Comparison Between Point Defect Generation by γ-rays in Bulk and Fibre Samples of High Purity Amorphous SiO_2

Benoit Brichard, *Member, IEEE*, Simonpietro Agnello, Laura Nuccio, and Laurent Dusseau, *Member, IEEE*

***Abstract*—We compare the E', H(I) and Si-ODC(II) contents in a low-OH high-purity a-SiO_2 both in bulk and fibre forms. The investigation includes the effects of hydrogen loading of the fibre. We found that the H(I) centre appears during irradiation and that its concentration tends to increase with the dose in fibers impregnated with molecular hydrogen. For the hydrogen-treated fibers, no experimental repeatability could be found in the measurements of E' and Si-ODC(II) although an acceptable agreement was still found in non-hydrogenated samples. This result suggests a possible complex reaction mechanisms under gamma radiation when the glass has a hydrogen excess.**

***Index Terms*—Fibre, gamma, hydrogen, point defects, silica.**

I. Introduction and Background

APPLICATIONS of amorphous SiO_2 (a-SiO_2) in optical and electronic devices for radiation environments are limited by the effects of ionizing radiation on the employed material. One of the principal causes of material degradation is the generation of point defects in a-SiO_2 (see [1] and [2] for a recent review). These defects act as traps for electrons or holes and give rise to optical absorption (OA), photoluminescence (PL) bands in the visible and UV spectral range and to electron paramagnetic resonance (EPR) signals. The generation processes of these radiation-induced defects can be considerably modified in presence of hydrogenated species (H or H_2). For instance earlier studies on irradiated optical fibres have shown that hydrogen can drastically reduce the radiation-induced absorption at 2 eV (600 nm) [3], [4]. Hydrogen-impregnated silica offers a great potential for the development of radiation-resistant fibres used for applications in the visible range[5]. Both theoretical and experimental considerations support the idea that this RIA reduction observed in the visible spectrum can be attributed to the reaction of hydrogen with the non-bridging oxygen holes centres (NBOHCs) which in turn yields hydroxyl groups[6]–[8].

Manuscript received September 8, 2007; revised March 12, 2008. Current version published September 19, 2008. B. Brichard was supported by the European Commission—EURATOM fusion technology program. The content of the publication is the sole responsibility of its authors and it does not necessarily represent the views of the Commission or its services.

B. Brichard is with the SCK•CEN, Boeretang 200 2400 Mol, Belgium (e-mail: bbrichar@sckcen.be).

S. Agnello and L. Nuccio are with the Department of Physical and Astronomical Sciences, University of Palermo, Via Archirafi 36, I-90123 Palermo, Italy.

L. Dusseau is with the University of Montpellier II, place Eugène Bataillon, 34 095 Montpellier, France.

Digital Object Identifier 10.1109/TNS.2008.2001706

Conversely it was however reported that the presence of hydrogen tends to increase the RIA in the blue-UV spectrum, especially if the fibre is irradiated at high dose (> 1 MGy)[9]. The reason for this behaviour is not precisely understood but it is believed to be related with the formation of oxygen-deficiency point defects which are found in different forms in irradiated silica. Probably the most widely studied of this category of defect is the E' centre ($O \equiv Si^{\bullet}$). Its structural model is a threefold coordinated silicon atom with an unpaired electron in a sp3 hybrid orbital. It is responsible for an electron paramagnetic resonance signal at $g \sim 2.0006$ and for an optical absorption band centered at 5.8 eV with a full width at half maximum (fwhm) of 0.8 eV and an oscillator strength $f = 0.4$[10]. Another paramagnetic point defect in silica is the hydrogen related H(I) centre ($O = Si^{\bullet} - H$). Its structure is similar to the E' centre, except for an hydrogen atom substituting one of the three oxygen atoms that are bonded to the silicon in the E' centre. The fingerprint of H(I) centre is an EPR hyperfine doublet with a splitting of about 7.4 mT [10]. The reasons for studying these two point defects in the framework of this work are their usefulness as probe for the radiation sensitivity of the material and the possibility to use the H(I) centre as a marker for the presence of hydrogen. An oxygen deficient centre (ODC) that has been hypothesized to be precursors of these two defects is the so called ODC(II) centre [10], [11], characterized by an optical absorption band centered at about 5 eV, inside which two photoluminescence bands, at 4.4 eV and 2.7 eV, can be excited [10]. The structural model for this defect is still the subject of controversies, as some authors suggest it is a non relaxed oxygen vacancy [12], and some others a twofold coordinated silicon [2], [13]. This latter hypothesis links the ODC(II) to the H(I) centre, as it is commonly thought that this defect is the result of the reaction between an hydrogen atom and the twofold coordinated silicon [10].

The understanding of these generation and inter-conversion mechanisms between point defects as well as a deeper knowledge of the influence of hydrogen are key factors for the development of radiation-resistant silica glass. In this work we report a series of EPR and photoluminescence (PL) measurements in an attempt to elucidate the role of hydrogen regarding the generation of oxygen deficient centres. We compare EPR signals resulting from the generation of H(I) and E' centres that are generated in a low OH pure silica fibres. Photoluminescence (PL) measurements have been also carried on these samples to detect Si-ODC(II).

An other important question also concerns the influence of the matrix in the generation processes of these point defects. This work addresses partly this aspect by reporting a comparative study on EPR measurements performed on both the fibre preform and the corresponding fibre irradiated in identical conditions.

II. Experimental Details

We selected a fibre preform fabricated by Hereaus-Tenevo (Germany) from a dry a-SiO_2 ($OH < 0.1$ ppm) and low chlorine ($Cl < 20$ ppm) material called STU [14]. This type of glass is known to be highly radiation-resistant [15]. This fibre preform was drawn into a step-index fibre of 200 μm diameter with a core/cladding ratio of 1.2 and a F-doped cladding. The fibre was coated with aluminium and some meters of the drawn fibre were then further soaked in a molecular hydrogen atmosphere at high temperature (> 100 ° C) and pressure (> 300 bars). The fibre remained in the autoclave until the H_2-content reached at least 10^{19} H^2/cm^3. The rationale behind the use of an aluminium coating is to prevent hydrogen escaping the fibre core. The drawing of the fibre and the hydrogen-loading process was conducted at the Fibre Optic Research Centre in Moscow.

In addition, several bulk samples of dimensions $5\times5\times1$ mm^3 were cut from the fibre preform and irradiated, simultaneously with the fibres, at several total doses from 0.5 up to 10 MGy and at a dose-rate of 19.5 Gy/s (SCK•CEN, Belgium) [16]. After removing the aluminium coating using a solution of $FeCl_3$ all the samples were carefully cleaned and sent to the University of Palermo for PL and EPR measurements.

The fibre samples for the EPR measurements were prepared cutting; ~ 0.5 m of fibre, corresponding to a silica volume of about 16 mm^3, into pieces of 5 mm of length, in order to fit the EPR spectrometer cavity dimensions. EPR measurements have been carried out using a Bruker EMX spectrometer working at 9.8 GHz (X band). The E' centre signal has been revealed with a microwave power $P = 0.8$ W and a modulation field with peak-to-peak amplitude $Bm = 0.01$ mT and frequency $fm = 100$ kHz. The 7.4 mT doublet has been revealed with a microwave power $P = 0.05$ mW and a modulation field with peak-to-peak amplitude $Bm = 0.4$ mT and frequency $fm = 100$ kHz. These EPR measurement conditions have been verified to not distort the EPR signal and to not induce microwave saturation effects. The defect concentration has been estimated by comparing the double integral of the EPR signal under consideration with the signal of E' centres in a silica sample whose defect concentration has been determined by spin-echo experiments. The relative concentrations estimated using this procedure are affected by a 10% error. A detection level of about 10^{13} spin/cm^3 has been estimated.

The same fibre pieces used in EPR measurements have been used to perform PL measurements. They have been mounted in a planar configuration placed at 45° with respect to the excitation beam, and the PL light has been collected in the direction opposite to the reflected beam (so called "back-scattering geometry"). A Jasco FP-6500 spectrometer, mounting a Xenon lamp of 150 W, has been used to detect the steady state PL emission in the range 2.5–5.0 eV, excited at 5.0 eV, with bandwidths of 5 nm for the excitation and 3 nm for the emission. The photobleaching induced by the Xenon lamp, evaluated by repeating the measurements on the fibre samples, was found to be negligible.

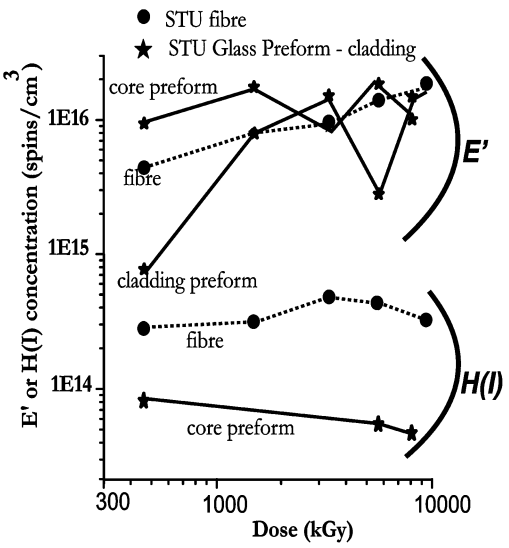

Fig. 1. E' and H(I) centres in the core and cladding STU glass preform (star) and in the as-drawn fibre (circle).

Irradiation tests have been carried out three times on the same samples over a period of 18 months in order to check about the repeatability.

III. Results

Prior to any irradiation tests we first determined the concentration of E' and H(I) centre in the pristine fibre preform (core and cladding) as well as in the hydrogen-treated and untreated STU fibres. Only EPR signals from E' centres could be detected in the untreated STU fibre and was 4.74 10^{13} (spins / cm^3). The preform and the fibre were then irradiated with γ-rays. Fig. 1 compares the results by showing the evolution of both E' and H(I) concentration as a function of the gamma dose in the STU fibre preform as well as in the as-drawn fibre. The E' concentration tends to be similar either in the preform or fibre and increases with dose.

By contrast the H(I) content tends to decrease or to remain stable with respect to the dose and independently of the fibre or the preform. The H(I) concentration is however slightly higher in the fibre than in the core preform. No H(I) centre has been detected in the cladding preform, i.e., where fluorine is present.

We also carried out PL measurements in the STU fibres with and without hydrogen. A PL response was obtained at 4.4 eV in both types of fibre (see Fig. 2) and is attributed to SiODC(II). We performed the experiment two times. While good agreement can be obtained with the STU fibre for two similar (but separated) experiments we could not obtain a satisfactory repeatability for the STU fibre treated with hydrogen. Compared to the first irradiation session the PL intensity of the hydrogenated STU fibre measured in the second irradiation session was much more intense and clearly well above the PL intensity recorded in the hydrogen-free fibre sample.

The corresponding evolution of the E' and H(I) content measured in the 1st and 2nd irradiation sessions are displayed at Fig. 3. Again we observed that the E' or the H(I) content are

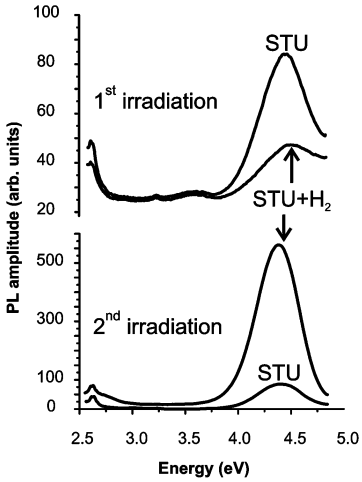

Fig. 2. PL band at 4.5 eV attributed to SiODC(II) in fibres irradiated at 10 MGy showing opposite behaviour in the hydrogenated fibres and the lack of repeatability in such samples.

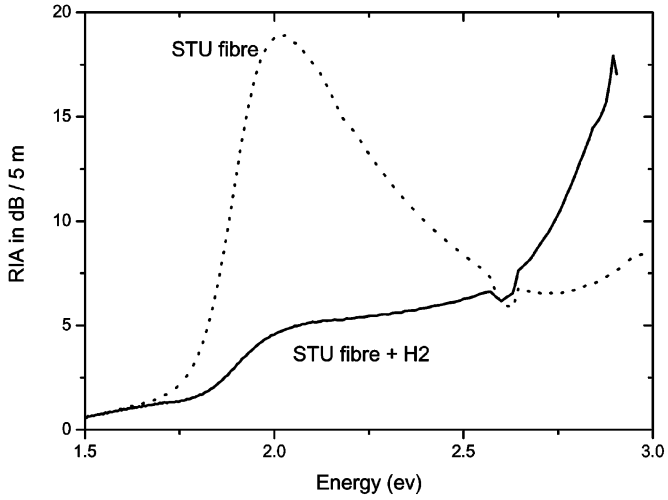

Fig. 4. Radiation-induced absorption (RIA) in normal and hydrogen-treated STU fibres irradiated at 5.5 Gy/s. The graph shows the radiation-sensitivity enhancement of the hydrogenated STU fibre in the 2.6–3 eV region. The E' and H(I) concentration corresponding to these RIA measurements are given at Fig. 3 as open symbols.

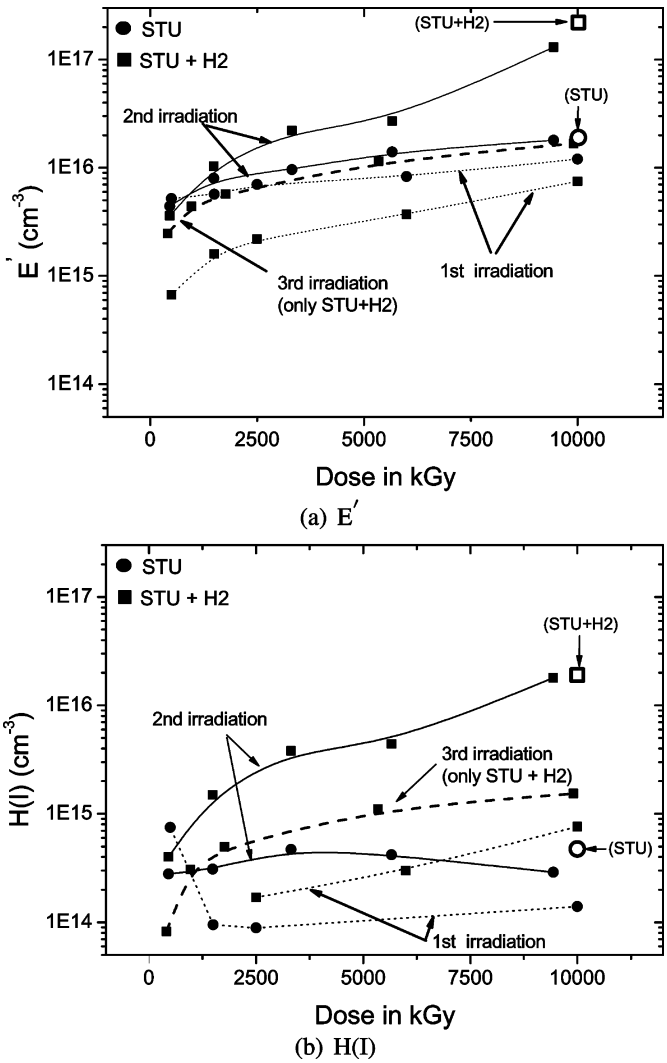

Fig. 3. Evolution of the E' and H(I) concentration in H_2-free (circle) and hydrogenated (square) STU fibres. for several irradiation sessions at 19.5 Gy/s. Data of the 1st irradiation are the same as those displayed at Fig. 1 and redrawn here for convenience. Open symbols refer to an additional measurement for fibre samples but irradiated at 5.5 Gy/s.

well reproducible for the hydrogen-free fibre sample within a factor 2 to 3 from one irradiation session to another. We see that the E' content increases with the dose whereas the H(I) content seems to remain almost constant or to decrease with the dose, in agreement the previous observations reported for the preform sample (see Fig. 1).

However the repeatability of our measurements is far less satisfactory concerning the hydrogenated fibre sample. Nevertheless, we observed a *qualitative* increase in the E' content inside a given hydrogenated fibre set. This increase is systematically accompanied by a rise of the H(I) content as well. From that point of view this result contrasts with the non-hydrogenated fibre or preform sample.

To confirm this result we conducted a 3rd irradiation session in similar conditions as the previous one. As displayed at Fig. 3 the results indeed confirm the clear increase of the E' and H(I) content in the hydrogenated fibre when considering the data per hydrogenated fibre sets.

As indicated at Fig. 4 we also performed (independently) an in-situ radiation-induced absorption (RIA) measurement on the hydrogenated and non-hydrogenated fibre samples. The fibres have been irradiated up to 10 MGy at a dose-rate of 5.5 Gy/s (about 4 times lower compared to the other measurements). Due to the action of hydrogen the RIA in the hydrogenated fibre sample is lower around 2 eV (reduction of the NBOHC content) but then rises steeply for photon energies above 2.6 eV. As mentioned earlier the presence of hydrogen tends indeed to enhance the radiation sensitivity in the blue-UV region. For comparison with the other data sets the E' and H(I) content corresponding to these RIA measurements have been also reported on Fig. 3 as single open square and circle data points. Interestingly, we note that the radiation sensitivity enhancement in the UV, characteristic of the hydrogenated fibre, actually corresponds to a high content of E' and H(I) as well as a high PL intensity.

IV. Discussion

The EPR measurements on the pristine sample show that E' centres are formed during the drawing process but they disappear when the fibre is further loaded with hydrogen. This observation suggests that the E' centres are likely to be converted in diamagnetic centres like Si-H. Nevertheless they do not form H(I) centres since these latter are not detected in any form of glass prior to irradiation. The comparison of the measurements between preform and fibre tells that, in the present case, the fibre drawing has a influence in the generation of point defects as already reported earlier[17]. Under radiation further defects are of course generated but the rate of change of the content seems to be fairly independent of the glass form. It is also worth to note that the cladding preform shows, at least in the low dose regime, a lower E' concentration. Note that no H(I) was detected even under radiation. This result underlies the positive role of fluorine to limit the formation of point defects as it was already reported earlier [18].

The H(I) centres are created after irradiation and their concentration rises with the dose when there is an excess of hydrogen but they are in general much less abundant compared to the E' centres. They also appear in the untreated STU fibre but their concentration does not increase with the dose. It means that a fix number of hydrogenated species are certainly introduced during the manufacturing process and that these hydrogenated species only react upon irradiation.

For the measurement of the E' concentration we observed an acceptable repeatability for the hydrogen-free fibre. Imai [19] reported the E' concentration to be higher than $10^{16}/\text{cm}^3$ when low-OH silica glasses are irradiated at 1 MGy, including hydrogenated samples. In the present case we found the E' concentration to be always less than 10^{16} spins/cm^3 at similar ionising doses which underlies the good radiation resistance of the presently investigated glass. However However no repeatability for the E' centres can be established in the hydrogenated fibre samples. This discrepancy makes the situation for E' centre less clear when the fibre is hydrogenated. In Imai's study [19] it was shown that, in the hydrogenated samples, more E' centres are induced when the dose increases. From that point of view the second irradiation session is in better agreement with the Imai's observations.

We also noted a similar discrepancy for the PL measurements related to SiODC(II) defects in hydrogenated fibres. The variation of the PL signal exhibits the same behaviour as that of the E' or H(I) centres in the hydrogenated samples. The PL intensity related to the SiODC(II) defect is significantly higher in the hydrogenated samples when the E' and H(I) content are high as well. It is therefore clear that radiation sensitivity involves of these defects. Unfortunately we can not identify a good reason explaining the anomalous behaviour observed in the hydrogenated STU fibre when irradiated in separated irradiation sessions. This fact suggests that a complex reactional behaviour takes place between hydrogen and silicon related defects generated under radiation, avoiding repeatability.

The RIA enhancement observed in the 3 eV region for hydrogenated fibres might be connected with the rise of the silicon dangling bonds, like E' and H(I). However, although E' and H(I) strongly absorb light with typical oscillator strengths of 0.1–0.5, their central peaks are located relatively far in the UV region, well above 3 eV. Even with a concentration of the order of 10^{17} cm^{-3} the possible contribution from these centres to the RIA would be extremely small ($< 10^{-13}$ dB/5m). Another possibility of this RIA enhancement could be actually linked with the associated SiODC(II) also apparently more abundant in hydrogenated fibres. Skuja reported a weak absorption band of SiODC(II) centered at 3.15 eV (fwhm:0.34 eV), i.e., close to the spectral absorption data obtained on the fibre. The oscillator strength $f \sim 10^{-6}$ associated to this band is nevertheless very weak, implying that the SiODC content should rise up to figure as high as 10^{19} cm^{-3} to obtain RIA of the order of dB/m at 3 eV.

V. Conclusion

We carried out EPR and PL measurements on a low OH high purity silica glass either in bulk or fibre forms. Only the E' centre could be detected in pristine hydrogen-free fibre samples and is likely to be due to the drawing process. Since no H(I) centres are present prior to irradiation it is concluded than Si-H bonds are formed in presence of hydrogen.

After irradiation H(I) centres are formed in all types of fibres. Their concentration tends to increase as a function of the dose but only in the hydrogenated fibres. This behaviour could contribute, directly or indirectly through the associated SiODC(II), to the RIA enhancement generally observed in the blue-soft UV spectral region when the hydrogenated fibre is irradiated at high gamma dose. This observation shows the limitation of hydrogen in protecting the glass under radiation. Hydrogen is efficient to suppress oxygen dangling bonds like NBOHC (defect absorbing at 2 eV)[5], [9] but as the dose increases this protective role becomes less efficient because more silicon dangling bonds are created. In turn they strongly enhance the soft UV region if the fibre is irradiated at high dose (> 1 MGy).

However, it is not clear what types of defects are actually responsible for the UV radiation-sensitivity enhancement as the evolution of the E' and SiODC(II) concentration was not reproducible in hydrogen treated fibres. At present we can not explain the discrepancies. Further investigations are therefore needed to clarify the role of hydrogen with respect to E', H(I) and SiODC(II) centres.

References

[1] D. Griscom, "The nature of point defects in silicon dioxide," in *Defects in SiO_2 and Related Dielectrics: Science and Technology*. Norwell, MA: Kluwer, 2000, pp. 117–161.

[2] L. Skuja, M. Hirano, H. Hosono, and K. Kajihara, "Defects in oxide glasses," *Phys. Stat. Solidi C: Conf.*, vol. 2, pp. 15–24, 2005.

[3] K. Nagasawa, Y. Hoshi, Y. Ohki, and K. Yahagi, "Improvement of radiation resistance of pure silica core fibres by hydrogen treatment," *Jpn. J. Appl. Phys.*, vol. 24, no. 9, pp. 1224–1228, 1985.

[4] A. Tomashuk, E. Dianov, K. Golant, and A. Rybaltovskii, "Gamma-radiation-induced absorption in pure-silica-core fibers in the visible spectral region: The effect of h2-loading," *IEEE Trans. Nucl. Sci.*, vol. 45, no. 3, pp. 1576–1579, Jun. 1998.

[5] B. Brichard, A. Fernandez, H. Ooms, F. Berghmans, M. Decreton, A. Tomashuk, S. Klyamkin, M. Zabezhailov, I. Nikolin, V. Bogatyrjov, E. Hodgson, T. Kakuta, T. Shikama, T. Nishitani, A. Costley, and G. Vayakis, "Radiation-hardening techniques of dedicated optical fibres used in plasma diagnostic systems in iter," *J. Nucl. Mater.*, vol. 329–333, pp. 1456–1460, 2004.

[6] M. Vitiello, N. Lopez, F. Illas, and G. Pacchioni, "H2 cracking at SiO_2 defect centers," *J. Phys. Chem.*, vol. 104, no. 20, pp. 4674–4684, 2000.

[7] J. Shelby, "Radiation effects in hydrogen-impregnated vitreous silica," *J. Appl. Phys.*, vol. 50, no. 5, pp. 3702–3706, 1979.

[8] B. Brichard, A. Tomashuk, V. Bogatyrjov, A. Fernandez, S. Klyamkin, S. Girard, and F. Berghmans, "Reduction of the radiation-induced absorption in hydrogenated pure silica core fibres irradiated in situ with gamma-rays," *J. Non-Cryst. Solids*, vol. 353, no. 5-7, pp. 466–472, 2007.

[9] A. Tomashuk, K. Golant, and E. Dianov, "Radiation-induced absorption and luminescence in specially hardened large-core silica optical fibers," *IEEE Trans. Nucl. Sci.*, vol. 47, no. 3, pp. 693–698, Jun. 2000.

[10] L. Skuja, "Section 1. Defect studies in vitreous silica and related materials: Optically active oxygen-deficiency-related centers in amorphous silicon dioxide," *J. Non-Cryst. Solids*, vol. 239, no. 1-3, pp. 16–48, 1998.

[11] C. Jones and D. Embree, "Correlations of the 4.77–4.28-ev luminescence band in silicon dioxide with the oxygen vacancy," *J. Appl. Phys.*, vol. 47, no. 12, pp. 5365–5371, 1976.

[12] H. Imai, K. Arai, H. Imagawa, H. Hosono, and Y. Abe, "Two types of oxygen-deficient centers in synthetic silica glass," *Phys. Rev. B*, vol. 38, pp. 12772–12772, 1988.

[13] L. Skuja, A. Streletsky, and A. Pakovich, "New intrinsic defect in amorphous SiO_2: Twofold coordinated silicon," *Solid State Commun.*, vol. 50, no. 12, pp. 1069–1072, 1984.

[14] G. Schotz and J. Vydra, "New silica fiber for broad-band spectroscopy," *ASP Conf. Ser.*, vol. 152, 1998.

[15] H. Henschel, O. Kohn, and U. Weinand, J. L. Autran, Ed., "A new radiation hard optical fibre for high dose values," in *Proc. Eur. Conf. Radiation and its Effects on Components and Systems*, 2002, vol. 1, pp. 179–185.

[16] A. Fernandez, B. Brichard, and F. Berghmans, "SCK·CEN gamma irradiation facilities for space radiation tolerance assessment programs," presented at the ata Workshop, NSREC, 2006.

[17] Y. Hibino and H. Hanafusa, "Defect structure and formation mechanism of drawing-induced absorption at 630 nm in silica optical fibers," *J. Appl. Phys.*, vol. 60, no. 5, pp. 1797–1801, 1986.

[18] K. Kajihara, Y. Ikuta, M. Oto, M. Hirano, L. Skuja, and H. Hosono, "UV-VUV laser induced phenomena in SiO_2 glass," *Nucl. Instrum. Meth. Phys. Res.*, vol. 218, pp. 323–331, 2004.

[19] H. Imai and H. Hirashima, "Intrinsic- and extrinsic-defect formation in silica glasses by radiation," *J. Non-Cryst. Sol.*, vol. 179, pp. 202–213, 1994.