Polyamorphic transformation induced by electron irradiation in a-SiO_2 glass

G. Buscarino,* S. Agnello, F. M. Gelardi, and R. Boscaino
Department of Physical and Astronomical Sciences, University of Palermo, Via Archirafi 36, I-90123 Palermo, Italy
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We report a study by electron paramagnetic resonance of amorphous silicon dioxide (a-SiO_2) irradiated by 2.5 MeV electrons in the dose range from 1.2×10^3 to 5×10^6 kGy. By measuring the change in the splitting of the primary ^{29}Si hyperfine doublet of the E'_γ centers we evidenced an irradiation induced *local* (around the defects) densification of a-SiO_2. Our data show that the local degree of densification of the materials is significantly higher than that obtained by mean density measurements, suggesting that the structural modifications induced by electron irradiation take place prevalently within confined defective regions of the material. The overall results we have found have permitted us to obtain a detailed quantitative description of the electron irradiation-induced densification process of a-SiO_2 and to point out relevant physical properties which have for many years remained elusive. Among them, we have found strong evidences that the processes of permanent densification induced by irradiation or by high hydrostatic pressure involve quite similar structural modification of the a-SiO_2 matrix.

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I. INTRODUCTION

Amorphous silicon dioxide (a-SiO_2) continues to attract wide scientific interest for its involvement in a wide variety of modern technologies.[1,2] Furthermore, it represents an extraordinary example of amorphous solid-state system and gives the opportunity to investigate some relevant topics in basic solid-state physics.[1–3] For these reasons, up to date many efforts have been devoted to characterize the microscopic and macroscopic properties of this material, with both experimental and theoretical methods.[1–3] In recent years, one of the subjects which has received increasing attention concerns the polyamorphic transformations induced in a-SiO_2 by application of high hydrostatic pressure or by irradiation.[4–10] Although it is well known that in both cases a permanent increase in the density of the material is induced, many aspects of the atomic scale structural changes occurring in the material as a consequence of these treatments remain at present elusive.[2,5–7,9] In addition, the analogies and the differences between the structural modifications that pressure or irradiation induce are currently a matter of large debate.[1,2]

Experiments on a-SiO_2 materials subjected to high hydrostatic pressure have proved that different degree of permanent densification of the material can be induced for different combinations of pressure and temperature.[1,2,11–15] The higher the temperature, the lower the hydrostatic pressure necessary to induce a given value of volume compaction.[12–14] Typically, a permanent densification of ~16% is induced with a pressure of ~5 GPa at $T=600$ K.[13] Mechanically densified a-SiO_2 has been the object of many experimental[8,9,13,15–27] and theoretical[6,23,28–38] works. These studies have pointed out that, as a general trend, the densification of the material takes place through a gradual reduction in the mean Si–O–Si bond angle and a slight increase in the Si–O bond length.[1,2,18,39]

On the other hand, the studies dealing with the effects of prolonged irradiation (with ionizing radiation or particles) on the structural properties of a-SiO_2 have pointed out some interesting and characteristic properties. First of all, the degree of densification of the material, δ, increases on increasing the irradiation dose following the power law[40–54]

$$\delta = \frac{\rho - \rho_0}{\rho} = cD^\kappa, \tag{1}$$

where ρ_0 and ρ are the densities of the pristine and of the irradiated materials, respectively, D is the absorbed irradiation dose, while the constants c and κ depend on the nature of the irradiation. Many experimental investigations have pointed out that $\kappa\simeq1$ for irradiations with fast neutrons[40] or with swift ions, as 140 keV He^+ and D^+,[40] whereas $\kappa\simeq2/3$ for irradiations with protons,[40] γ rays,[40,41,44,45,49,50] electrons,[40–43,46,47] or UV light.[48,51–55] Although it is believed that these two different values of κ originate from the different types of interactions occurring between irradiation and matter, a detailed explanation of the physical origin of this effect is at present lacking. Furthermore, while the power law characterized by $\kappa\simeq1$ can be explained on the basis of simple physical considerations,[40,56] the origin of that with $\kappa\simeq2/3$ remains at present not understood.[40–54]

Although the power dependence described by Eq. (1) usually holds over a range of radiation doses of several orders of magnitude, two relevant deviations are known to occur: one in the low and the other in the high-dose limit. In fact, various experimental investigations have reported that in some cases, in the low-dose limit, the densification induced in the materials was lower than that predicted on the basis of Eq. (1).[41,42] The occurrence of this effect is dependent on the material properties and on the details of the irradiation and has been tentatively attributed to concurrent impurity-related (H or Al) radiation-induced structural effects opposing to the general densification process acting on the bare a-SiO_2 matrix.[41,42,57,58] The second deviation from the power law of Eq. (1) consists in the occurrence of a saturation of the degree of densification δ as a function of the irradiation dose to a value of ~4%. The saturation of the densification in correspondence of this value has a general nature, as it takes place independently from the specific properties of the start-

ing material and from the nature of the irradiation.[39–43,59] Although the existence of this limit value is universally believed to represent a key feature characterizing the radiation-induced densification process, the physical properties which this relevant property is founded on are at present unknown. The exhausted system, which is ~4% denser than the pristine material, obtained by prolonged irradiation of a-SiO_2 is usually referred to as *metamict phase*. Interestingly, it has been also reported that the same (metamict) phase can be obtained by prolonged irradiation of quartz samples with neutrons.[56,60–64] Consequently, the metamict phase is generally believed to represent the characteristic amorphous structure which SiO_2 transforms to after exhaustive irradiation, essentially independently of the nature of the irradiation and of the structure of the pristine material.[59,65]

The structural alterations induced by irradiation on a-SiO_2 have been widely studied by many different experimental techniques, such as small-angle x-ray[10] and Raman[66,67] scattering, infrared (IR) absorption,[68–70] nuclear magnetic resonance,[71,72] electron paramagnetic resonance (EPR),[73–76] photorefractive index,[56,62,63,77,78] and birefringence measurements,[58] as well as by theoretical methods.[5,37,79,80] The results indicate that, in analogy with the case of mechanically densified materials, the irradiated systems are characterized by a reduced mean Si–O–Si bond angle and a slightly increased Si–O bond length. However, in spite of these analogies, it was put forward that a higher amount of Si–O–Si angle variation is necessary to induce a given percentage of macroscopic densification by irradiation rather than by application of high pressure.[39,59,65] On the basis of this quantitative inconsistency it is believed that the microscopic processes responsible for the densification of a-SiO_2 induced by irradiation and by hydrostatic pressure are fundamentally different.[39,59,65]

While the structural modifications and the inherent permanent compaction induced in a-SiO_2 by high hydrostatic pressure involve homogeneously the whole volume of the sample, the process of densification induced by irradiation may show a more complex and fascinating scenario.[59] By studying *in situ* the effects of electron irradiation in quartz by transmission electron microscopy (TEM), Hobbs and Pascucci[81,82] have found that the progressive transformation of the material under irradiation takes place through the heterogeneous nucleation of localized structurally modified (amorphous) regions dispersed into an essentially unperturbed (crystalline) matrix. These observations are based on the possibility to make contrast between amorphous and crystalline regions in TEM images. On increasing the irradiation dose the volume of the portion of the material modified by irradiation gradually increases. This process goes on until almost the whole volume of the sample becomes altered by irradiation and then the matrix globally converts into the metamict phase. To explain these features Hobbs and Pascucci[81,82] proposed that the transformation of the material is triggered by the irradiation-induced generation of high local concentration of point defects which decreases the connectivity of the matrix and allows local structural rearrangements. In principle, as suggested by the same authors,[81,82] a similar heterogeneous process may take place in a-SiO_2 under irradiation. However in the latter case, due to the amorphous nature of the pristine material, there is no way to obtain enough contrast in TEM images between perturbed and unperturbed regions of the material and, consequently, a definitive conclusion on the nature of the process of structural modification induced by electron irradiation in a-SiO_2 cannot be drawn using that technique.[81]

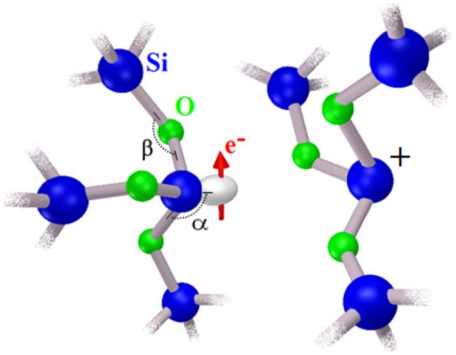

FIG. 1. (Color online) Microscopic structure of the E'_γ center in a-SiO_2. The arrow represents an unpaired electron (e^-) in a Si sp^3 orbital and the symbol + indicates a trapped hole. α is the angle between the symmetry axis of the unpaired electron orbital and the Si–O bond, whereas β is the Si–O–Si bond angle.

In order to gain new insight into this relevant issue here we report a study on the effects of electron irradiation on the *local* (within the defective regions of the material) degree of densification of a-SiO_2. To this aim the densification is investigated by the irradiation induced E'_γ point defect. Since its properties depend on the spatial arrangement of a few atoms around the defect, it acts as a probe of the local properties of the material. Assuming that the densification of a-SiO_2 is triggered by the generation of point defects,[81,82] then the E'_γ center *selectively* explores the local polyamorphic transition induced by irradiation. The E'_γ center has been widely studied and its generally accepted model consists in a puckered positively charged oxygen vacancy (Fig. 1): $O{\equiv}Si^{\bullet}\ {}^{+}Si{\equiv}O$ (where $\equiv$ represents the bonds to three oxygen atoms, $^{\bullet}$ an unpaired electron, and $^{+}$ a trapped hole).[1,2,83,84] This defect is characterized by a slightly orthorhombic EPR line shape with principal g (spectroscopic splitting factor) values $g_1 \simeq 2.0018$, $g_2 \simeq 2.0006$, and $g_3 \simeq 2.0003$ and by a pair of EPR lines split by $\simeq 41.8$ mT.[1,2,83,84] The doublet arises from the hyperfine interaction of the unpaired electron with a ^{29}Si nucleus (nuclear spin $I=1/2$, natural abundance 4.7%).[83] The potentiality of the E'_γ center as a structural probe of a-SiO_2 has been pointed out both in experimental[18,83–85] and theoretical[86] works. These works have evidenced that the constant A_{iso}, the isotropic part of the above-mentioned hyperfine interaction, depends on the angle α between the symmetry axis of the unpaired electron orbital and the Si–O bond, on the Si–O–Si bond angle β, and on the length of the Si–O bonds involved in the $O{\equiv}Si^{\bullet}$ moiety (see Fig. 1). In particular, it has been shown that A_{iso} increases on decreasing the bond angle β or on increasing the angle α or the Si–O bond length.[83,86,87] Furthermore, in an experimental investigation focused on mechanically densified a-SiO_2,

Devine and Arndt[18] have found that the constant A_{iso} monotonically increases on increasing the density of the material.

II. EXPERIMENTAL DETAILS

The materials here considered are high-purity industrial a-SiO_2 obtained by fast quenching of melted natural quartz powders under controlled atmosphere:[88] Infrasil 301 (I301),[89] Puropsil A (QPA),[90] Herasil 1 (H1),[89] and Homosil (HM).[89] The hydroxyl groups contents of these materials are: ≤ 8, ~ 15, ~ 150, and ~ 150 ppm by weight, respectively,[89,90] as estimated before any irradiation by measuring the amplitude of the IR band peaked at ~ 3670 cm^{-1} and by using the value 77.5 l mol^{-1} cm^{-1} for the molar extinction coefficient.[91] For each material we used a set of optically polished samples $5 \times 5 \times 0.5$ mm^3 in size.

The electron irradiations were performed in helium atmosphere by a Van de Graaf accelerator (current=20 μA, electron energy=2.5 MeV, dose rate=20 kGy/s). Six separate samples were considered for each material. One sample was preserved from any irradiation (D0), whereas the remaining five samples were irradiated at the doses: 1.2×10^3 kGy (D1), 1.2×10^4 kGy (D2), 1.2×10^5 kGy (D3), 1.2×10^6 kGy (D4), and 5.0×10^6 kGy (D5). Hereafter the samples subjected to these treatments will be referred to as MATERIAL_NICKNAME/n, with $n=0,1,2,3,4,5$, respectively. The temperature of the samples was monitored during each irradiation and it was found to reach a maximum value of ~ 330 K.

EPR measurements were carried out at room temperature at frequency ~ 9.8 GHz with a Bruker EMX spectrometer working in the first-harmonic unsaturated mode (FH-EPR) and in high-power second-harmonic mode (SH-EPR).[84,92] In particular, due to its high sensitivity, the latter method was used to detect the primary ^{29}Si hyperfine doublet of E'_γ centers. All spectra were acquired with a magnetic field modulation frequency of 100 kHz. Concentrations of defects were determined, with relative accuracy of 10%, by comparing the double numerical integral of the FH-EPR spectra with that of the E'_γ center in a reference sample. The defects concentration in the reference sample was evaluated, with absolute accuracy of 20%, using the instantaneous diffusion method in spin-echo decay measurements carried out in a pulsed EPR spectrometer.[93]

III. EXPERIMENTAL RESULTS

A. Main EPR line of the E'_γ center

A preliminary EPR characterization has pointed out that no EPR signals can be detected in the pristine materials, indicating that the concentration of paramagnetic point defects in the samples before irradiation falls below the detection limit. In contrast, after irradiation the main FH-EPR line shape attributed to the E'_γ center is easily detected in all materials. This result is presented in Fig. 2 for the samples QPA/1, QPA/3, and QPA/5. Note that the weak EPR signal indicated by the arrow in the figure is due to another E'-type defect (induced in very small concentrations), the E'_δ center,[92,94–96] which is of no interest in the present work and will not be further considered. The EPR lines reported in Fig. 2 are normalized to their double numerical integral and horizontally shifted to overlap the position of the first positive peak. We attributed the value $g_1=2.00180$ to the position of first positive peak in the FH-EPR spectra and we used it as a reference to estimate the other two principal g values.[1,92,97] With this procedure we obtained $g_2=2.00063 \pm 0.00002$ and $g_3=2.00036 \pm 0.00002$ which are in quite a good agreement with the well-known values pertaining to the E'_γ center in a-SiO_2.[1,92]

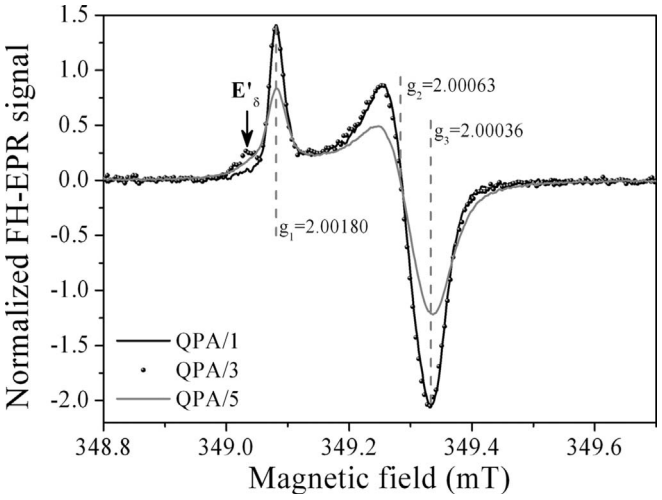

FIG. 2. FH-EPR spectra of the E'_γ center measured in the QPA material irradiated with electrons at the doses D1, D3, and D5. The FH-EPR spectra are normalized to the double numerical integral of the spectrum and horizontally shifted to overlap the position of the first positive peak. The weak EPR signal indicated by the arrow is due to the presence in the QPA/3 sample of another E'-type defect, the E'_δ center (Refs. 92 and 94–96) in very small concentrations.

As it is evident from the comparison shown in Fig. 2 while the FH-EPR line shapes of the E'_γ center observed in the samples QPA/1 and QPA/3 are virtually identical to each other that measured for the sample QPA/5 is significantly broader. Similar effects were also observed in the other irradiated materials here considered. The occurrence of this broadening effect in correspondence of the highest irradiation dose was studied in a previous work on the same samples.[98] In that experimental investigation, on the basis of several evidences, the broadening was proposed being related to the mutual interaction of the paramagnetic centers via the magnetic dipolar interaction. It was concluded that at high doses the concentration of paramagnetic centers induced by irradiation is high enough ($>10^{18}$ spins/cm^3) to determine a relevant contribution of the dipolar interaction to the overall width of the E'_γ center FH-EPR line.[98]

The concentrations of defects as a function of the irradiation dose obtained for the considered materials are reported in Figs. 3(a) and 3(b). As shown in Fig. 3(a), no relevant variations in the concentration of E'_γ centers are observed between D1 and D4 for QPA and I301, whereas in correspondence of the dose D5 a sudden rise of the defects concentration is measured. Note that, in agreement with our previous conclusions regarding the origin of the broadening effect acting on the FH-EPR spectrum of the E'_γ centers at high doses,

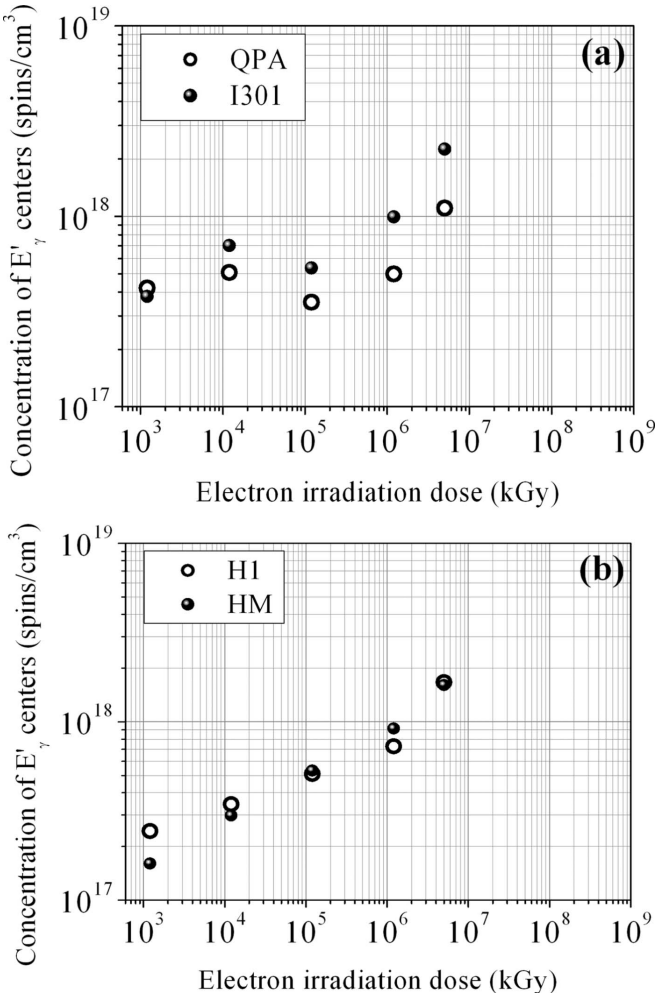

FIG. 3. Concentration of the E'_γ centers induced in the materials (a) QPA and I301, and (b) H1 and HM as a function of the electron irradiation dose, as determined by double numerical integral of the FH-EPR spectra. The experimental error bars are comparable with the symbols sizes.

the concentration of defects estimated in QPA/5 is significantly higher than those obtained in the other samples of the same material irradiated at lower doses. As reported in Fig. 3(b), at variance to QPA and I301, in the H1 and HM materials the concentration of E'_γ centers grows monotonically with dose. It is worth noting that the concentrations of defects reached in the high-dose limit ($D \geq$ D3) are comparable in all the considered materials.

B. Primary ^{29}Si hyperfine structure of the E'_γ center

In this work to better characterize the properties of the E'_γ center we have also studied its primary ^{29}Si hyperfine structure. In particular, we have estimated the constant A_{iso} by measuring the splitting of the hyperfine doublet from the SH-EPR spectra, defined as the difference in magnetic field units between the mean positions in the spectrum of each line component of the doublet. This method is supported by the results of previous extensive computer line-shape simulations of the ^{29}Si hyperfine structure of the E'_γ center performed by Griscom *et al.*,[83] by Devine and Arndt,[18] and by Stesmans *et al.*[85] The spectra obtained for the samples QPA/1, QPA/3, and QPA/5 are reported in Fig. 4(a). In Figs. 4(b) and 4(c) the low- and the high-magnetic field components of the doublet are zoomed in, respectively. In Fig. 4(a) the position of the main EPR line of the E'_γ center and that of its ^{29}Si hyperfine doublet are indicated by arrows, for clarity. The other EPR lines evident in the spectra in the range from ~335 to ~360 mT are due to paramagnetic point defects of a-SiO_2 distinguishable from the E'_γ center[1,2] and will not be further considered. To facilitate the comparison, the EPR spectra reported in Fig. 4 are normalized to the signal amplitude of the high-field component of the ^{29}Si hyperfine doublet of the E'_γ center. As it is evident in Fig. 4, our results clearly show that the hyperfine splitting of the E'_γ center significantly increases on increasing the irradiation dose, indicating that relevant structural alterations of the material take place. These splitting changes occur with fixed center of gravity of the pair. Furthermore, we found that in spite of the change in the hyperfine splitting, no relevant modifications in the EPR line shapes of each of the two components of the doublet are detectable. This result indicates that the dipolar broadening effects which, as discussed above, alter the main FH-EPR spectrum of the E'_γ center at high doses, give negligible contribution to the shape of the hyperfine lines. The latter property is obvious if one considers that each hyperfine line is at least ~16 times wider than the main resonance of the E'_γ center and, consequently, it is negligibly affected by the dipolar broadening effects. Finally, it is worth noting that no obvious correlation is evident between the value of the hyperfine splitting and the width of the E'_γ main EPR line (compare Figs. 2 and 4), nor between the value of the hyperfine splitting and the concentration of defects [compare Figs. 3(a) and 4].

To evaluate the relative changes of A_{iso} we define the quantity

$$\varepsilon = \frac{A_{iso} - A^0_{iso}}{A_{iso}}, \tag{2}$$

where A^0_{iso} is a value of reference of the isotropic hyperfine constant used to calculate the relative changes of A_{iso} induced by irradiation. Here we fix A^0_{iso}=41.8 mT, in agreement with previous experimental investigations indicating that the value of the hyperfine splitting of the E'_γ center measured in a wide variety of materials in the low-dose limit is (41.8 ± 0.08) mT.[85,92] The values of ε estimated in all the materials irradiated at the different considered doses are collected in Fig. 5. Note that the experimental points corresponding to the lowest dose D1 are not shown in the figure, as no detectable variations in A_{iso} from A^0_{iso} were found in the various materials. At variance, as a general trend, on further increasing the irradiation dose an increase in A_{iso} is induced.

As it can be easily recognized in Fig. 5, in the limit of high irradiation doses the quantity ε follows a similar trend in all the investigated materials. By a fit procedure we found that in each material the data for $D \geq$ D3 can be properly described by the following characteristic power law:

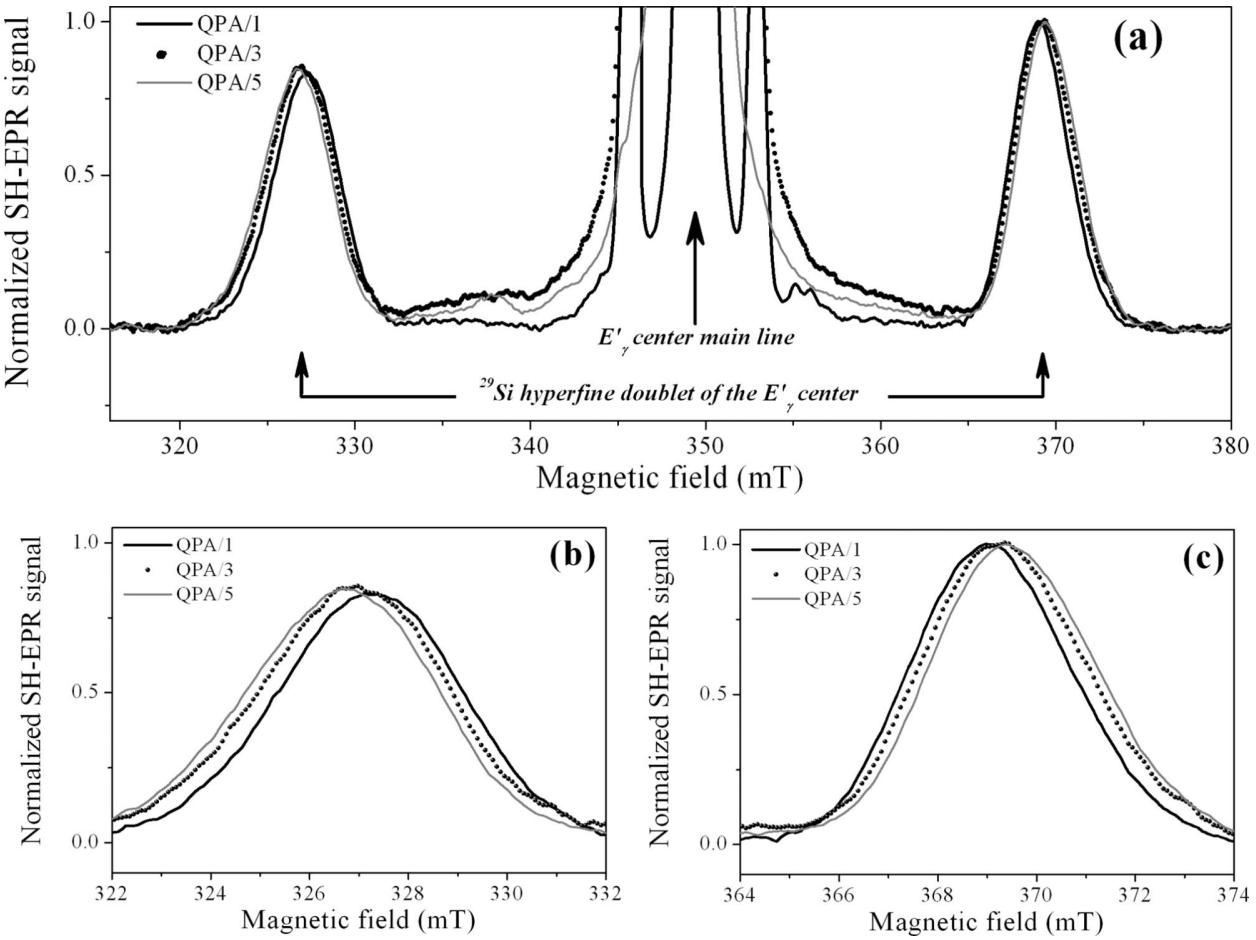

FIG. 4. (a) SH-EPR spectra of the ^{29}Si hyperfine doublet of the E'_γ center measured in the QPA material irradiated with electrons at the doses D1, D3, and D5. The SH-EPR spectra are normalized to the signal amplitude of the high-field component of the hyperfine doublet. In (b) and (c) the low- and the high-magnetic field components of the doublet are zoomed in, respectively. In (a) the SH-EPR signals between ~335 and ~360 mT are due to other point defects not considered in this work.

$$\varepsilon = bD^{\nu}, \tag{3}$$

where $b=(2.0\pm0.3)\cdot10^{-3}$ and $\nu=0.160\pm0.004$, and the dose is measured in kGy. The errors associated to these parameters are representative of the overall variability observed in the complete set of considered materials. The curve obtained from Eq. (3) with $b=2\times10^{-3}$ and $\nu=0.16$ is compared to the experimental data in Fig. 5 (dotted line). This comparison evidences that this power-law dependence is rigorously observed in the high-dose limit by all the considered materials.

As it is evident from Fig. 5, for doses lower than D3 the measured constant A_{iso} is typically lower than that expected on the basis of the power-law dependence of Eq. (3). This trend is quite similar as that typically observed in the degree of densification δ as a function of the irradiation dose.[42] In fact, as discussed in Sec. I, for many materials the measured value of δ in the low-dose limit is typically lower than that expected on the basis of the power law of Eq. (1). In those cases it was tentatively suggested that upon irradiation an impurity-related (H or Al) concurrent process takes place, which tends to oppose to the radiation-induced densification. The similarity between the deviations observed in the low-

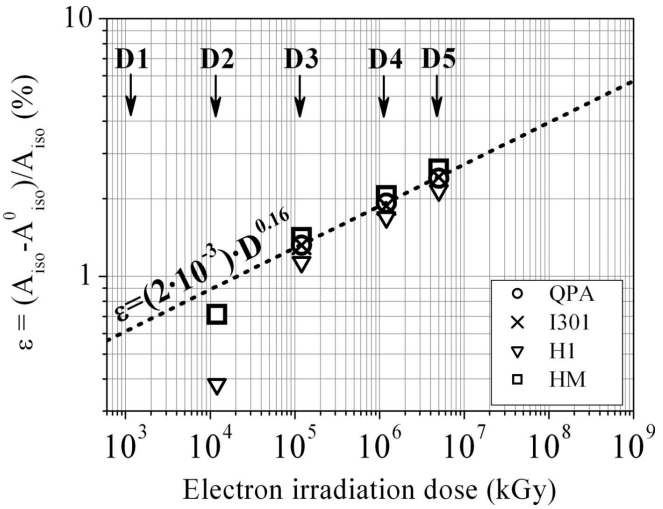

FIG. 5. Relative changes in the hyperfine constant A_{iso} with respect to the reference value $A^0_{iso}=41.8$ mT, estimated in the considered materials as a function of the electron irradiation dose. The experimental error bars are comparable with the symbols sizes. The curve obtained from Eq. (3) for $b=2\times10^{-3}$ and $\nu=0.16$ (dotted line) is also reported, for comparison.

dose limit for the quantities δ (in previous works) and for ε (in the present work) suggests that they could share a common origin. This suggestion is also supported by the fact that it is widely recognized that the constant A_{iso} of the E'_γ center actually depends on the local density of the a-SiO_2 matrix around the defect.[18,85] Consequently, if a process alters the local density of the material, it should thereby also alter the value of the constant A_{iso}.

An alternative explanation of the fact that for doses lower than D3 the measured value of ε is less than expected may be due to the growth of local mechanical stress. It should originate prevalently at the edge of the regions of the material structurally modified by irradiation and it could limit the inherent process of local densification. Since this effect involves the border of the modified regions, it is expected to be more relevant in the low-dose limit when the volume of the regions modified by the irradiation is very small,[81,82] whereas it should become negligible on increasing the irradiation dose and consequently the volume of the modified regions. These features are compatible with the data reported in Fig. 5.

IV. DISCUSSION

A. Interpretation of the variation in A_{iso} induced by irradiation

The most intriguing property emerged from the present experimental investigation consists in the observation that the relative change in the parameter A_{iso} in the high-dose limit ($D \geq$ D3) follows a general trend represented by the power law of Eq. (3) with $b \simeq 2 \times 10^{-3}$ and $\nu \simeq 0.16$ (see Fig. 5). In principle, the results obtained for the constant A_{iso} should be translated into detailed information on the microscopic structure of the material surrounding the E'_γ center. However, since A_{iso} depends on many local structural parameters of the defect, such as α, β, and the length of the Si–O bonds involved in the $O \equiv Si^\bullet$ moiety (see Fig. 1), practically, it is not a simple task. Another way to proceed is to restrict ourselves looking for mean information on the properties of the material around the defect. For example, by studying a series of a-SiO_2 samples densified at different levels by application of high pressure at elevated temperatures, Devine and Arndt[18] found that the ^{29}Si hyperfine splitting of the E'_γ center increases on increasing the degree of densification of the material. In particular, they found that for $\delta < 5\%$ the relative change in the density is approximately equal to the relative change of A_{iso}: $\delta \simeq \varepsilon$. However, it is worth noting that since the equivalence of the structural processes induced in a-SiO_2 by high pressure or by irradiation has not been established yet, the applicability of the result of Devine and Arndt to the present case is not guaranteed. Keeping this observation in mind, here we tentatively assume that the equality $\delta \simeq \varepsilon$ holds in our case. By using Eq. (3) and considering the best values obtained from the fits, we have

$$\delta \simeq \varepsilon \simeq (2 \times 10^{-3}) D^{0.16} \tag{4}$$

This conclusion is in strong disagreement with the results of the experimental investigations which have well established that for irradiation with electrons the relative increase in the material density follows the power law[40,42]

$$\delta_{exp} \simeq (1.75 \times 10^{-7}) D^{0.66}, \tag{5}$$

which is a particular case of Eq. (1). Looking for the possible reasons determining this failure, we recognize that we have tacitly assumed that, as a consequence of irradiation, the structure of the whole volume of the material changes *homogeneously*. This condition could, in principle, be not satisfied. In order to take into account the possibility that the irradiation-induced structural alteration of the material could occur in an inhomogeneous way, in the following we will pose the basis of a new model. In line with the observations of Hobbs and Pascucci for electron irradiated quartz,[81,82] here we assume that at any given irradiation dose the a-SiO_2 sample can be described as a mixture of two components: the first consists in the portion of the material whose structure has been significantly modified by irradiation, whereas the second consists in the portion of the material which has not been modified by irradiation yet. We indicate with V_m and V_p the total volumes occupied into the sample by the first (with modified structure) and the second (with pristine structure) components, respectively. Analogously, we indicate their local densities as ρ_m and ρ_0. If we indicate with V and ρ the whole volume and the mean density of the sample, respectively, we have

$$V = V_p + V_m \tag{6}$$

and

$$\rho = \rho_o \left(\frac{V_p}{V} \right) + \rho_m \left(\frac{V_m}{V} \right). \tag{7}$$

By using Eq. (6), Eq. (7) can be rearranged as follows

$$\rho = \rho_o + (\rho_m - \rho_0) \left(\frac{V_m}{V} \right), \tag{8}$$

which permits to obtain δ as

$$\delta = \frac{\rho - \rho_0}{\rho} = \left(\frac{\rho_m - \rho_0}{\rho} \right) \left(\frac{V_m}{V} \right). \tag{9}$$

Now we define the quantity

$$\delta_m = \frac{\rho_m - \rho_0}{\rho_m}, \tag{10}$$

which represents the local relative density change in the component of the material whose structure has been altered by irradiation. From Eq. (9) and by using the definition of Eq. (10) one finally obtains

$$\delta \simeq \delta_m \left(\frac{V_m}{V} \right), \tag{11}$$

where we have used the approximation

$$\frac{\rho_m - \rho_0}{\rho} \simeq \frac{\rho_m - \rho_0}{\rho_m}, \tag{12}$$

which is valid for $\frac{\rho_m}{\rho} \simeq 1$. Equation (11) simply states that if the density of only one component of the system changes,

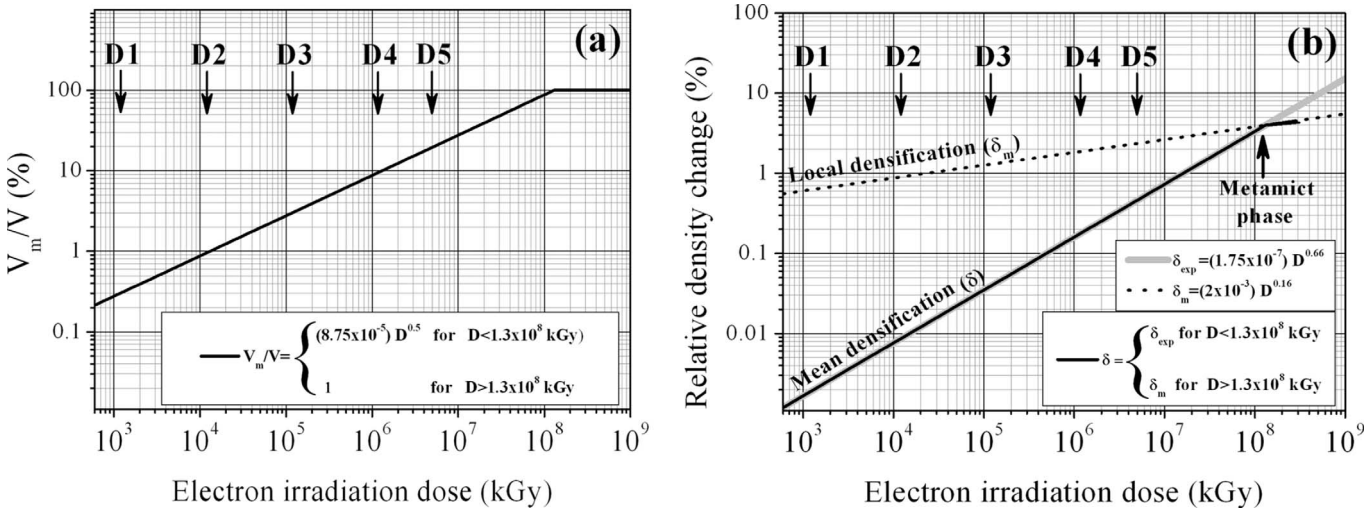

FIG. 6. (a) Volume fraction of the material structurally modified by electron irradiation, $\frac{V_m}{V}$, as a function of the accumulated dose. (b) Evolution of the mean densification of the material (black line) as a function of the irradiation dose. The power-law dependencies for δ_m [Eq. (14)] (broken line) and for δ_{exp} [Eq. (5)] (gray line) are also shown, for comparison. All quantities reported in (a) and (b), but the power-law dependence δ_{exp}, are obtained basing on the model discussed in detail in the text and describing the radiation-induced densification processes of a-SiO_2.

then the relative density variation in the mixture (the whole macroscopic solid in our case) is given by the relative density change in the modified component (δ_m) weighted by the fraction of the whole volume occupied by it ($\frac{V_m}{V}$).

Now, by tentatively assuming again that the results obtained by Devine and Arndt[18] for pressure densified materials are applicable to the present case of irradiation induced densification, we have

$$\delta_m \simeq \varepsilon. \tag{13}$$

Note that in Eq. (13) we have assumed that the E'_γ point defects present in the material are prevalently localized into the structurally modified portion of the whole volume, whose relative density change induced by irradiation is δ_m. This assumption is justified if, as suggested by Hobbs and Pascucci,[81,82] the radiation-induced structural alteration in the material takes advantage of the local degree of freedom originating from the presence of point defects. From Eqs. (3) and (13) we obtain

$$\delta_m \simeq \varepsilon \simeq (2 \times 10^{-3}) D^{0.16}, \tag{14}$$

which is valid for electron irradiation. Finally, substituting Eqs. (5) and (14) into Eq. (11) we obtain

$$\left(\frac{V_m}{V}\right) \simeq (8.75 \times 10^{-5}) \sqrt{D}, \tag{15}$$

which is valid for $\frac{V_m}{V} \leq 1$ and where, we recall, the dose D is measured in kGy. Equation (15) gives the ratio between the portion of volume occupied by the structurally modified material (V_m) and the whole volume of the sample (V) as a function of the irradiation dose. The function of Eq. (15) is plotted in Fig. 6(a). As shown, our model predicts that the ratio $\frac{V_m}{V}$ increases on increasing the irradiation dose up to a dose $D \simeq 1.3 \times 10^8$ kGy. In correspondence of this value the whole volume of the sample results altered by irradiation. As a consequence, for doses higher than 1.3×10^8 kGy, Eq. (15) does not apply anymore and we simply have $\frac{V_m}{V} = 1$, as shown in Fig. 6(a). In Fig. 6(b) we plot the relative density change, δ, of the whole sample consisting of a mixture of the two components (black line). For the sake of comparison, the power-law dependencies for δ_m [Eq. (14)] (broken line) and for δ_{exp} [Eq. (5)] (gray line) are also reported in the same figure. As shown, the relative density change δ follows the power law of Eq. (5) up to a dose $D \simeq 1.3 \times 10^8$ kGy, whereas for higher doses the condition $\frac{V_m}{V} = 1$ is fulfilled and Eq. (11) reduces to $\delta = \delta_m$.

Figure 6(b) remarks that our model predicts that the densification of the material δ as a function of dose abruptly changes slope and tends to saturate for $D \simeq 1.3 \times 10^8$ kGy, corresponding to the minimum dose value for which the condition $\frac{V_m}{V} = 1$ is fulfilled. In our scheme, this exhausted system in which the whole available volume of the sample has been structurally modified by irradiation represents the metamict phase. Data of Fig. 6(b) predict that this state should be characterized by a mean densification $\delta \simeq 4\%$ and by an E'_γ hyperfine splitting such that $\varepsilon \simeq 4\%$. Both these predictions are in excellent agreement with the results of the experiments, giving strong support to our approach. Indeed, as discussed in Sec. I, the former is a well-known property of the metamict phase pointed out in a wide variety of experimental works,[59] whereas the latter is corroborated by a previous investigation of Douillard *et al.*[74–76] In particular, by studying the metamict phase obtained by irradiation with ^{86}Kr ions (energy=8.2 MeV/amu and fluence=6×10^{12} ions cm^{-2}) of a quartz sample, Douillard *et al.*[74–76] estimated $\varepsilon \simeq 3.9\%$, which is in a very good agreement with the value predicted by our analysis.

Our model puts forward that the deviation of the densification of the material from the power-law dependence of Eq.

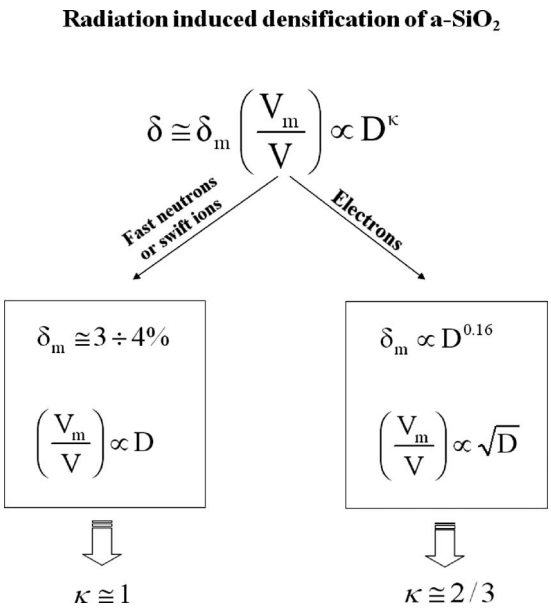

FIG. 7. Scheme summarizing the main properties of the processes of densification induced by irradiation with fast neutrons or swift ions and with electrons.

(1) in correspondence to the value of ~4% is a consequence of the fact that the whole volume of the sample has been structurally modified by electron irradiation. This conclusion is quite similar to that proposed many years ago for the process of densification induced by fast neutrons and swift ions, whose densification curve follows the power-law dependence of Eq. (1) with $\kappa \simeq 1$.[40,56] Indeed, in that case it was proposed that each heavy particle striking the material causes the definitive transformation of a little volume τ from the pristine structure to that of the metamict phase, characterized by a density ~4% higher than that of the unirradiated material. On increasing the number of impinging energetic particles one observes a densification linearly increasing with the energy deposited on the sample. The function δ appropriate to this case can be obtained from Eq. (11) by taking $\delta_m \sim 4\%$ and $V_m = N\tau$, where N is the number of impinging neutrons or ions which have reached the sample. The energy deposited into the material is proportional to N. When almost the whole volume of the sample has been converted into the metamict phase, then the densification saturates to a maximum value of about ~4%.

In Fig. 7 we present a scheme in which the general properties of the processes of densification induced by irradiation with fast neutrons or swift ions and with electrons are summarized. This simple scheme puts forward that the main differences between irradiation with energetic heavy particles and with electrons consists in a reduced efficiency of the latter with respect to the former in generating stable structural alterations. Indeed, fast neutrons or swift ions irradiation events cause the definitive transformation of a portion of the whole volume to a phase (the metamict one) ~4% denser than the ordinary a-SiO_2 materials. At variance, the degree of densification induced by irradiation with electrons is typically lower than ~4% and increases on increasing the dose proportionally to $D^{0.16}$. Furthermore, in the case of heavy particles irradiation, the volume fraction of the sample structurally modified increases linearly with the energy deposited, $\frac{V_m}{V} = \frac{N\tau}{V} \propto D$, whereas in the case of electrons irradiation it increases more slowly, $\frac{V_m}{V} \propto \sqrt{D}$.

The conclusion that electron irradiation, unlike the energetic heavy particles one, creates a lower degree of structural alteration in the material is not surprising. Indeed, it is energetically possible for each impinging heavy particle striking the sample to create a local *fusion* of a little volume τ of the material.[56,59,60,99] Subsequently, the structure of the material within the volume τ is rapidly frozen as a consequence of the fast exchange of thermal energy originating by the interaction of the volume τ with the surrounding material which is at room temperature. At variance, when electrons impact on a-SiO_2 a large number of secondary electrons with lower energy are generated, whose effect is mainly that to generate localized electronic excitations distributed over an extended portion of the whole volume of the sample. Statistically, in only *few cases* these excitations will actually generate stable and isolated point defects.

By following the general scheme proposed by Hobbs and Pascucci,[81,82] here we assume that although the point defects induced by electron irradiation are initially uniformly distributed into the whole volume of the sample, they subsequently diffuse away from the original site and contribute to the nucleation of confined high-defective (densified) regions statistically dispersed into the whole volume of the material. An increasing number of defect nucleates into each densified region on increasing the irradiation dose. This effect causes an increase with dose both in the mean radius of each structurally modified region and in the degree of densification within it. These two features are described in our model by the quantities $\frac{V_m}{V}$ [Eq. (15)] and δ_m [Eq. (14)] as a function of dose, respectively.

B. Comparison between the densification processes induced by irradiation and by pressure

As discussed in Sec. I, in previous works[39,59,65] it was put forward that a higher amount of Si–O–Si angle variation is necessary to induce a given percentage of macroscopic densification by irradiation rather than by application of high pressure. This inconsistency was raised and widely discussed by Devine[39] and Dooryhée *et al.*[59] and is based on the observation that exhaustive irradiation of a-SiO_2 induces a densification of ~4% with a corresponding variation in the mean Si–O–Si bond angle of $10° \pm 2°$.[39] At variance, when the material is mechanically densified at a level of $11\% \pm 2\%$, the Si–O–Si angle variation is only of $7° \pm 1°$.[39] In these two systems the overall change of the Si–O–Si bond angle is almost comparable, whereas their densification differ by a factor ~3. Dooryhée *et al.*[59] suggested that the lack of a one-to-one correspondence between the variation in the Si–O–Si bond angle and the densification of the materials (independently on the method of densification), arises from different ring[100] size distribution into the material. Different methods of compaction lead the Si–O–Si chains involved in the ring structures to fold in quite different ways. For a given value of the mean Si–O–Si bond angle, the higher the folding

efficiency of the Si–O–Si chains, the higher the resulting density of the material. On the basis of these considerations the authors concluded that the microscopic structures of materials densified by irradiation or by high hydrostatic pressure are significantly different.[59]

The main result of the present work is to have proved that if one assumes that the condition $\delta_m \simeq \varepsilon$ holds for both radiation and pressure densified materials, then a general quantitative description of the electron irradiation induced densification process of a-SiO_2 can be obtained, which agrees with the most relevant properties pointed out in the experiments. However, if one believes that irradiation and pressure densified materials possess quite different medium-range microscopic structures, as proposed by Dooryhée *et al.*,[59] then it seems strongly surprising that both give $\delta_m \simeq \varepsilon$. In contrast, we believe that the validity of the equality $\delta_m \simeq \varepsilon$ independently on the method of compaction, suggested by our results, strongly supports the conclusion that strict and fundamental similarities exist between a-SiO_2 materials densified by irradiation or by high hydrostatic pressure. It is worth noting, in fact, that the quantitative relation between ε and the local densification of the material around the defect, δ_m, should be extremely dependent on the details of the short- and medium-range microscopic structure of the material. In fact, in principle, the hyperfine splitting of the E'_γ center depends on the atomic scale structure of a few atoms around the unpaired spin (see Fig. 1),[83,86,87] whereas the local density of the material is defined on a larger volume of the sample centered on the defect.[2,28] As a consequence, the folding properties of the Si–O–Si chains involved in the ring structures of a-SiO_2, discussed by Dooryhée *et al.*,[59] are expected to influence the latter property (related to δ_m), whereas they should not affect significantly the former (related to ε).

Summarizing, the conclusion drawn by Devine[39] and Dooryhée *et al.*[59] suggests that the microscopic structural effects induced in a-SiO_2 by irradiation are not equivalent to those induced by high hydrostatic pressure. At variance, a strong indication in the opposite direction comes from our experimental data. The reason of this apparent contrast may reside in the significantly different irradiation doses considered in the two cases. Indeed, Devine[39] and Dooryhée *et al.*[59] founded their discussion on a-SiO_2 materials exhausted by irradiation, i.e., essentially on the metamict phase. In contrast, in our study we have considered irradiation doses more than one order of magnitude lower than that necessary to reach the metamict phase. This difference may be very relevant. Indeed, since the rings properties pertain to the medium-range structure of the material, the modifications induced by irradiation in the ring size statistic should dramatically depend on the actual mean spatial extent of each single densified region. Our results indicate that for doses significantly lower than that necessary to obtain the metamict phase the structurally modified portions of the material are confined within small regions embedded into an essentially unperturbed a-SiO_2 matrix. Basing on the results of Hobbs and Pascucci[81] one expects that the mean radius of these regions ranges from less than one nanometer up to few tens of nanometers, for the doses here considered. Such small spatial extension of the structurally modified regions may significantly limit the ability of the matrix to modify the local ring size statistic in minimizing the energy of the system. In contrast, in the metamict phase all the volume of the sample is structurally modified and consequently no significant spatial constraints apply. In the latter case one expects that the elasticity of the system is maximum, allowing more relevant alterations in the ring size statistic. On the basis of these observations we suggest that, as far as the irradiation dose is significantly lower than that necessary to obtain the metamict phase, then the microscopic structural effects induced in a-SiO_2 by irradiation and by high hydrostatic pressure are essentially equivalent. At variance, when almost the whole volume of the sample becomes structurally modified, a relevant alteration in the ring size statistic takes place, as discussed in detail by Dooryhée *et al.*,[59] which makes the final structure of the material (the metamict phase) significantly different from that with comparable density obtainable by application of high hydrostatic pressure.

V. CONCLUSIONS

In conclusion, we reported here an experimental investigation of the effects on a-SiO_2 materials of 2.5 MeV electron irradiation in the dose range from 1.2×10^3 up to 5×10^6 kGy. By measuring the change in the splitting of the primary ^{29}Si hyperfine doublet of the E'_γ centers we evidenced an irradiation-induced local (around the defects) densification of a-SiO_2.

The overall results we found have permitted us to obtain a detailed and quantitative description of the radiation-induced densification process in a-SiO_2. This objective has been accomplished by introducing a model in which the irradiated materials are assumed to be composed of a mixture of two components: the first consists in the portion of the material whose structure has been significantly modified by irradiation, whereas the second consists in the portion of the material which has not been modified by the irradiation yet. On increasing the irradiation dose both the volume fraction occupied by the structurally modified material, $\frac{V_m}{V}$, and its degree of local densification, δ_m, increase. The process of point defects generation is directly responsible of the gradual increase with dose of these two quantities. Basing on the results on the hyperfine structure of the E'_γ center we found that the local densification follows the characteristic power law $\delta_m \propto D^{0.16}$. Furthermore, by comparing our model to the results obtained in previous works focused on the radiation-induced densification of a-SiO_2 upon electron irradiation, we recognized that the gradual structural alteration of the volume of the material takes place following the power-law dependence $\frac{V_m}{V} \propto \sqrt{D}$.

One of the main goals of the model we propose here consists in the fact that, in strict agreement with the results of many experimental investigations, it predicts that the densification of the material δ as a function of dose deviates significantly from the power law of Eq. (1) in correspondence of $D \simeq 1.3 \times 10^8$ kGy, approaching the saturation value of $\sim 4\%$. In our simple scheme, these features naturally occur when almost the whole volume of the sample has been

structurally modified and, consequently, no more portions of the whole volume can be further transformed from the pristine structure to that modified by the irradiation.

Finally, we have found strong evidences indicating that, as far as the irradiation dose is significantly lower than that necessary to reach the metamict phase, then the microscopic structural effects induced in a-SiO_2 by irradiation and by high hydrostatic pressure are essentially equivalent.

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*buscarin@fisica.unipa.it

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