Twofold coordinated Ge defects induced by gamma-ray irradiation in Ge-doped SiO_2

A. Alessi,[1,*] S. Agnello,[1] F. M. Gelardi,[1] S. Grandi,[2] A. Magistris,[2] and R. Boscaino[1]

[1]*Department of Physical and Astronomical Sciences, University of Palermo, Via Archirafi 36, I-90123, Palermo, Italy*
[2]*Department of Physical Chemistry, University of Pavia, Via Taramelli 16, I-27100, Pavia, Italy*
[*]*Corresponding author: alessi@fisica.unipa.it*

Abstract: We report an experimental study by photoluminescence, optical absorption and Electron Paramagnetic Resonance measurements on the effects of exposure of Ge-doped amorphous SiO_2 to γ ray radiation at room temperature. We have evidenced that irradiation at doses of the order of 1 MGy is able to generate Ge-related defects, recognizable from their optical properties as twofold coordinated Ge centers. Until now, such centers, responsible for photosensitivity of Ge-doped SiO_2, have been induced only in synthesis procedures of materials. The found result evidences a role played by γ radiation in generating photosensitive defects and could furnish a novel basis for photosensitive pattern writing through ionizing radiation.

OCIS codes: (160.2750) Glass and other amorphous materials; (160.5335) Photosensitive materials; (160.2220) Defect-center materials; (060.3738) Fiber Bragg gratings, photosensitivity; (350.5610) Radiation;

References and links

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1. Introduction

Ge doped amorphous SiO_2 (a-SiO_2) is a widely employed material for the realization of fiber optics and other optical devices. These applications are related also to the high ultraviolet (UV) photosensitivity that for example enables the production of fiber Bragg gratings, sensors, multiplexers and filters [1, 2]. The higher photosensitivity of Ge doped silica with respect to pure one has been connected to the presence of an optical absorption (OA) band peaked at ~5.15 eV (named $B_{2\beta}$ band) [2] with a full width at half maximum (FWHM) of ~ 0.46 eV [3-5].

This band is correlated to two photoluminescence (PL) bands peaked at 3.2 eV (β band) and 4.3 eV (α_E band) having FWHM of 0.43 eV and 0.48 eV, respectively [4, 5]. The absorption band has been associated to a transition from a point defect ground singlet state (S_0) to its first excited singlet state (S_1). The α_E band is attributed to the inverse transition of absorption ($S_1 \rightarrow S_0$) while, in this energy level scheme, the β band is associated to the transition from the first excited triplet state (T_1), supplied by an intersystem-crossing (ISC) process ($S_1 \rightarrow T_1$), to the S_0 [4, 5]. This overall optical activity has been attributed to a diamagnetic Ge oxygen deficient defect, and previous works have pointed out that its most probable microscopic structure is that of a twofold coordinated Ge (=$Ge^{\bullet\bullet}$), where the (=) represents the bonds with two oxygen atoms, and ($^{\bullet\bullet}$) indicates an electron lone pair: from this structural model the defect takes the name Ge lone pair center (GLPC) [6, 7]. The optical proprieties of GLPC have been widely studied to enrich their comprehension and because the defects embedded in an amorphous matrix can be used to understand the environment that is coupled with them by the non radiative process [4, 5, 8].

Up until now the GLPC has been observed in materials just after their production, or by subsequent specific treatments in H_2 atmosphere sometimes followed by UV light exposure [6, 9, 10], and a limiting constraint for generation of this defect has been the oxygen deficiency of the synthesis atmosphere [6]. The successive writing procedure is carried out by exposure to the UV light that induces selective bleaching of the ~5.15 eV absorption band [11] associated to GLPC, and employing interference patterns emerging from a phase mask to obtain spatially resolved effects [2]. The obtained periodical change of the absorption coefficient is intrinsically related to refractive index change of the medium by the Kramers-Krönig equations, and is the basis of Bragg gratings and other devices preparation. No other mechanisms for the generation of GLPC, apart from those above reported, has been observed yet. Some findings of this kind could be effective in modifying the properties of the material and in enhancing its photosensitivity.

In this work we report on the generation of stable GLPC by exposure of Ge-doped silica to γ-ray at room temperature. Our results could furnish a basis for novel devices employing ionizing radiation for the preparation of spatial structures on target materials for successive UV writing, a point that has been found to be relevant for novel optics applications [12].

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2. Experimental procedures

The measurements reported here were done on two sol-gel Ge doped silica samples, and in particular the sample named A has Ge content of 10^4 part per million (ppm) molar, while the sample named B has a content of 10^3 ppm mol. The investigated materials are produced by a mixture of TEOS (tetra-etil-orthosilicate) and TEOG (tetra-etil-orthogermanate). The starting aerogels have been densificated using two different temperature routes. In particular, sample A was heated up to 1200°C with a rate of 0.3°C/min and then it was kept at this temperature for 0.75 hours, finally, it was cooled to room temperature. In the heating stage a flux of O_2 + N_2 was used up to 800°C, then it was changed to normal atmosphere for the remaining part of the temperature route. The sample B was heated up to 1150 °C with a rate of 0.3 °C/min, and it was kept to this temperature for a time of 24 hours, and finally it was cooled to room temperature. During the heating a flux of O_2 was used up to 700 °C, and then, after half an hour in He, the atmosphere was switched to vacuum (~10^{-8} atm).

The optical activity has been investigated using a spectrophotometer Jasco V-560 in the spectral range 2-6 eV to estimate the absorption coefficient, while the photoluminescence measurements were acquired, in the range 2.5-5 eV, with a spectrofluorometer Jasco FP6500 using a 150 W Xenon lamp source. In these kind of measurements the samples were placed in a 45° back scattering configuration and the experimental spectra were corrected for the spectral efficiency of the detection system and for the spectral dispersion. The PL time decay measurements were carried out using a Varian Cary Eclipse fluorescence spectrophotometer. We have performed also electron paramagnetic resonance (EPR) measurements using a Bruker EMX spectrometer working at 9.8 GHz to detect the presence of paramagnetic centers related to GLPC. All the measurements here reported were recorded at room temperature.

3. Results and discussion

In the sample A no PL and EPR activities were found before the γ-ray irradiation, as well as no evidence of the $B_{2\beta}$ band was found in the OA spectrum (Fig. 1(a)). The sample was then γ-ray irradiated up to 1 MGy exposing it to a ^{60}Co source at room temperature.

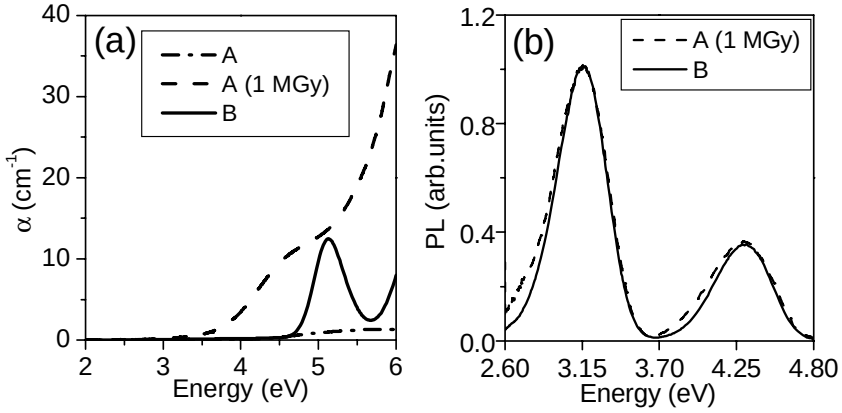

Fig. 1. (a). OA spectra of sample A before and after γ irradiation to 1 MGy and that of the sample B are reported; (b) PL spectra under excitation energy 5.0 eV acquired on sample A γ-irradiated at 1 MGy and on sample B, normalized to the maximum at ~3.2 eV.

As reported in Fig. 1(a), after irradiation, the absorption spectrum shows the appearance of a signal in the ultraviolet range. A photoluminescence excited at 5.0 eV is also found, whose spectrum, reported in Fig. 1(b), shows two luminescence bands centered at ~3.2 eV and 4.3 eV. It is important to underline that this latter band is clearly evidenced after the correction of

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the PL for the absorption coefficient value in the 3.5-4.8 eV spectral range (shown in Fig. 1(a)).

A comparison of the PL in the irradiated sample A with that observed in the as grown sample B is reported in Fig. 1(b), and it shows that the PL bands are essentially the same with an almost equal amplitude ratio in both samples. It is worth to note that in sample B the OA band peaked at 5.15 eV (Fig. 1(a)) confirms the presence of GLPC centers due to the material synthesis. At variance the presence of induced absorption linked with other Ge related centers [3, 7] prevents to distinguish the $B_{2\beta}$ band in irradiated sample A.

In Fig. 2(a), the PL spectra in the range 2.5 - 3.7 eV of irradiated sample A recorded using different excitation energies (5.51, 5.00, 4.81, 4.70 eV) are shown. These spectra evidence spectral changes of the 3.2 eV band compatible with already reported data for GLPC centers induced during materials synthesis [4]. A more detailed comparison is reported in Fig. 2(b), where the variations of the 3.2 eV maximum position and of its FWHM (inset) as a function of the excitation energy (E_{exc}) are shown for irradiated sample A and as grown sample B.

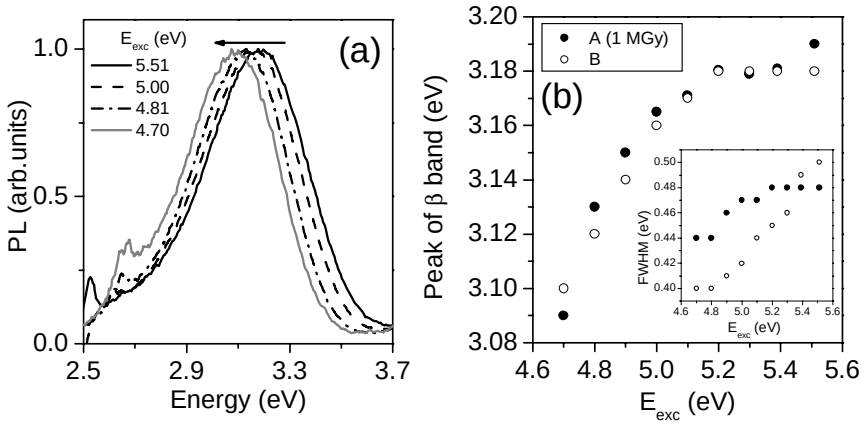

Fig. 2. (a). normalized PL spectra of 3.2 eV band recorded on sample A γ irradiated at 1 MGy exciting at different energies, (b) variation of the peak position as function of excitation energy: (●) 1 MGy irradiated sample A, (○) sample B; in the inset the dependence of FWHM on excitation energy is reported: (●) 1 MGy irradiated sample A, (○) sample B.

The peak position of the 3.2 eV band of the irradiated sample A changes with the E_{exc} in the same way of the non irradiated sample B, in particular it increases almost monotonically on increasing E_{exc}. At variance, the FWHM in the investigated materials depend on E_{exc} in different ways. In details, in sample B it increases monotonically with E_{exc}, while in the irradiated sample A the FWHM has lower dependence changing only from 0.44 to 0.48 eV (with an error of ~ 0.01 eV). The correction procedure for the high absorption in irradiated sample A gives a large error of the α_E band peak position avoiding the accurate investigation of its dependence on excitation energy.

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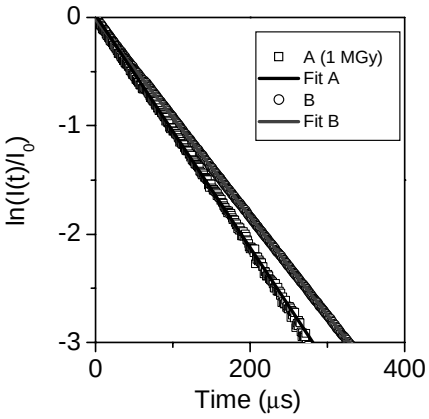

Fig. 3. PL emission at 3.2 eV as a function of time under pulsed excitation at 4.9 eV: (□) experimental data of 1 MGy irradiated sample A, (○) experimental data of sample B, the reported data are normalized to the maximum emission; the full lines represent best fits.

To further compare the PL activity of the irradiated sample A with that of sample B we investigated the PL time decay of the 3.2 eV band, under pulsed excitation at 4.9 eV. In Fig. 3, the $\ln(I(t)/I_0)$ ($I(t)$ indicating the PL intensity as a function of time and I_0 the initial intensity), is reported. For both samples the decay is a single exponential and the estimated lifetimes are $\tau = (97 \pm 2)$ μs in the irradiated sample A, and $\tau = (109 \pm 2)$ μs in the sample B, this latter being in good agreement with the value reported by Skuja [5].

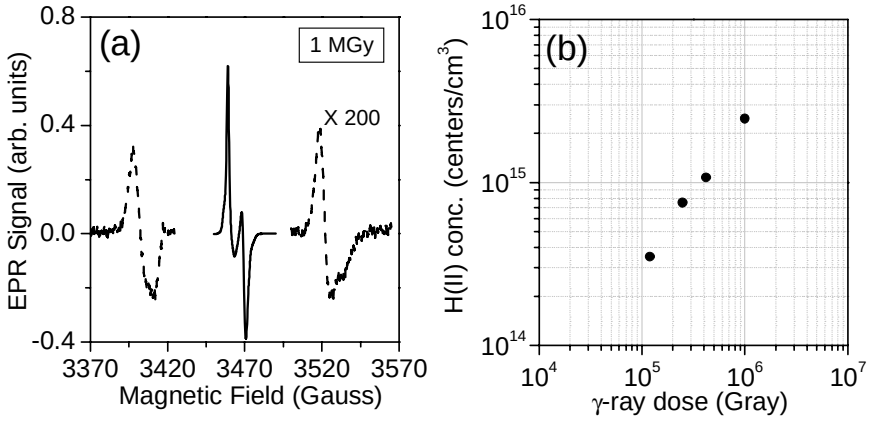

Fig. 4. (a). EPR doublet (dashed line, magnified by a factor 200) associated to the H(II) defect as detected in sample A irradiated at 1 MGy; the central part of the spectrum (continuous line), reporting the region near g = 2, is due to the superposition of Ge(1) and E'-Ge centers; (b). H(II) centers concentration as a function of the accumulated dose in sample A.

The signal [13, 14] of H (II) defect [5] is present in the EPR spectra of irradiated sample A, as shown in Fig. 4(a), and is characterized by a doublet split by ~118 G. The H (II) center is a product of GLPC and it results from the reaction with a H atom [5, 14]. In particular the H atom binds itself with one of the two electrons of the lone pair, giving the structure $=Ge^{\bullet}-H$. This kind of defect is paramagnetic, and its EPR spectrum consists of two components generated by the hyperfine interaction of the electron spin with the nuclear spin of the H atom [5, 13]. The central part of the spectrum reported in Fig. 4(a) shows the region near g = 2 and evidences the presence of Ge(1) and E'-Ge centers [2, 3]. In Fig. 4(b), the concentration growth of the H (II) centers as a function of the accumulated dose is shown as determined using the signal of both the hyperfine lines after every irradiation step. It is important to note

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that the EPR signal of H (II) defect has been detected at minor dose values than the PL signal of GLPC. This happens because of the higher sensitivity of the EPR measurement technique and for the presence, in 3-6 eV range, of other OA active centers that subtract light to GLPC ones.

From the comparison of the here reported data we can argue that the γ irradiation has induced GLPC centers in sample A. In fact, we observe the characteristic two PL bands centered at ~3.2 eV and ~4.3 eV with a ratio between them very similar to that of PL bands linked to GLPC centers produced during sample synthesis (*native centers*) and observed also in natural silica. At the same time the peak position of 3.2 eV induced PL component depends on excitation energy similarly to the native one, whereas its FWHM shows lower dependence. This difference can be attributed to different effects of the defect environment [4, 5]. From the time decay data we can argue that the same cause originates the small differences in lifetime of native and irradiation induced GLPC defects. The different values could be due, for example, to a more efficient non radiative decay channel connecting T_1 to S_0 in the induced defect. The generation of GLPC in sample A is further supported by the experimental detection of the paramagnetic defect H(II) generated by a reaction of this defect with an H atom [4, 5].

A detailed description of the microscopic process of GLPC generation by irradiation is beyond the scope of the present paper and needs further investigation. However, it is worth to note the analogy with high purity a-SiO_2 where it has been found that by ion implantation [15-17] or gamma irradiation [18, 19] the photosensitive twofold coordinated Si (=$Si^{\bullet\bullet}$), featuring an absorption band at 5.06 eV and two related emissions at 4.4 eV and 2.7 eV [5], can be induced. These features suggest that the main generation mechanism of twofold coordinated Si defects involves the displacing of O from bonding configuration, due to knock–on or radiolysis processes. Such a generation process should depend on the structure of the material (for example on the strength of Si-O bonds) but not on its OH content. This hypothesis is also supported by experimental results [19] showing no correlation between twofold coordinated Si and OH groups content in gamma irradiated high purity a-SiO_2.

On the basis of these considerations, the GLPC generation process by ionizing radiation in our sample A, having about 1000 ppm by weight of OH and no detectable H_2, can be attributed to oxygen displacements without directly involving the H species. In this context, also large differences in OH content between sol-gel and MCVD or VAD materials could not be relevant for the generation of GLPC by ionizing radiation.

4. Conclusions

We have studied the effects of gamma radiation in sol-gel Ge-doped samples, and we have evidenced the presence of induced GLPC defects. This finding shows the occurrence of a relevant photosensitivity process in Ge-doped silica as GLPC are responsible for refractive index change. In addition, our results showing the possibility to induce GLPC with ionizing radiation, suggest that such radiation could be used to spatially activate the amorphous system enabling to write a photosensitive pattern through for example electron or X ray beams.

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