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In situ observation of β-ray induced UV optical absorption in a-SiO_2: Radiation darkening and room temperature recovery

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ABSTRACT

We studied the optical absorption in the 3.0–6.2 eV range induced in bulk amorphous SiO_2 by β-ray irradiation up to ~1 MGy at room temperature. The induced absorption was measured *in situ* both during irradiation and in the post irradiation time. Our data evidence E'_γ center as the main defect induced by irradiation and the partial decay of their absorption band at about 5.8 eV after irradiation. A quantitative analysis of the time evolution of the induced absorption shows that the transmission recovery observed after irradiation is compatible with the reaction of radiation-induced defects with H-related (H_2, H_2O) species diffusing in the amorphous matrix.

1. Introduction

The investigation of irradiation-induced point defects in amorphous SiO_2 (a-SiO_2) has constituted a debated research domain for many years, aiming to unveil the limiting features for the technological application of this widely used material [1]. A particular relevance is attributed to defects inducing optical absorption (OA) bands in the ultraviolet region, as they hamper novel UV laser applications. One of the foremost UV-absorbing defects is the E'_γ center, due to its ubiquitous presence and high generation efficiency upon irradiation [1–3]. Even if largely studied, the generation mechanism of this defect is not unequivocally determined and both the formation from precursor sites and that from unperturbed SiO_2 units have been proposed [3]. Furthermore, the influence of interstitial species on defect generation, stabilization and recovery has been poorly studied, or principally focused on the investigation of the effects induced by H species purposely added to the material [4,5]. To clarify this aspect, it is mandatory to use *in situ* experimental techniques, able to monitor the generation of the defects already during the irradiation time and to observe short-term post-irradiation effects. Indeed, this approach can shed light on the mechanisms originating the centers and can help clarifying the influence of diffusing species reacting with the defects [6,7].

Starting from the 70s, several attempts were done to investigate defects generation by *in situ* OA measurements in bulk samples [8,9]. Nevertheless, these investigations were usually done in the infrared–visible range, with few data up to the ultraviolet (UV) where the OA band of the E'_γ center, the most radiation sensitive defect, shows up [2]. Furthermore, many studies mainly concerned optical fiber samples, possibly affected by peculiar features such as drawing-induced stresses or fiber-specific precursor sites [4,5,9].

Recently, we have studied the defects generation under β-ray irradiation by *in situ* optical absorption measurements up to the UV in bulk high purity a-SiO_2 materials [10]. This experimental procedure enabled to characterize the processes leading to defect generation and to investigate the post irradiation bleaching of induced absorption bands. However, these measurements were somehow affected by the instrumental detection limit at ~5.5 eV, preventing a clear study of the E'_γ center. We report here a novel study of the induced OA up to 6.2 eV in high purity a-SiO_2 samples

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during and after irradiation at room temperature by β-rays. The experiments aim to better investigate the generation of the E'_γ center and in particular to evidence the presence of defects recovery effects in the post irradiation, as already evidenced when the defects are generated by other irradiation sources [7,9].

2. Experimental details

Commercial high purity silica samples were used: a natural dry, Infrasil 301 (hereafter named I301, OH groups, $\sim 1 \times 10^{17}$ cm^{-3}, metallic impurities content about 20 ppm by weight, supplied by Heraeus [11]); and a synthetic dry, ED-B (OH groups $\sim 2 \times 10^{17}$ cm^{-3}, metallic impurities content <10 ppb by weight, supplied by Tosoh quartz [12]). We employed bulk samples having size $5 \times 5 \times 1$ mm^3 with the largest surfaces optically polished.

Irradiation was carried out at room temperature in He atmosphere by 2.5 MeV β-rays in a Van de Graaff accelerator. The dose rates were ~30 and ~6 kGy/min for the I301 and ED-B samples, respectively. OA measurements in the spectral range 3.1–6.2 eV were carried out both during and after irradiation by an Avantes fiber optic spectrophotometer equipped with a deuterium lamp and a charge coupled device (CCD) detector, with a time resolution of 1 s. The samples were mounted with the largest surfaces forming a 90° angle to the optical beam direction and 45° to that of the β beam, collimated on the sample. Preliminary tests evidenced that the effects of irradiation on the employed fibers were negligible and only low levels of bremsstrahlung radiation in the irradiation chamber affected the fibers. Furthermore, a reference fiber was used to drive a signal along a similar path to that of the probing fiber. By monitoring the transmission through this second fiber it was possible to independently estimate spurious effects and to verify that their influence on the sample spectra was always negligible.

Stationary E'_γ center concentration was determined by electron paramagnetic resonance measurements at room temperature by a BRUKER EMX spectrometer working at 9.8 GHz. Measurements were carried out under non distorting conditions (modulation field amplitude 0.01 mT, microwave power 800 nW). The concentration of defects was determined by comparing the double integral of the EPR signal with that of a reference sample [13]. The estimated concentration error is 20%.

Infrared, IR, absorption spectra of the samples were measured before and some months after the irradiation by using a Bruker Vertex70 Fourier transform-IR spectrophotometer using the spectral resolution of 1 cm^{-1}. The absorption band at 3670 cm^{-1} [14], was used to determine the OH content of the samples, whereas the signal around 3300 cm^{-1} was used to estimate the H_2O content [15]. The concentration of H related species was estimated using ε extinction coefficient 77.5 l mol^{-1} cm^{-1} [14] and 81 l mol^{-1} cm^{-1} [15], for OH and H_2O, respectively. The uncertainty in the concentration estimation is 5%.

3. Results

Only the sample I301 presents an absorption band peaked at 5.15 eV before irradiation. This band, attributed to Ge oxygen deficient defects (Ge-ODC(II)), had ~0.46 cm^{-1} amplitude, and is usually associated to two photoluminescence bands centered at ~3.1 and ~4.2 eV [2]. As shown in the inset of Fig. 1, where for simplicity only the spectrum after 330 s of irradiation is reported, the exposure to β-rays induces absorption from 3 up to 6.2 eV in the I301 sample. A Gaussian band peaked at (5.71 ± 0.02) eV, with full width at half maximum (FWHM) (0.75 ± 0.02) eV, can be isolated in the spectrum together with a wide band of much lower amplitude at about 4 eV. This latter contribution will not be considered further. As reported in Fig. 1, the study during irradiation evidenced that the absorption in the 5.7–5.8 eV range increases rapidly up to ~23 cm^{-1} after 330 s of irradiation, corresponding to an accumulated dose of 135 kGy. As soon as the irradiation is stopped a fast absorption reduction is found in the first ~100 s, followed by a much slower decrease rate. No variations of the spectroscopic parameters of the 5.7 eV band are observed during the post-irradiation stage.

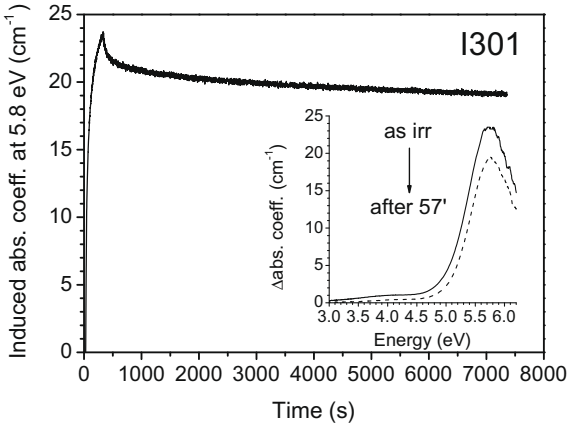

Fig. 1. Induced absorption measured in natural dry silica I301 during and after irradiation; noise is the main cause of error in absorption estimation. In the inset, absorption spectra at the end of irradiation (135 kGy, continuous line) and 57 min after irradiation (dash line) are reported.

The effects of irradiation on the ED-B sample are reported in Fig. 2. As shown in the inset, irradiation induces absorption in the UV range beginning from ~4.3 eV. A Gaussian band peaked at (5.70 ± 0.02) eV with FWHM (0.78 ± 0.02) eV is the principal feature detected in the spectra. The characteristics of this band are indistinguishable from those of the I301 sample, and agree with the typical features of the absorption band associated to the E'_γ center [1,2], thus allowing to individuate its presence in the investigated samples.

As shown in Fig. 2 for the ED-B sample, the kinetics of absorption in the 5.7–5.8 eV range shows a large increase during the first ~500 s of irradiation, followed by a slower growth. This sample is characterized by a higher radiation hardness than the I301. Indeed, at the maximum accumulated dose of 1.35 MGy, the induced absorption is ~11 cm^{-1}, much lower than the absorption of I301

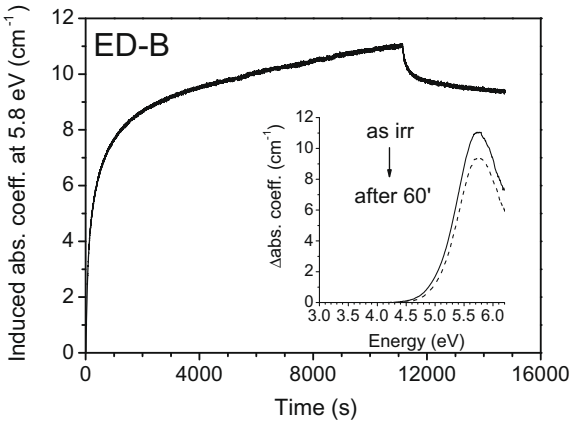

Fig. 2. Induced absorption measured in synthetic dry silica ED-B during and after irradiation; noise is the main cause of error in absorption estimation. In the inset, absorption spectra at the end of irradiation (1.35 MGy, continuous line) and 60 min after irradiation (dash line) are reported.