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Hyperfine structure of the E'_δ centre in amorphous silicon dioxide

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Abstract

We report a comparative study by electron paramagnetic resonance (EPR) of the E'_δ point defect and of the 10 mT doublet in γ-ray irradiated amorphous silicon dioxide. Our experimental investigation, carried out on three distinct materials and for an overall variation of one order of magnitude of the concentration of defects, shows a quite general linear correlation between the two EPR signals. This result definitively supports the attribution of the 10 mT doublet to the hyperfine structure of the E'_δ centre, originating from the interaction of the unpaired electron with a nucleus of ^{29}Si ($I = 1/2$).

1. Introduction

In the past five decades many efforts have been dedicated to the study of amorphous silicon dioxide (a-SiO_2) [1–4], primarily because this material is employed in many technologically relevant devices in the fields of optics and microelectronics. However, the proper working of these devices is often prevented by the growth of point defects in the a-SiO_2 matrix, induced in the manufacturing process or due to exposition to ionizing radiation [3, 4].

One of the most important point defects in a-SiO_2, especially in the field of microelectronics, is the E'_δ centre [1–4]. The main spectroscopic evidence of this defect consists in a nearly symmetric electron paramagnetic resonance (EPR) line shape with $g \sim 2.002$ [5], where g is the spectroscopic splitting factor. Since its first observation [5], a relevant matter was the identification and the characterization of the hyperfine structure, arising from the interaction of the unpaired electron of this centre with a nucleus of ^{29}Si ($I = 1/2$, 4.7% natural abundance). In the experiments made by Griscom *et al* [5], a sample was x-ray irradiated at 77 K to induce E'_δ centres and successively it was subjected to a series of isochronal thermal treatments at higher temperature. Since in the temperature range from 520 to 670 K the main EPR resonance of the E'_δ centre was found to anneal with a similar rate with respect to a pair of lines split by 10 mT, this doublet was supposed to constitute the hyperfine doublet of the E'_δ

centre. Furthermore, in the same work it was shown that for temperatures lower than 520 K no similar annealing rate occurs. This disagreement was attributed to the presence under the 10 mT doublet of the EPR signals arising from the $M_s = -1 \leftrightarrow M_s = 0$ and $M_s = 0 \leftrightarrow M_s = +1$ transitions of a distinct point defect in a spin triplet state (pair of coupled electrons with total spin $S = 1$) [5]. This triplet centre is usually observed in the same materials in which the E'_δ centre is induced [5–8], and is also characterized by a resonance with $g \sim 4$, due to the weakly allowed transition $M_s = -1 \leftrightarrow M_s = +1$ [5].

Further support for the attribution of the 10 mT pair to the hyperfine doublet of the E'_δ centre has been given by our recent experimental study of a room-temperature γ-ray irradiated oxygen deficient silica, *Pursil 453* [8]. This sample was subjected to isochronal thermal treatments and, also in this case, a similar annealing behaviour was observed above ∼450 K for the E'_δ and for the 10 mT doublet [8]. However, a detailed quantitative analysis of the correlation between these two EPR signals was not attempted.

A sure ascription of the 10 mT doublet to the hyperfine interaction of the E'_δ centre represents a basic step towards the determination of a definitive microscopic model of this defect. In fact, until now, four different microscopic structures have been proposed for the E'_δ centre (for an exhaustive review of the models see [8]) [5–7, 9]. The simplest of these consists in an ionized single oxygen vacancy, with the two silicon atoms in a dimer configuration and nearly equally sharing the unpaired electron wavefunction [6]. This model has been supported by many computational works mainly on the basis of the predicted hyperfine doublet split by ∼10 mT [10–17], in agreement with that proposed by Griscom *et al* [5]. In the other proposed models the E'_δ centre is supposed to consist in an unpaired electron delocalized over a pair of nearby oxygen vacancies [7, 8], or of a nanocluster of five silicon atoms [8, 9]. In order to support one or other model, a key role is played by the intensity ratio between the 10 mT doublet and the main resonance line of the E'_δ centre, that should assume distinct values depending on the number of Si atoms surrounding the unpaired electron. In this respect, the value of ∼0.16 recently determined for such a ratio suggests that the unpaired electron wavefunction is delocalized over four Si atoms [8].

In spite of its relevance, as comes from the above discussion, the experimental studies supporting the attribution of the 10 mT doublet to the hyperfine structure of the E'_δ centre are at present very limited. In order to bridge this gap we have performed an experimental investigation on three distinct materials subjected to isochronal and isothermal treatments at two distinct temperatures, aiming to demonstrate the general strict correlation between the EPR signal of the 10 mT doublet and that of the E'_δ centre. The reported study extends and completes experimental results partially reported in [18]. We here include new and more comprehensive experimental data and also a more detailed discussion of the effects of the thermal treatments. The present paper is intended to represent a dedicated experimental investigation in which the attribution of the 10 mT doublet to the hyperfine structure of the E'_δ centre is definitively established.

2. Experimental details

The materials considered here are commercial-type a-SiO_2. Two of these are obtained from fused quartz, QC and Pursil 453 [19], while the third, KUVI [20], is synthesized by a vapour axial deposition technique. The optical absorption spectra of these materials show an intense band peaked at ∼7.6 eV of amplitude of ∼20 cm^{-1} for KUVI, and larger than 100 cm^{-1} for Pursil 453 and QC, characterizing them as oxygen-deficient silicon dioxide [21]. Furthermore, all these materials have an Al atom content of about 10^{17} cm^{-3} [19, 20]. One sample of Pursil 453 was irradiated at a dose of $\sim 10^3$ kGy and successively was subjected to an isochronal

thermal treatment from 330 to 800 K (the details of this experiment are reported in [8]). Two samples of the same KUVI material, hereafter referred to as KUVI/1 and KUVI/2, were simultaneously irradiated at a dose of ∼124 kGy and successively subjected to a series of isothermal treatments at a fixed temperature of 580 and 630 K, respectively. Finally a sample of QC was irradiated at ∼73 kGy and isothermally treated at 630 K. All the γ-ray irradiations were performed at room temperature. Isothermal treatment experiments were performed at different steps. In each step the sample was kept at a fixed temperature for a time t_0 and then was returned to room temperature to perform the EPR measurements. The time t_0 was varied from 30 s up to many minutes. EPR measurements were carried out at room temperature with a Bruker EMX spectrometer working at frequency $\nu \sim 9.8$ GHz in the first derivative unsaturated mode (FH-EPR) and in the high-power second-harmonic scheme (SH-EPR). The main resonance of the E'_δ and the $g \sim 4$ transition of the triplet centre were acquired with the first method, while the 10 mT doublet was detected with the high-sensitivity SH-EPR technique, due to its low intensity.

3. Results and discussion

We have reported [8] that in the sample Pursil 453 subjected to isochronal thermal treatments a growth of concentration of E'_δ centres occurs, concomitantly to the annealing of the paramagnetic $[AlO_4]^0$ defects. These features were supposed to arise from a hole transfer process from $[AlO_4]^0$ to the site precursors of E'_δ centres, thermally activated above 500 K. Here we have verified that a similar process occurs in the samples KUVI/1, KUVI/2 and QC, isothermally treated at 580, 630 and 630 K, respectively. In particular, we have found that the concentrations of E'_δ centres and of the 10 mT pair increase up to a total time of the isothermal treatment of ∼500 s; after that the hole transfer process is exhausted and both signals progressively anneal out. In all the irradiated samples the $g \sim 4$ resonance of the triplet was also detected. However, at variance from E'_δ centres, no growth of concentration occurs after thermal treatment. Furthermore, we have verified that after a treatment of about 60 s above 500 K this EPR signal disappears definitively, indicating the irreversible annealing of the triplet centre, in agreement with previous findings [5].

In figure 1(a), the FH-EPR spectrum of the sample KUVI/2 thermally treated for 60 s at $T = 630$ K is reported. In this spectrum the partially superimposed resonance lines of E'_δ and of the more common E'_γ centre are evident [1, 5, 22]. The FH-EPR signal intensity for the E'_δ centre was estimated from the height of the first positive peak in the spectrum of figure 1(a). In this portion of the spectrum, in fact, only the E'_δ centre contributes and no superposition with the resonance line of the E'_γ occurs [5]. In figure 1(b), we report the SH-EPR spectrum acquired over an extended region for the same sample. The inner pair of EPR lines of figure 1(b), split by 7.4 mT, are due to a hydrogenated point defect [23], while the outer pair, split by 10 mT, is the candidate hyperfine doublet of the E'_δ centre [5]. Due to the superposition of many EPR resonances, to estimate the SH-EPR signal of the 10 mT pair a fit procedure was necessary. Since in the central part of the SH-EPR spectra the signal intensity is saturated, the right and the left components of the 10 mT doublet were analysed separately. The procedure used to fit the SH-EPR spectra is illustrated in figure 2 for the right part of the spectrum. We have found that the experimental data can be properly fitted by a superposition of three Gaussian profiles: one describes the tail on the left of the spectra, while the other two Gaussians take into account the right components of the 7.4 mT and the 10 mT doublets. Finally, the SH-EPR intensity of the right component of the 10 mT doublet was obtained by simple integration of the Gaussian profile peaked at ∼354 mT. With a similar procedure the SH-EPR signal intensity of the left component of the 10 mT doublet was also estimated.

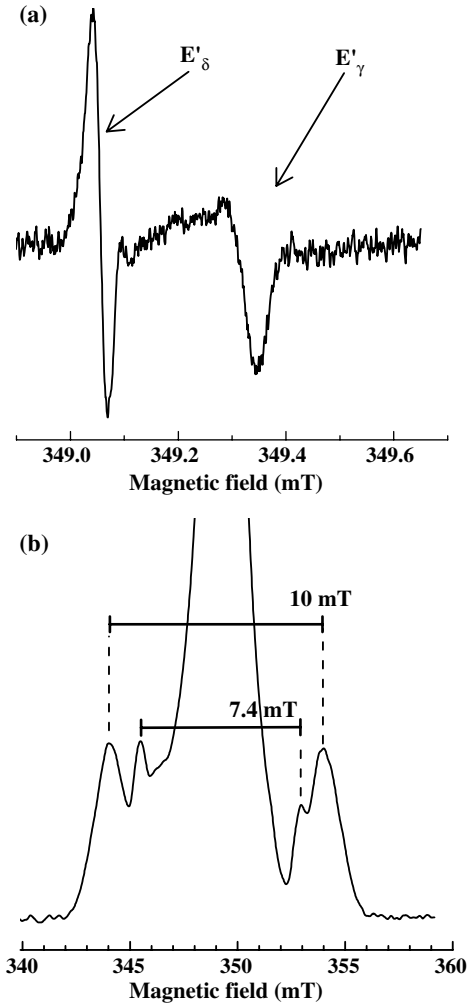

Figure 1. (a) FH-EPR spectrum for the sample KUVI/2 thermally treated for ∼60 s at $T = 630$ K, showing the partially superimposed resonance lines of E'_δ and E'_γ centres. (b) SH-EPR spectrum for the same sample acquired over an extended region and showing the 10 mT pair.

In figure 3(a) the SH-EPR signal intensity of the right component of the 10 mT as a function of the left component is reported, as detected during isothermal treatments of sample KUVI/2. The times near to the data points indicate the total duration of the isothermal treatments, while the straight line shows the linear dependence, for comparison. This figure points out a good linear correlation between the data points, indicating that the pair of lines split by 10 mT arises from a single paramagnetic centre and that the two components of the pair share nearly equal intensity. In figure 3(b) the total SH-EPR intensity of the 10 mT pair as a function of the FH-EPR intensity of the E'_δ centre is reported. Also in this case the two EPR signals are strictly correlated, supporting the assignment of the 10 mT doublet to the E'_δ centre.

The degree of generality of this result depends on the possibility to extend it to more than one material and for a large variation of the concentration of defects. To this aim, the same analysis here described for KUVI/2 was performed for Pursil 453, KUVI/1 and QC. The

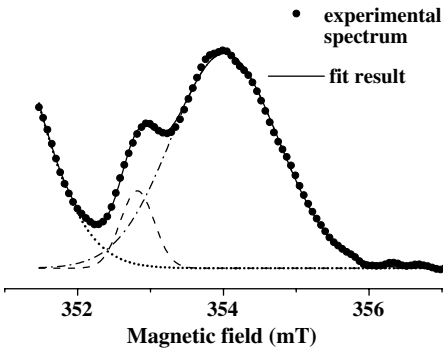

Figure 2. Right component of the 10 mT doublet detected by SH-EPR measurements. Broken lines indicate the three Gaussian components used to fit the experimental data.

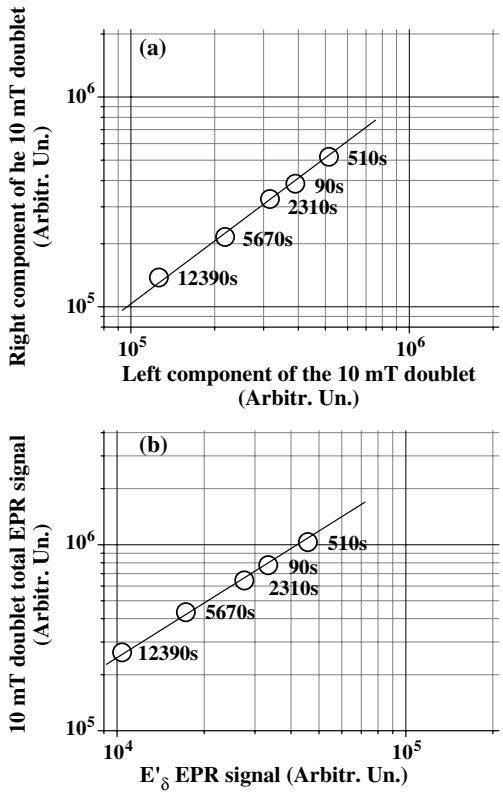

Figure 3. (a) SH-EPR signal intensity of the right component of the 10 mT as a function of the left component during isothermal treatments of sample KUVI/2. (b) SH-EPR total intensity of the 10 mT doublet as a function of the FH-EPR signal intensity of the E'_δ centre main resonance for the same sample. The dimensions of the symbols are comparable with the error on the measurements. The total durations of the isothermal treatments are indicated near to the data points. The straight lines, with slope 1, are superimposed on the data, for comparison.

experimental data obtained for the latter samples are collected in figure 4 and clearly show a severe correlation between the 10 mT doublet and the E'_δ centre for three distinct materials and for an overall variation of the EPR signals intensities of one order of magnitude.

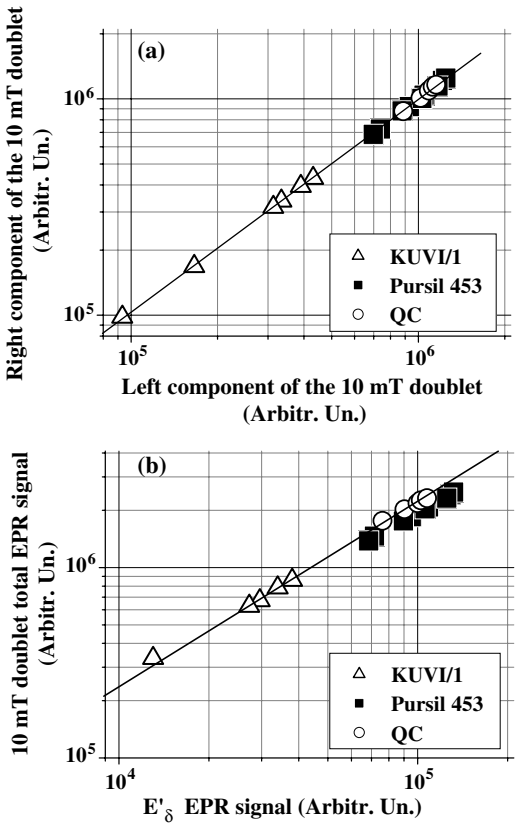

Figure 4. (a) SH-EPR signal intensity of the right component of the 10 mT as a function of the left component during isothermal treatments of samples Pursil 453, KUVI/1 and QC. (b) SH-EPR total intensity of the 10 mT doublet as a function of the FH-EPR signal intensity of the E'_δ centre main resonance for the same samples. The dimensions of the symbols are comparable with the error on the measurements. The straight lines, with slope 1, are superimposed on the data, for comparison.

4. Conclusions

In conclusion, our results quantitatively support the attribution of the 10 mT doublet to the hyperfine structure of the E'_δ centre, arising from the hyperfine interaction of the unpaired electron of the E'_δ centre with a nucleus of ^{29}Si ($I = 1/2$). Furthermore, the present work validates and enforces all the experimental and theoretical studies focused on the 10 mT doublet to explore the microscopic structure of the E'_δ centre in amorphous silicon dioxide [8, 10–14].

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