delta g_{1,3}=0.001\,47$ at $D=0.5$ kGy and $\Delta g_{1,3}=0.001\,42$ at $D=5000$ kGy. These gradual line-shape variations occur between 10 and 1000 kGy. The line shape reported for the 0.5 kGy irradiated sample is characteristic of the low-dose region whereas that observed at 5000 kGy is peculiar of the high dose. For convenience, hereafter we adopt the symbols $L1$ and $L2$ for the low- and high-dose line shapes, respectively. We note that $\Delta g_{1,2}$ and $\Delta g_{1,3}$ found for $L2$ are in strict agreement with those reported by Griscom for the E'_γ; as suggested by the simulated spectra[18] $L2$ could be related to an orthorhombic symmetry whereas $L1$ to an axial one. The phenomenology just reported for the I301 is a feature common to all the other materials. Indeed, we observe the line shape $L1$ after low γ doses, with the uncertainty of 0.001 mT, and the same line shape $L2$ after high γ doses in all the silica types considered here. It is worth noting that we have verified that the variation from $L1$ to $L2$ is not related to the concentration of centers, i.e., to dipole-dipole interaction.[4] As an example, the line shape $L2$ is observed also in synthetic wet material (not reported here) at a concentration of 4×10^{15} spins/cm^3, whereas at the same concentration of E'_γ centers the line shape $L1$ is observed in both natural and synthetic dry materials. We can infer that these variations of the line shape are intrinsic to the process of defect generation as they occur in all the materials.

To further investigate the line-shape variation, we carried out a series of thermal treatments in the sample I301 previously irradiated at 4000 kGy in which we recorded the line shape $L2$ and $C_s=3.3\times10^{17}$ spins/cm^3. Various isochronal treatments with time fixed to 25 min were carried out at normal atmosphere in the temperature range $350\leqslant T\leqslant910$ K in an electric furnace with T stabilized within ±3 K. After each treatment the sample returned to room temperature before EPR measurements. For $T<370$ K no significant variation occurs in the line shape nor in C_s, as shown in the inset of Fig. 1(b). A gradual change from $L2$ toward $L1$ occurs for $370\leqslant T\leqslant460$ K. Actually, as shown in Fig. 1(b), the line shape after the treatment at 460 K coincides with that in the same material exposed to a dose of 0.5 kGy. A noteworthy aspect is that after these treatments, C_s is 2.9×10^{17} spins/cm^3 indicating that only a very low quantity of centers has been destroyed and ruling out definitively that the line-shape changes are due to dipole-dipole interaction. At higher temperature we observe an additional reduction of C_s down to 2.7×10^{17} spins/cm^3 and a very small variation of

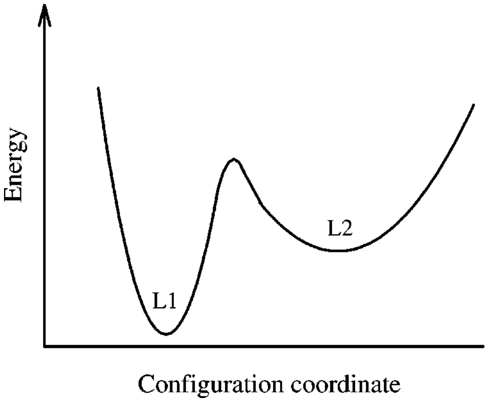

FIG. 2. Total energy for the structural configurations of the E'_γ centers related to the experimental line shapes $L1$ and $L2$.

the line shape; at $T = 520$ K we found $\Delta g_{1,2} = 0.001\,25$ and $\Delta g_{1,3} = 0.001\,47$, very close to $L1$. Finally, on increasing the temperature further, only a reduction of C_s occurs and temperatures as high as 800 K are required to obtain its large decrease, consistently with recent literature data.[18] Similar results were obtained as well in all the investigated materials. Here we limit ourselves to report on a somewhat different thermal treatment carried out in the synthetic dry material S300. After γ irradiation at the dose of 10^4 kGy, we measured $C_s \approx 1.1 \times 10^{17}$ spins/cm^3 and a line shape $L2$, as shown in Fig. 1(c). The sample was heated for nearly 9 hr at 500 K in a He-filled dewar. So long a heat treatment caused only a slight decrease of C_s down to 7×10^{16} spins/cm^3 but an evident variation of the line shape from $L2$ to $L1$. This result is relevant as the very high purity of synthetic material with respect to the natural one rules out the possibility that the line-shape modification can be ascribed to impurity-related effects.

Results reported above suggest that the E'_γ center possesses a structural configuration of minimum energy and a metastable state. An axial line shape $L1$ is observed after low-dose irradiation and can be associated to those centers whose formation is energetically favored. On increasing the dose, other centers are formed in a metastable configuration state associated with an orthorhombic line shape $L2$. A conversion from $L2$ to $L1$ is induced by warming and can be explained considering that some thermal vibration energy is employed in a structural conversion, where the metastable centers switch to the more stable ones. A qualitative representation of these features is outlined in Fig. 2 where the energy related to a given configuration is reported as a function of a generic configuration coordinate. The energy well associated with the line shape $L1$ is expected to be lower and narrower with respect to that of $L2$, explaining both the major energy stability and the minor broadening of the g-value distribution experimentally detected. An energy barrier between the two wells, corresponding to a thermal energy of ~34 meV ($T \sim 400$ K), separates the two configurations thus explaining the thermally activated conversion.

Now we try to interpret our results in terms of the existing models of the E'_γ centers. We consider the asymmetrically relaxed positively charged oxygen vacancy.[12] In this model the unpaired electron points toward the vacancy so that the observed variation of the line shape should be attributed to the perturbative role of Si$^+$.[18,26] In particular, the $L1$ center should result from the backward puckering of Si$^+$, which bonds to a normal bridging O, being stabilized and energetically favored. $L2$ would be the unpuckered E'_γ center, Si$^+$ being the origin of the orthorhombic character. The above scheme seems suitable to explain our results, however it presents some faults. Indeed, theoretical calculations for the positively charged oxygen vacancy predict only one energy minimum for the puckered state and an unpuckered state with the unpaired electron shared between the two Si.[14] The latter structure is expected to give rise to a consistent line-shape variation and also a significant variation in the hyperfine structures at 42 mT, not experimentally observed. Moreover, the conversion from the oxygen vacancy to the E'_γ center has not been clearly proven experimentally[6] and, in particular, our previously reported results[27] show that this conversion mechanism, if present, could be responsible for the generation of just a negligible part of the induced E'_γ center in our samples.

In view of this partial failure, we wish to put forward an alternative explanation for our results relying on a model of the E' center as the only $\equiv$Si$^\bullet$ moiety without a vacancy construct and the faced Si$^+$. We tentatively assign the configuration $L1$ of the $\equiv$Si$^\bullet$ moiety to an E'_β-like center,[18] in which the bonds of the three basal O with the near neighbors Si are on the same side of the unpaired electron orbital (backward projection). A similar atomic arrangement was proposed for E'_2 in quartz[28] and E'_β (generated at low temperature),[18] to justify a more symmetric line shape. Consequently, we assume that in the configuration $L2$ these bonds are in the opposite side of the unpaired electron (forward projection). The interconversion from $L2$ to $L1$ corresponds to Si$^\bullet$ crossing through the plane of the basal O atoms. We note that this movement does not affect the structure of the moiety and is expected to manifest as small variations in the line shape without changing the strong hyperfine structure, as experimentally observed. In this scheme the E'_β-like structure is energetically favored with respect to the other; in this sense our interpretation deviates from the prediction of the vacancy model where the energy minimum is expected when Si$^\bullet$ is forward projected attracted by Si$^+$. On the other hand, our interpretation seems to be consistent with the Uchino, Takahashi, and Yoko's model where the $\equiv$Si$^\bullet$ moiety could have two energy configurations, corresponding to two different distances from Si$^+$ in BHODC, with a minimum in the backward projection. We note, however, that in this model the g-value perturbation induced by Si$^+$ was not estimated.

To summarize, we have shown that E'_γ centers in silica have a configuration of minimum energy characterized by an axial line shape and a metastable state with an orthorhombic line shape separated by an energy barrier of ~34 meV. These results are interpreted assuming that the E'_γ center is confined to be an electron in a dangling orbital of a single silicon atom ($\equiv$Si$^\bullet$) coherently with the majority of reported spectroscopic features.[3,5,9,18] The line-shape variations observed are attributed to a migration of Si through the plane of the bonding O atoms. This model is suitable to explain the generation of the defect also from precursors different from the oxygen vacancy.[1,6,27,29]

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