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Optical absorption band at 5.8 eV associated with the E'_γ centers in amorphous silicon dioxide: Optical absorption and EPR measurements

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Line shape modifications induced by thermal treatment in the optical absorption and electron paramagnetic resonance (EPR) signals associated with the E'_γ center are experimentally investigated in various types of γ-irradiated amorphous silicon dioxide (a-SiO_2). The g values of the EPR main resonance line of the E'_γ center show a shift correlated with the peak energy variation of the absorption band at about 5.8 eV associated with this defect. These spectroscopic changes are proposed to originate from structural modifications of the defect environment. The correlation is theoretically explained considering that the spin-orbit interaction couples the g-tensor's elements and the electronic energy level distribution of the defect. Our results suggest that the optical band at 5.8 eV is due to an intracenter electron promotion from the Si—O bonding states to the dangling bond of the $O\equiv Si^\bullet$ moiety.

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I. INTRODUCTION

The E' centers in amorphous silicon dioxide (a-SiO_2) constitute from almost 50 years widespread investigated point defects.[1–3] Among the reasons of interest for these studies is the use of a-SiO_2 in many technological applications from microelectronics, as insulating layer of metal-oxide-semiconductor devices, to optics, as, for example, in fibers for light transmission. For all these applications, point defects and, in particular, the E' centers, cause charge traps and optical absorption bands determining the device failure.[1–6]

Of special interest in the family of E' centers is the E'_γ.[2,3,7] It is a paramagnetic point defect characterized by an almost axially symmetric g tensor, giving a characteristic electron paramagnetic resonance (EPR) signal around $g \approx 2.0006$ and by an hyperfine doublet split by 42 mT. On the basis of these spectral features, the microscopic model proposed for this defect, tested by many experimental and theoretical studies, consists in a dangling bond of a threefold coordinated silicon atom with the unpaired electron in an approximately sp^3 hybrid orbital: $O\equiv Si^\bullet$ (the symbol $\equiv$ represents single bonds to three oxygen atoms and the symbol $^\bullet$ stays for the unpaired electron).[2,3,8–13] Various origins of this point defect have been evidenced and many precursors have been suggested, both intrinsic, as the monovacancy of oxygen $O\equiv Si—Si\equiv O$ giving a charged E'_γ by trapping a hole, $O\equiv Si^{\bullet +}Si\equiv O$,[8–13] and extrinsic, as the $O\equiv Si—H$ and $O\equiv Si—Cl$ groups giving neutral E'_γ by the rupture of the bond and the release of the impurity, $O\equiv Si^\bullet + X$ (where $X = H, Cl$).[5,14] This assortment of precursors explains the ease of formation of E'_γ centers by mechanical stress or irradiation of a-SiO_2 materials and the observation of complex kinetics of growth of the concentration of the E'_γ under irradiation.[14,15] By contrast, it leaves open the question on the microscopic structure of the environment of the $O\equiv Si^\bullet$ moiety and the effects it could have on the spectral features of this defect.

Interestingly, independently from the precursor and from the procedure or type of irradiation (UV, x ray, γ ray, and β ray) that originates the defect, an optical absorption (OA) band centred at about 5.8 eV has been correlated to the E'_γ center.[5,6,16,17] Although this experimental evidence suggests that the electronic transition associated with the optical band should involve the $O\equiv Si^\bullet$ moiety, its nature has been extensively debated and mainly three electronic processes have been proposed and discussed.[6,18–23] On the basis of the observation of an analogous band peaked at 6.3 eV for the surface E' center, an intracenter electron transition involving states of the basal O atoms of the $O\equiv Si^\bullet$ moiety and the unpaired electron orbital has been proposed.[18,21] In contrast, another transition that has been suggested for the charged monovacancy structure, $O\equiv Si^{\bullet +}Si\equiv O$, consists in a charge transfer process from the $Si^\bullet$ atom on which the unpaired electron of E'_γ is localized to the facing one, Si^+.[19] *Ab initio* calculations provided the evidence that only the latter transition shows an oscillator strength compatible with the experimental one and drove the authors to the conclusion that this charge transfer process should apply for E'_γ.[21] This conclusion, however, is in contrast with the experimental observation of analogous oscillator strengths for bulk and surface E'_γ centers, where a charge transfer cannot occur.[6] Another model suggested that the OA originates from the $O\equiv Si^\bullet$ moiety terminating in the conduction band states,[20] and recent quantum calculations, applying the embedded cluster method to the charged monovacancy model, have shown that the electronic transition associated with the OA is due to a superposition of electron transition from the $O\equiv Si^\bullet$ toward delocalized states in the lower part of the conduction band and transition from valence band states perturbed by the defect to unoccupied states of the $O\equiv Si^\bullet$ moiety.[22,23]

Another still open question regarding the OA associated with the E' centers regards the attribution of two bands to these defects. In detail, the first work correlating the absorption band at 5.8 eV to the EPR signal of the E'_γ center suggested that another band was present peaked at 5.4 eV.[16] These two bands showed different thermal stabilities and were tentatively associated with two variants of E' in a-SiO_2 by similarity with the E'_1 and E'_2 centers of irradiated α-quartz.[6,16] This distinction has been reiterated and the two bands at 5.8 and 5.4 eV have been tentatively associated with E'_γ and E'_β, respectively.[5] Even if tentative and not fully clarified, until recently, this distinction has been used to interpret the modifications of the OA observed in γ- and x-ray irradiated commercial a-SiO_2 samples.[24,25]

It has been recently shown that the EPR signal associated with E'_γ undergoes line shape changes both during irradiation and upon thermal treatments.[7,26–28] These modifications are evidenced by two typical line shapes denominated as L1 and L2, one corresponding to a more axial and the other to a more orthorhombic g tensor, respectively, and they have been attributed to a structural variation in the center.[7,27] A preliminary study has suggested that these structural modifications also affect the peak position of the OA band at 5.8 eV associated with E'_γ.[28] In the present work, a parallel investigation by OA and EPR measurements is reported for various types of a-SiO_2. It is shown that the modifications of the EPR and OA signals associated with the E'_γ center are well correlated independently from the material, supporting the attribution of the 5.8 eV OA band peak shift to a structural relaxation of E'_γ. We interpret this correlation considering that the spin-orbit interaction links the g-tensor values and the electronic state energies of the defect, and we find an indication that the OA band is due to an electron promotion from the Si—O bonding states to the unpaired electron orbital of the $O\equiv Si^\bullet$ moiety.

II. EXPERIMENTAL DETAILS

Here, we report the results obtained in four commercial a-SiO_2 materials representative of the standard types I–IV:[29] a natural dry, *Silica EQ906* (type I; nominal OH content of 20 ppm by weight);[30] a natural wet, *Herasil1* (type II; nominal OH content of 150 ppm by weight);[31] a synthetic wet, *Suprasil1* (type III; nominal OH content of 1000 ppm by weight);[31] and a synthetic dry, *Suprasil300* (type IV; with nominal OH content of less than 1 ppm by weight).[31] The following names will be used hereafter: Q906, Her1, S1, and S300. Samples with size of $5\times5\times1\ \mathrm{mm}^3$ were used, with the largest surfaces optically polished.

Each sample was preliminary exposed to γ-ray irradiation at a dose rate of $\sim$3 kGy/h at room temperature in a ^{60}Co source. The accumulated doses are 1800 kGy for Q906, 3000 kGy for Her1, 5000 and 8000 kGy for S1, and 8000 kGy for S300. The dose values were chosen to have a concentration of defects high enough and an EPR line shape of the E'_γ centers corresponding to that L2 evidenced for types I–IV a-SiO_2.[27]

EPR measurements were carried out at room temperature by using a Bruker EMX spectrometer working at 9.8 GHz (*X* band). To avoid line shape distortions and microwave saturation effects, the input power was fixed at 800 nW and the amplitude of the modulation field at 100 kHz was set at 0.01 mT. In order to determine the main spectroscopic g values of the E'_γ center from the EPR spectra,[32] accurate measurements of the microwave frequency have been carried out during the spectra acquisition, enabling us to evaluate the g's differences with a maximum error of $\pm0.000\,02$.

The concentration of the E'_γ centers was estimated by comparison of the double integral of the EPR signal to that of a sample in which the E'_γ center concentration was directly determined through the instantaneous diffusion method in spin echo decay measurements by using a pulsed EPR spectrometer.[33] The error associated with these concentrations is estimated to be $\sim$20%.

OA measurements in the range 3.0–6.2 eV have been carried out by a double beam spectrophotometer Jasco V-570, using a bandwidth of 2 nm ($\sim$0.05 eV at 5.8 eV). The accuracy of the measured amplitude was 10%. Further measurements in the range 4.6–8.0 eV, which extends into the vacuum-UV region, were carried out by employing a single beam ACTON SP-150 spectrophotometer working in N_2 flux atmosphere and using a bandwidth of $\sim$2.8 nm.

After the γ-ray irradiation, all the samples were subjected to the same sequence of isochronal thermal treatments in the temperature range 330–950 K in air atmosphere. For any given temperature, each sample was kept inside an electric furnace for 25 min and successively it was cooled to room temperature for measurements. The furnace temperature was controlled by a digital system and was stabilized within ±3 K.

III. EXPERIMENTAL RESULTS

No EPR signal was detected in unirradiated samples. After irradiation at the final doses, all the samples showed the E'_γ center signal. The concentration of these defects differs somehow from sample to sample depending on the irradiation history. As reported in Fig. 1(a), minor differences in the EPR line shapes are found. From the reported spectra, the principal values of the g tensor have been estimated,[32] and in Table I a summary of the differences of g_2 (zero crossing position) and g_3 (minimum position) with respect to g_1 (maximum position) is reported together with the concentration of the centers. The values of $\Delta g_{1,2}=(g_1-g_2)$ and $\Delta g_{1,3}=(g_1-g_3)$ found are in agreement with those reported for E'_γ centers with the L2 type of line shape.[3,7,27] This peculiarity of the EPR line shape speaks for a prevalent contribution to the EPR spectra by E'_γ centers generated from oxygen vacancies, where the orthorhombic symmetry of the L2 line shape originates from the perturbative role played by the $^+Si\equiv O$ moiety.

As reported in Fig. 1(b), the OA measurements of the irradiated samples have shown that various bands are induced and, among them, the OA band at about 5.8 eV associated with the E'_γ centers emerges in all the samples. It can be observed that this band dominates the spectra of Q906 and Her1, and in the synthetic samples an additional band is clearly distinguishable in the low energy side of the spectra. An analysis with Gaussian bands of the OA spectra of all the considered samples has been carried out by using four bands. These bands have been singled out in the spectrum of the S300 sample, in which the absorption is more structured. As shown in the inset of Fig. 1(b), the latter spectrum has been fitted with a band peaked at 4.8 eV with a full width at half maximum (FWHM) of 0.94 eV, a band peaked at 5.02 eV (FWHM=0.36 eV), a band at 5.74 eV (FWHM=0.75 eV), and a band at 6.25 eV (FWHM=0.59 eV). The spectral features of the first three bands are in agreement with those usually reported for the nonbridging oxygen hole center, the oxygen deficient center [ODC(II)], and the E'_γ center,

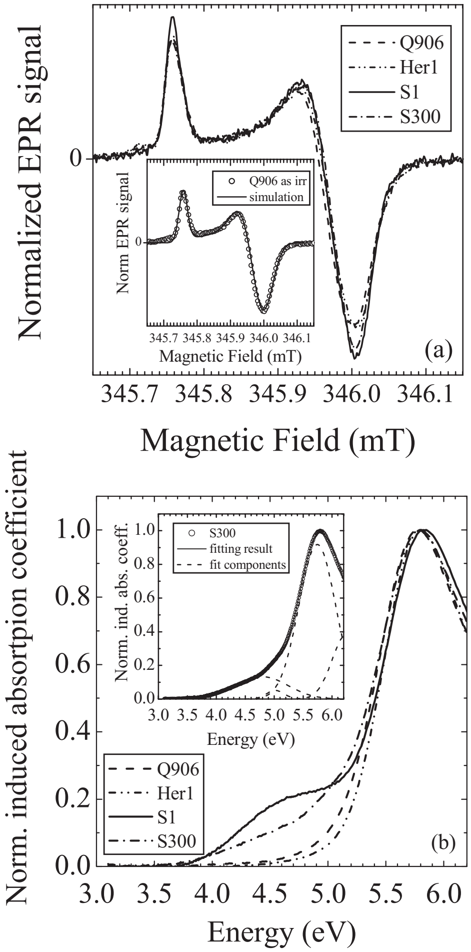

FIG. 1. (a) EPR spectra normalized to the double integral of the as-irradiated samples. The data are horizontally shifted to make the first maximum coincide; in the inset, the simulation of the spectrum with the SIMFONIA software (Ref. 35) is compared to the experimental spectrum of the Q906 sample. (b) Induced optical absorption spectra of the as-irradiated samples normalized to the maximum absorption coefficient; in the inset, experimental spectrum (circles) of sample S300 fitted using Gaussian bands. The fit result is indicated by a full line and the component bands by dashed lines.

respectively.[6] The latter band is instead introduced to take into account the absorption profile on the high energy shoulder of the E'_γ center band. It is worth noting that the presence of the band of the ODC(II) is also supported by photoluminescence measurements.[34] The same Gaussian decomposition has been used for the other samples by fixing all the band spectral features but for the E'_γ band. From this decomposition, it emerges that the band associated with the E'_γ centers gives more than 70% of the UV absorption in all the investigated samples. Furthermore, the spectral features of this band change, somehow depending on the sample, as summarized in Table I.

After the irradiation, the samples have been thermally treated. It is found that the EPR signal of the E'_γ centers undergoes gradual modifications of shape and, finally, the same line shape is attained in all the samples, as reported in Fig. 2(a). This line shape is characterized by the values $\Delta g_{1,2}=0.001\,25$ and $\Delta g_{1,3}=0.001\,47$ in agreement with the L1 type of line shape.[26] It is worth noting that in the natural dry sample, the spectroscopic changes by thermal treatments occur when the E'_γ center concentration variation is less than 10%.

In order to further substantiate the empiric determination of the g-tensor main values,[32] we have carried out EPR powder pattern spectra simulations employing the SIMFONIA software by Bruker.[35] This enables us to determine the g-tensor main values by using Gaussian line shape functions. We fixed the value of g_1 and varied g_2 and g_3 and the linewidths (FWHM) for all the main g values until reasonable agreement was found between experimental data and simulations. As shown in the insets of Figs. 1(a) and 2(a), for the Q906 sample irradiated and thermally treated at 510 K, respectively, reasonably good simulations of the spectra can be obtained. It is worth noticing that the simulation of each experimental spectrum requires different principal g values, their estimated error being $\pm 0.000\,02$. A summary of the results is reported in Table II, where it can be observed that the differences of g-tensor main values are in agreement with the empiric determination of the same differences. Similar agreement was also found for the other investigated samples.

Together with the EPR signal, we have observed modifications in the OA spectra, as reported in Fig. 2(b) for the Her1 material. Apart from the amplitude variations of the other bands, it is found that the E'_γ center OA band undergoes amplitude variations and a blueshift. This effect is found in all the investigated samples and occurs in opposite direction to previous findings.[16] In the inset of Fig. 2(b), the OA spectra corresponding to the EPR ones reported in Fig. 2(a) are shown. It can be observed that the peak position of the band related to the E'_γ centers is almost coincident for all the

TABLE I. Sample name, irradiation dose, concentrations of E'_γ centers, differences between the g-tensor main values [$\Delta g_{1,2}=(g_1-g_2)$ and $\Delta g_{1,3}=(g_1-g_3)$], and spectral features of the absorption band at about 5.8 eV of the investigated samples before the thermal treatments.

					Absorption band	
Sample	Dose (kGy)	E'_γ concentration (centers/cm^3)	$\Delta g_{1,2}$ (10^{-3})	$\Delta g_{1,3}$ (10^{-3})	Center (eV)	FWHM (eV)
Q906	1800	1.4×10^{17}	1.15	1.43	5.70	0.75
Her1	3000	1.5×10^{17}	1.16	1.43	5.75	0.68
S1	8000	5.0×10^{16}	1.17	1.43	5.77	0.70
S300	8000	8.6×10^{16}	1.19	1.43	5.74	0.75

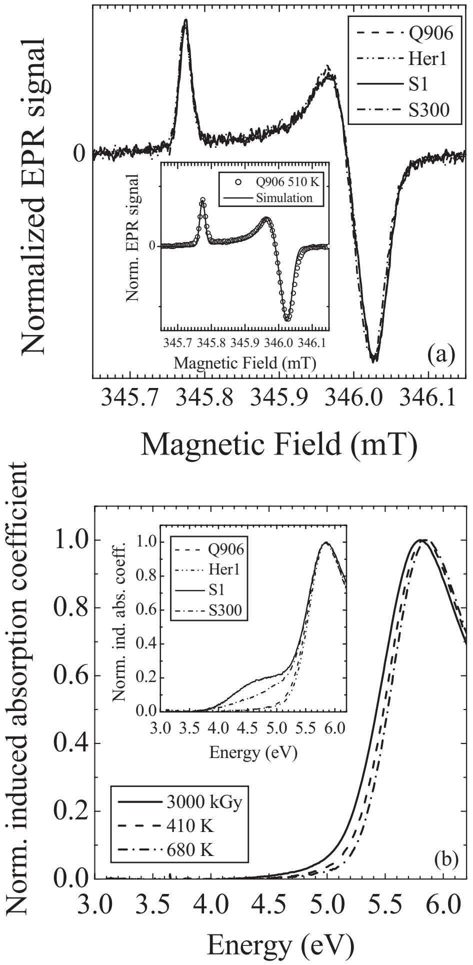

FIG. 2. (a) EPR spectra normalized to the double integral of the samples thermally treated at 510 K for Q906, 600 K for Her1, 490 K for S1, and 700 K for S300. The data are horizontally shifted to make the first maximum coincide; in the inset, the simulation of the spectrum with the SIMFONIA software (Ref. 35) is compared to the experimental spectrum of the Q906 sample. (b) Induced optical absorption spectra of the H1 sample as irradiated and thermally treated at 410 and 680 K normalized to the maximum absorption coefficient; in the inset, induced optical absorption spectra of the samples thermally treated at 510 K for Q906, 600 K for Her1, 490 K for S1, and 700 K for S300 normalized to the maximum absorption coefficient.

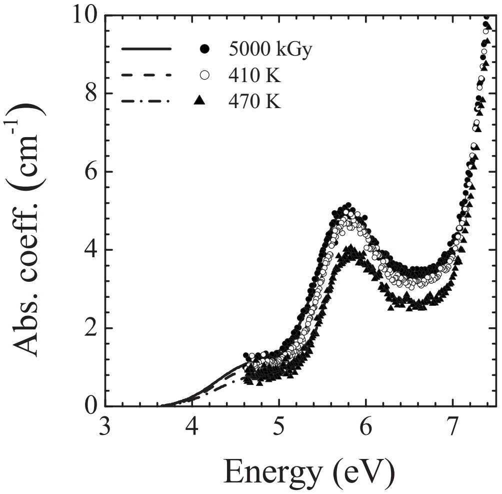

FIG. 3. Optical absorption spectra in the UV (lines, double beam spectrophotometer) and VUV (points, single beam spectrophotometer) of the S1 sample as irradiated at 5000 kGy and after thermal treatments at 410 and 470 K.

samples. The Gaussian decomposition of the spectra acquired after each thermal treatment has been carried out using the same procedure illustrated above, by fixing all the band spectral features but for the band associated with the E'_γ center. A good fitting of the data is obtained for all the temperatures, confirming amplitude reduction of all the component bands and blueshift of the E'_γ center band. This effect gradually occurs for all the samples in the same temperature range in which the EPR line shape is modified and, finally, the E'_γ center band is peaked at 5.79 ± 0.01 eV for all the thermally treated samples. A further investigation of OA modifications by thermal treatments has been carried out with material S1 extending the spectra to the vacuum-UV range in a sample irradiated at 5000 kGy. In Fig. 3, the OA spectra are reported for the as-irradiated sample and for some temperatures at which the modifications are also found in the EPR line shape. It can be observed that the E'_γ OA band peak shifts toward higher energy on increasing the thermal treatment temperature; furthermore, a monotonic amplitude reduction of the overall OA above 6 eV is evident. These findings rule out the possibility that the shift of the E'_γ OA band peak can be attributed to changes of absorption at higher energy. Indeed, we note that the absorption at ~6.6 eV maintains almost the same amplitude ratio with respect to the ~5.8 eV peak. A Gaussian decomposition procedure similar to the one applied for the UV range, with free parameters only for the E'_γ center OA band, has confirmed that the peak position of this band undergoes a blueshift by thermal treatment.

In order to investigate the relationship between the changes in the optical band and those in the EPR line shape associated with the E'_γ centers, we have determined for each sample and for the various thermal treatments the shift of the

TABLE II. Powder pattern line shape simulation (Ref. 35) results for sample Q906; main g values and differences between the g-tensor main values [$\Delta g_{1,2}=(g_1-g_2)$ and $\Delta g_{1,3}=(g_1-g_3)$].

Sample	g_1	g_2	g_3	$\Delta g_{1,2}$ (10^{-3})	$\Delta g_{1,3}$ (10^{-3})
Q906 as irradiated	2.00173	2.00059	2.00032	1.14	1.41
Q906 thermally treated at 510 K	2.00173	2.00049	2.00027	1.24	1.46

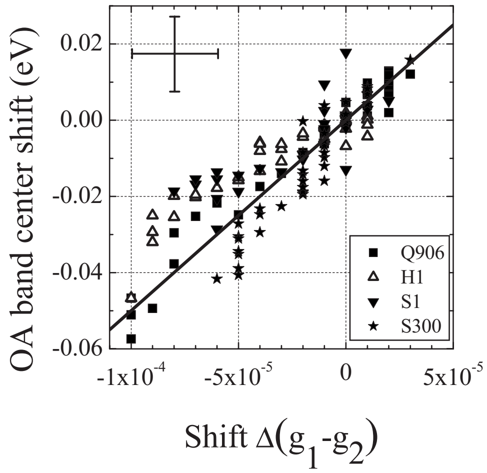

FIG. 4. Shifts induced by the thermal treatments of the peak position of the Gaussian band at about 5.8 eV, derived from the fitting of the optical absorption spectra, as a function of the variation of $\Delta g_{1,2}=(g_1-g_2)$ of the corresponding EPR spectra for E'_γ. The differences are calculated with respect to the values obtained from the spectra reported in Figs. 2(a) and 2(b) (inset). The straight line is obtained by inserting in Eq. (3) $|\lambda|=0.02$ eV, $\beta^2=0.65$, $E_b=5.8$ eV, and $E_t=8.5$ eV.

peak position of the OA band with respect to the value found for the spectra in the inset of Fig. 2(b) and the shift of $\Delta g_{1,2}$ relative to the value of the spectra of Fig. 2(a). In Fig. 4, these shifts are reported for all the investigated samples and they show a good correlation for all the thermal treatments, suggesting a connection between the thermally induced spectroscopic changes.

IV. DISCUSSION

The above reported data evidence that the EPR line and the OA band associated with E'_γ undergo correlated modifications, as shown in Fig. 4 for the changes of the OA band peak position and of the EPR signal g values. The differences between one and the other spectral features are small but above the experimental uncertainty and can be induced by irradiation or by thermal treatments. The variations of the EPR line shape induced by the thermal treatments can be attributed to changes in the defect environment and, in particular, these treatments bring the center toward a more axially symmetric surrounding.[7,27] The details of the microscopic structural modification induced in the defect could consist in a relaxation from a forward unpaired electron orbital configuration (the orbital points in the opposite direction with respect to that of the back bonds between basal O and nearest neighbor Si in the $O\equiv Si^\bullet$ moiety)[13,36] to a backward configuration. On this basis, it can be concluded that the shift of the 5.8 eV OA band reflects the various structural configurations of the E'_γ centers.

In the charged oxygen vacancy model for the E' center in α-quartz, the suggestion has been given that the electron could be trapped by the Si atoms facing the vacancy on a short bond or on a long bond (in this latter case with an additive H atom linked to the other Si).[16] These configurations have been named E'_1 and E'_2, in α-quartz, and their analogous configurations in silica are usually named E'_γ and E'_β and are associated with OA bands at 5.8 and 5.4 eV, respectively.[5,16] It has been suggested that by thermal treatments[16] and irradiation,[25] the two defects are responsible for the changes of the OA shape. In our experiments, from the difference of the absorption spectra of the as-irradiated samples and those of the corresponding thermally treated ones [reported in Fig. 2(b)], a band peaked at 5.4 eV having FWHM of 0.5 eV can be evidenced (not reported here). This band could be related to that usually employed to fit the OA spectra assuming the presence of E'_β centers.[16,25] If the changes observed in the OA spectra were due to the E'_β center annealing, as should be guessed from the bleaching of a band at 5.4 eV, a related modification of the EPR line shape should also occur. In detail, since the EPR component associated with the E'_β centers has an axial g tensor,[7] removal of E'_β should give rise to an EPR line shape of lower symmetry. This is in evident contrast to our experimental findings that the thermal treatments induce an increase of symmetry in the EPR line shape. Basing on our observation that spectral changes occur at almost constant concentration of E' centers and also on the basis that a gradual modification of the line shape in the EPR spectra occurs, it is more reasonable to assume that the E'_γ structural changes give rise to the spectral modifications rather than the presence of a further defect, E'_β, whose concentration changes in an anticorrelated manner to that of E'_γ.

In connection to the correlation of the changes in the EPR spectral features with the changes in the optical features of the E'_γ center reported in Fig. 4, it should be considered that the shifts of the g-tensor principal values from the free electron value, $g_e=2.0023$, are related to the energy separation of the electronic ground and excited states of the paramagnetic molecular group by the spin-orbit coupling.[37–41] For the E'_γ center, the unpaired electron is strongly localized in an sp^3-like hybrid orbital of Si,[38,42] so it is legitimate to assume that the electronic orbitals used for the calculation of the g shifts mainly pertain to the molecular cluster ($O\equiv Si^\bullet$) formed by the Si hosting the unpaired electron and the bonded basal O atoms.[39,40] It is further considered that in a first approximation, the g tensor of the E'_γ center approximates the axial symmetry expected for an electron in a broken tetrahedron configuration.[39,40] On this basis, using perturbation theory treatment of the spin-orbit interaction, the shifts of the g-tensor principal values are dependent on the energy separation between the dangling bond electron ground state and the Si—O bonding and antibonding states of the molecular cluster according to the following formulas:[39–41]

$$g_\parallel \cong g_e, \tag{1}$$

$$g_\perp \cong g_e + \left(\frac{1}{E_b} - \frac{1}{E_a}\right)|\lambda|\beta^2, \tag{2}$$

where E_a and E_b, as sketched in Fig. 5, represent the separation in energy between the dangling bond electron state and the antibonding and bonding states localized at the de-

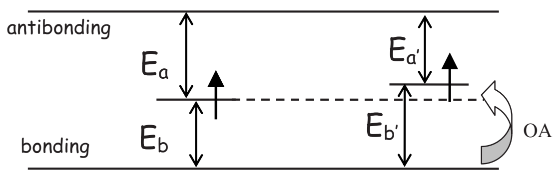

FIG. 5. Schematic energy level diagram showing the unpaired electron state of the E'_γ center between the $O\equiv Si^\bullet$ moiety bonding and antibonding states. E_b and E_a are the energy separations of the unpaired electron state from the bonding and antibonding states, respectively. On the right part of the diagram, the change due to thermally induced structural modifications is sketched together with the electronic transition associated with the optical absorption of the E'_γ center.

fect, respectively, $g_\parallel$ and $g_\perp$ correspond to the principal g-tensor values, $|\lambda|$ is the modulus of the spin-orbit interaction constant for the $3p$ electron of atomic Si, and β^2 is the percentage of $3p$ character in the dangling bond orbital of the unpaired electron. The difference of principal g values is derived from Eqs. (1) and (2) and its variation is given by

$$\begin{aligned}\delta\Delta g_{\parallel,\perp} &\cong \delta\Delta g_{1,2} = \delta(g_1 - g_2)\\ &\cong \left[\frac{1}{(E_t - E_b)^2} + \frac{1}{E_b^2}\right] \cdot |\lambda|\beta^2 \cdot \delta E_b, \end{aligned} \tag{3}$$

in which we have assumed that $(E_a + E_b) = E_t = \text{const}$. This assumption is motivated by the observation that by thermal treatments, the 42 mT hyperfine doublet of E'_γ does not change splitting.[43,44] This result suggests that the orbital of the unpaired electron is essentially unchanged and as a consequence also the moiety, $O\equiv Si^\bullet$, in which it resides. From Eq. (3), it is expected that the change of $\Delta g_{1,2}$ is related to the variation of E_b (or analogously of E_a). In our experimental results reported in Fig. 4, a correlation between the change of $\Delta g_{1,2}$ and the shift of the OA band peak position is found. This result suggests that the energy of the electronic transition associated with the E'_γ center OA should be equal to E_a or E_b. In this respect, individuating which one of the latter two energies coincides with the OA band peak energy E_{OA} will give information on the electronic transition process associated with the OA. In fact, E_b is related to the electron promotion from the Si—O bonding states to the dangling bond orbital, whereas E_a is related to a promotion of the unpaired electron to Si—O antibonding states.[38–40] It is useful to note that our experimental observations, Fig. 4, evidence that when $\Delta g_{1,2}$ increases, the peak of the OA band has a blueshift ($\delta E_{\text{OA}} > 0$). On the basis of Eq. (3), it can then be assumed that $E_{\text{OA}} = E_b$; indeed, under this hypothesis, a blueshift of the OA peak energy ($\delta E_{\text{OA}} = \delta E_b > 0$, see Fig. 5) should give an increase of $\Delta g_{1,2}$ (by contrast, if $E_{\text{OA}} = E_a$, a blueshift of the peak energy would give a decrease of $\Delta g_{1,2}$). We can conclude that the OA process should be mainly ascribed to an electron promotion from the bonding states of the $O\equiv Si^\bullet$ moiety to the dangling bond unpaired electron state. It is interesting to note that assuming $|\lambda| = 0.02$ eV, as estimated for the $3p$ atomic orbital of Si,[39] and $\beta^2 = 0.65$, as estimated for the E'_γ center,[8,38] from Eq. (3) we obtain good agreement between theory and data inserting $E_b = 5.8$ eV and $E_t = 8.5 \pm 0.5$ eV, as shown in Fig. 4. The obtained value of E_t is compatible with band gap values of silica, somehow supporting that bonding and antibonding states at the defect should reside near band gap levels.[2,3]

Recent computational works based on the embedded cluster method have predicted that the transition associated with the E'_γ center should consist in a charge transfer from valence band states to unoccupied states of the $O\equiv Si^\bullet$ moiety in agreement with our prediction.[22,23] Furthermore, they have shown that structural changes in the E'_γ center lead to changes in the OA in addition to changes in the g-tensor's values.[22,23] Even if these predictions qualitatively agree with our experimental observations of spectral changes, the computations show that changing the E'_γ center configuration from forward- toward back-projected, the OA band energy position has a redshift. Since the back-projected E'_γ center corresponds to the more axially symmetric EPR line shape in those calculations, a similar configuration should correspond to that found after the thermal treatments of the materials considered in the present work. However, our experimental findings show a blueshift of the peak of the E'_γ OA band, which is in quantitative contrast to computed predictions.[22,23] On these basis, the changes from forward- toward back-projected configurations cannot be the explanation of our findings. At variance, it is guessed that the $^+Si\equiv O$ structure, facing the $O\equiv Si^\bullet$ moiety in the charged oxygen vacancy model for the E'_γ center, could be responsible for the observed spectroscopic changes. In this case, in fact, it is reasonable that the energy of the occupied dangling bond state could change without a relevant variation, to a first approximation, of the energy levels of the three Si—O back bonds involved in the $O\equiv Si^\bullet$ molecule, as they are rigidly connected to the rest of the a-SiO_2 matrix. By contrast, if the conversion of EPR and OA features were due to a structural change involving the $O\equiv Si^\bullet$ moiety, then all the energetic levels of this molecular group should change and the correlation described by Eq. (3), in which $E_a + E_b$ has been considered a constant, should fail. Consequently, the quite good agreement shown in Fig. 4 suggests that the thermally induced conversion of spectroscopic features should involve a change of the perturbative effect of the structure facing the $O\equiv Si^\bullet$ moiety in the charged oxygen vacancy model for E'_γ, instead of a structural change of the $O\equiv Si^\bullet$ moiety itself.

V. CONCLUSIONS

We have reported that postirradiation heating of silica materials induces variations in the EPR line shape and in the optical absorption band at about 5.8 eV associated with the E'_γ center. These changes are shown to be correlated, indicating that they have the same origin, and we evidenced that they should be attributed to a structural modification of the neighborhood of the $O\equiv Si^\bullet$ moiety. This change of structure is interpreted in terms of the modification of the perturbative role of the $^+Si\equiv O$ structure in the charged oxygen vacancy model for the E'_γ center.

The link between changes of the EPR resonance line g values and the shift of the optical absorption band peak energy is explained by the use of the broken tetrahedron model for the E'_{γ} center and the relation among the energy level distribution of the molecular structure and the g tensor due to the spin-orbit coupling. The direction of the shift of the g-tensor main values and of the energy of the optical band peak have also enabled us to suggest that the electronic transition associated with the optical absorption of the E'_{γ} center is due to an electron promotion from the defect related bonding states to the unpaired electron level furnishing further insight on this widely studied defect.

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

[2] *Structure and Imperfections in Amorphous and Crystalline Silicon Dioxide*, edited by R. A. B. Devine, J. P. Duraud, and E. Dooryhée (Wiley, Chichester, 2000).

[3] *Defects in* $\mathrm{SiO_2}$ *and Related Dielectrics: Science and Technology*, edited by G. Pacchioni, L. Skuja, and D. L. Griscom (Kluwer Academic, Dordrecht, 2000).

[4] F. B. McLean, H. B. Boesch, Jr., and T. R. Oldham, in *Ionizing Radiation Effects in MOS Devices and Circuits*, edited by T. P. Ma and P. V. Dressendorfer (Wiley, New York, 1989).

[5] D. L. Griscom, J. Ceram. Soc. Jpn. **99**, 899 (1991).

[6] L. Skuja, J. Non-Cryst. Solids **239**, 16 (1998).

[7] D. L. Griscom, Nucl. Instrum. Methods Phys. Res. B **1**, 481 (1984).

[8] D. L. Griscom, E. J. Friebele, and G. H. Sigel, Jr., Solid State Commun. **15**, 479 (1974).

[9] M. Boero, A. Pasquarello, J. Sarnthein, and R. Car, Phys. Rev. Lett. **78**, 887 (1997).

[10] T. Uchino, M. Takahashi, and T. Yoko, Phys. Rev. Lett. **86**, 5522 (2001).

[11] Zhong-Yi Lu, C. J. Nicklaw, D. M. Fleetwood, R. D. Schrimpf, and S. T. Pantelides, Phys. Rev. Lett. **89**, 285505 (2002).

[12] M. M. G. Alemany and James R. Chelikowsky, Phys. Rev. B **68**, 054206 (2003).

[13] S. Mukhopadhyay, P. V. Sushko, A. M. Stoneham, and A. L. Shluger, Phys. Rev. B **70**, 195203 (2004).

[14] H. Imai and H. Hirashima, J. Non-Cryst. Solids **179**, 202 (1994).

[15] V. A. Mashkov, W. R. Austin, L. Zhang, and R. G. Leisure, Phys. Rev. Lett. **76**, 2926 (1996).

[16] R. A. Weeks and E. Sonder, in *Paramagnetic Resonance II*, edited by W. Low (Academic, New York, 1963), p. 869.

[17] R. Boscaino, M. Cannas, F. M. Gelardi, and M. Leone, Nucl. Instrum. Methods Phys. Res. B **113**, 373 (1996).

[18] A. A. Bobyshev and V. A. Radtsig, Kinet. Katal. **29**, 638 (1988).

[19] D. L. Griscom, in *Proceedings 33rd Frequency Control Symposium* (Electronics Industries, Washington, DC 1979), p. 98.

[20] D. L. Griscom, J. Non-Cryst. Solids **73**, 51 (1985).

[21] G. Pacchioni, G. Ieranó, and A. M. Marquez, Phys. Rev. Lett. **81**, 377 (1998).

[22] S. Mukhopadhyay, P. V. Sushko, V. A. Mashkov, and A. L. Shluger, J. Phys.: Condens. Matter **17**, 1311 (2005).

[23] L. Giordano, P. V. Sushko, G. Pacchioni, and A. L. Shluger, Phys. Rev. B **75**, 024109 (2007).

[24] Y. Kawaguchi and N. Kuzuu, J. Appl. Phys. **80**, 5633 (1996).

[25] N. Kuzuu and H. Horikoshi, J. Appl. Phys. **97**, 093508 (2005).

[26] L. Zhang and R. G. Leisure, J. Appl. Phys. **80**, 3744 (1996).

[27] S. Agnello, R. Boscaino, G. Buscarino, M. Cannas, and F. M. Gelardi, Phys. Rev. B **66**, 113201 (2002).

[28] S. Agnello, R. Boscaino, G. Buscarino, and F. M. Gelardi, J. Non-Cryst. Solids **351**, 1801 (2005).

[29] G. Hetherington, K. H. Jack, and M. W. Ramsay, Phys. Chem. Glasses **6**, 6 (1965).

[30] Quartz and Silice, Nemours, France, Catalogue No. OPT-91-3.

[31] Heraeus Quartzglas, Hanau, Germany, Catalogue No. POL-0/102/E.

[32] F. K. Kneubühl, J. Chem. Phys. **33**, 1074 (1960).

[33] S. Agnello, R. Boscaino, M. Cannas, and F. M. Gelardi, Phys. Rev. B **64**, 174423 (2001).

[34] S. Agnello and L. Nuccio, Phys. Rev. B **73**, 115203 (2006).

[35] SIMFONIA software, Bruker BioSpin.

[36] D. L. Griscom and M. Cook, J. Non-Cryst. Solids **182**, 119 (1995).

[37] J. A. Weil, J. R. Bolton, and J. E. Wertz, *Electron Paramagnetic Resonance* (Wiley, New York, 1994).

[38] R. H. Silsbee, J. Appl. Phys. **32**, 1459 (1961).

[39] G. D. Watkins and J. W. Corbett, Phys. Rev. **134**, A1359 (1964).

[40] F. J. Feigl and J. H. Anderson, J. Phys. Chem. Solids **31**, 575 (1970).

[41] G. Gobsch, H. Haberlandt, H. J. Weckner, and J. Reinhold, Phys. Status Solidi B **90**, 309 (1978).

[42] D. L. Griscom, Phys. Rev. B **20**, 1823 (1979).

[43] G. Buscarino, S. Agnello, and A. Parlato, Phys. Status Solidi C **4**, 1301 (2007).

[44] G. Buscarino, Ph.D. thesis, University of Palermo, Italy, 2007; arXiv:0711.4029 (unpublished).