

Generation and excitation of point defects in silica by synchrotron radiation above the absorption edge

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We report photoluminescence measurements carried out on amorphous SiO₂ upon excitation by synchrotron light. Exposure of the as-grown material to above-edge light at low temperature induces the formation of nonbridging oxygen hole centers (NBOHC), localized in a thin layer below the surface limited by the penetration depth (tens of nm) of impinging light. After concluding the exposure to 11 eV light, stable defects are revealed by observing their characteristic 1.9 eV photoemission band excited at 4.8 eV. The local concentration of induced defects, supposedly formed by nonradiative decay of excitons, is very high (close to $\sim 10^{21}$ cm⁻³) and independent of the previous history of the material. On the other side, we also observe the 1.9 eV emission upon excitation between 9 and 14 eV, accompanied by the 2.5 eV luminescence ascribed to self-trapped excitons. This 1.9 eV band exhibits a temperature dependence different from that measured by excitation within the absorption bands at 4.8 and 6.4 eV of NBOHC, and is proposed to arise from the fact that NBOHC are generated by above-edge light in their excited electronic state.

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I. INTRODUCTION

Amorphous silicon dioxide (SiO₂), or silica, is an insulator playing an archetypal role in current physics of amorphous solids, as well as a material widely used in applications including optical fibers, optical components for photolithography, and metal-oxide-semiconductor transistors. The wide applicability of this solid is vastly founded on its high optical transparency extending from the infrared up to the vacuum ultraviolet (VUV) absorption edge, located at $E_0 \sim 8.5$ eV.¹⁻³

The optimal features of silica are limited by the formation of point defects, usually induced by exposure to ionizing or high-power laser radiation and giving rise to wide absorption bands limiting the transparency range.¹⁻⁴ The two most common point defects in silica, virtually responsible of the whole UV absorption of irradiated high purity silica specimens, are the paramagnetic dangling bonds localized on Si (also known as E' center) and on O [nonbridging oxygen hole center (NBOHC)] atoms.¹⁻⁴ The microscopic structure of these two defects can be represented as $\equiv\text{Si}^\bullet$ (E' center),⁵ and $\equiv\text{Si}-\text{O}^\bullet$ (NBOHC),^{6,7} where the \equiv symbol stands for three back bonds with oxygen atoms, while \bullet represents an unpaired electron. While the optical activity of E' center consists of an absorption band peaked at 5.8 eV,^{1,4} that of NBOHC is more complex. Indeed, the latter gives rise to two absorption bands in the UV range, peaked at 4.8 and 6.4 eV, accompanied by a much weaker band at 2.0 eV.⁸⁻¹¹ All the three absorptions excite a long-living (10 μs) emission at 1.9 eV which is the most distinctive feature of this defect.⁷ NBOHC is currently studied as an important model defect having some almost unique features among defects in oxides related to its weak coupling with the vibrations of the matrix.¹²⁻¹⁵

While the detrimental influence of point defects on the performance of silica in applications is a well established fact, defects are still the subject of ongoing research aimed to clarify several poorly understood aspects of their generation

processes, the factors determining their stability or instability, as well as some of their most basic spectroscopic properties. In regard to the formation mechanisms, while several works have investigated the generation of E' and NBOHC centers induced by high-power laser (up to 7.9 eV photon energy) or ionizing radiation,¹⁶⁻²⁶ little information is available on possible generation of these defects upon exposure of SiO₂ to low power above-edge VUV radiation.

Although the position $E_0 \sim 8.5$ eV of the edge can be operatively defined by VUV absorption measurements, the physical interpretation of the electronic transitions responsible for absorption above E_0 is still debated, and the same occurs for the value of the band-gap energy, reported by different authors to be either near 9 eV or near 11 eV.^{1,27-29} While silica shows measurable photoconductivity starting from 8.9 eV, photoconductivity and photoemission signals markedly increase only above 11 eV, this being accompanied by qualitative variations of the photoelectron energy distribution curve.^{1,27} Hence, it has been argued that the observed photoemission below 11 eV was due to secondary processes and not to band-to-band transitions, while $E_g \sim 11$ eV must be interpreted as the actual band-gap energy.²⁷ Following this interpretation, absorption between E_0 and E_g is mainly related to excitons and defect formation upon exposure to light in this spectral range is expected to be mainly driven by exciton dynamics.^{1-3,19,27,30,31}

We report here experimental data evidencing the ability of VUV synchrotron radiation with photon energy above E_0 to generate luminescent NBOHC centers in extremely high concentrations near the surface of an ordinary silica sample. While these results bear some practical relevance related to the use of synchrotron as a photoexcitation source for silica, they also evidence previously unknown aspects of the generation processes of defects in silica by VUV radiation and of the excitation mechanisms of the 1.9 eV luminescence characteristic of NBOHC defects.

II. EXPERIMENTAL SECTION

We performed measurements on two “wet” synthetic commercial amorphous SiO₂ samples (nickname: Suprasil311, Heraeus Quarzglas), manufactured by hydrolysis of SiCl₄ in a H₂/O₂ flame, highly pure (concentration of metallic impurities below 1 ppm (ppm) by weight) except for the presence of Si—OH impurities in a concentration of [Si—OH]= 2.8×10^{19} cm⁻³.³² Specimens were $5 \times 5 \times 0.5$ mm³ sized, as obtained by cut of a single $50 \times 5 \times 0.5$ mm³ slab. One of the two samples, hereafter referred to as W_0 , was used as-received. This sample features no detectable luminescence or absorption signals before the experiment. The second sample, named W_β and initially identical to W_0 , was prepared for the experiment by irradiation with β rays performed in a Van de Graaff accelerator (2.5 MeV electrons energy) with a $1.2 \cdot 10^6$ kGy dose. Such a treatment induces in the sample the formation of several point defects, the main being the E' center and the NBOHC, easily detectable by their characteristic 5.8 and 4.8 eV absorption bands. Preliminary photoluminescence (PL) measurements on the 1.9 eV emission band of the NBOHC excited at 4.8 eV allowed to estimate its concentration [NBOHC]= 1.2×10^{18} cm⁻³ by comparison with a reference sample where the intensity of the 2.0 eV absorption band of NBOHC could be measured. The absorption coefficient at 4.8 eV was measured to be 8 cm⁻¹. For comparison purposes, we performed measurements also on an as-grown “dry” synthetic SiO₂ sample (commercial nickname: Suprasil F300, trademark of Heraeus Quarzglas), produced by reaction of O₂ with SiCl₄ in water-free plasma. This sample, hereafter referred to as D_0 , features a very low concentration of Si—OH impurities ([Si—OH]< 8×10^{16} cm⁻³).³²

We acquired PL spectra under excitation with synchrotron radiation at the SUPERLUMI experimental station in DESY-Hamburg (HASYLAB-Beamline I). In the experiments described in this paper, synchrotron radiation serves both as an irradiation source able to generate NBOHC, and as a photo-excitation source of their 1.9 eV emission band. The excitation wavelength was selected via a 2 m monochromator allowing an excitation bandwidth of 0.3 nm. The cross section of the synchrotron beam was about 2.5 mm². For the purposes of this experiment it is relevant to know the photon flux of the beamline at the sample position. From beamline’s calibration data,³³ its order of magnitude in our experimental conditions can be estimated to fall between 10^{13} – 10^{14} photons/(cm² s) at $E=11$ eV. The emission spectrum was detected in front-face geometry with the sample in high vacuum (10^{-9} – 10^{-8} mbar). The signal was dispersed by a 300 lines/mm monochromator with 500 nm blaze, and detected by a charge coupled camera cooled by liquid N₂. The emission bandwidth was 10 nm. Each reported spectrum was corrected for the response and dispersion of the detecting system and scaled for the intensity of the synchrotron beam at the exciting photon energy. The exciting spectrum was estimated prior to the experiments by recording the excitation profile of a sodium salicylate reference sample. Temperature was controlled by a liquid He flow cryostat.

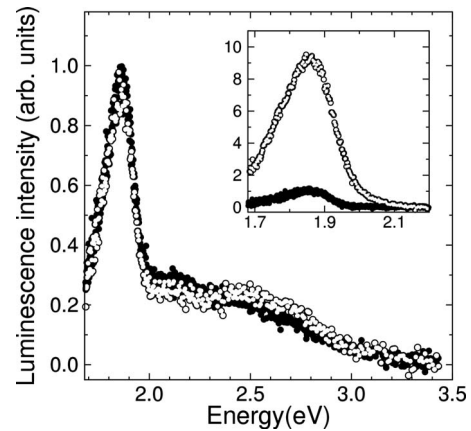


FIG. 1. Photoluminescence signal measured at $T=10$ K in as-grown (full symbols) W_0 and β irradiated (empty symbols) W_β silica samples under excitation by synchrotron light of 11.02 eV photon energy. Inset: signal measured in the two samples under 4.8 eV excitation.

III. RESULTS

The as-grown W_0 sample was cooled down to $T=10$ K and excited by synchrotron radiation with 11.02 eV photon energy, falling above the absorption edge of amorphous silica. Under these conditions, the sample emits a composite luminescence signal, shown in Fig. 1, consisting in a well resolved peak at 1.86 ± 0.02 eV with 0.20 ± 0.03 full width at half maximum (FWHM) and a broad band centered at 2.5 eV. The spectral features of the 1.86 eV peak are consistent with the characteristic emission signal of the NBOHC in silica;⁷ hereafter this signal will be simply referred to as the 1.9 eV band. Based on literature, the broad emission signal peaked at 2.5 eV can be attributed to self-trapped-exciton (STE) luminescence.^{1,27} After this first measurement performed under above-edge excitation, the W_0 sample showed the 1.9 eV signal also under 4.8 eV excitation, as reported in the inset of the same figure. The intensity of the band was found to be roughly the same (1.0 arb. units peak value) under the two excitations, while the 2.5 eV band was not detected under 4.8 eV excitation. It is worth noting that before exposing the sample to above-edge light, the signal of the NBOHC excited at 4.8 eV was absent in W_0 , as usual in as-grown silica. In other words, the 1.9 eV emission appeared in this sample only after the first exposure to above-edge light.

Differently from the W_0 specimen, the irradiated W_β sample already featured an intense 1.9 eV luminescence band under 4.8 eV excitation before any experiment performed with above-edge excitation. When W_β was subjected to the same sequence of measurements performed on W_0 , the following results were obtained: upon 11.02 eV excitation, W_β showed an emission spectrum with similar spectral features and almost identical intensity to that detected in the W_0 sample (Fig. 1). By contrast, when excited at 4.8 eV, the intensity of the 1.9 eV band observed in W_β was about nine times higher than that detected in W_0 (inset of Fig. 1).

We studied the excitation profile of these PL signals by recording the emission spectra in W_0 upon excitation at sev-

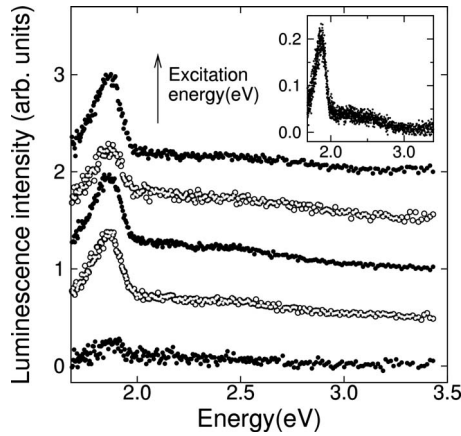


FIG. 2. Photoluminescence signals measured at $T=10$ K in W_0 sample under excitation by synchrotron light of 8.71, 10.25, 11.02, 13.33, and 14.1 eV photon energies. Spectra were vertically shifted for the sake of clarity. Inset: signal detected in D_0 sample by 10.25 eV excitation.

eral photon energies E_{exc} (Fig. 2) from 8 to 14 eV. We observed that the excitation profile features a threshold energy of ~ 8.7 eV, below which no emission is observed (except when exciting within the 4.8 or 6.4 eV absorption bands of the defect). Above the threshold, both the 1.9 eV and the 2.5 eV bands grow with E_{exc} , most of the growth occurring in the $8.7 \text{ eV} < E_{exc} < 10 \text{ eV}$ interval. Only weak variations are then observed for $E_{exc} > 10 \text{ eV}$. Also the ratio between the 1.9 and 2.5 eV components weakly depends on E_{exc} . In the inset of Fig. 2 we report the luminescence spectrum measured at $T=10$ K on the D_0 sample upon 10.25 eV excitation. The emission signal has a similar shape to that observed in the W_0 sample, with a ~ 4 times lower intensity.

In Fig. 3 we report the temperature dependence of the 1.9 and 2.5 eV bands excited at 11.02 eV, as obtained by measuring the emission spectrum of the W_0 sample at several temperatures. The thermal quenching of both signals appears

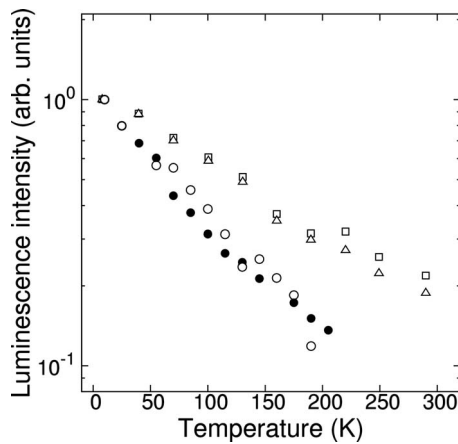


FIG. 3. Intensity of the 1.9 eV (empty circles) and 2.5 eV (full circles) luminescence signals detected in as-grown silica W_0 under excitation at 11.02 eV as a function of temperature. Intensity of the 1.9 eV signal as measured upon 4.8 eV excitation (triangles) and 6.4 eV excitation (squares). Data were normalized to the value measured at $T=10$ K.

to be active since the lowest measurement temperature. The 1.9 eV signal decreases by a factor of ~ 7 when temperature grows from 10 to 200K. The temperature dependencies of the 1.9 and 2.5 eV signals can be compared by normalizing both of them to the respective values detected at $T=10$ K. Such a comparison evidences a close agreement between the two curves. Contrastingly, the latter are different from the ordinary temperature dependence of the NBOHC signal, defined by the measurement of the 1.9 eV band under 4.8 or 6.4 eV (or 2.0eV, not reported) excitation. Indeed, by such a measurement we observe the 1.9 eV signal decreasing only by a factor of ~ 3 in the same temperature interval, and by a factor of ~ 5 when going up to 300 K. In regard to the STE emission at 2.5 eV, both its excitation threshold (Fig. 2) at about 8.7 eV, and the temperature dependence (Fig. 3) turn out to be consistent with literature data.²⁷ The fact that the thermal quenching of STE emission begins from 10K without featuring a lower threshold temperature, is typical of disordered materials such as amorphous SiO_2 , while it is not observed in crystalline SiO_2 .²⁷ This property suggests that a wide statistical distribution of activation energies controls the nonradiative decay process responsible for thermal quenching.

IV. DISCUSSION

The appearance (Fig. 1) of the characteristic NBOHC luminescence signal at 1.9 eV upon exposure to 11 eV light, in an as-grown silica previously not showing any detectable luminescence activity, leads to two conclusions: (a) VUV light above the absorption edge triggers the generation of stable NBOHC defects in the silica matrix, as demonstrated by their subsequent observation upon 4.8 eV excitation (inset of Fig. 1); (b) above-edge light is also able to excite the 1.9 eV emission of NBOHC defects. The result (b) can be reasonably interpreted as an evidence of NBOHC being generated by above-edge light in their excited electronic state, which is a common situation in molecule photodissociation processes.^{34,35} In this sense, the emission at 1.9 eV upon 9–14 eV excitation (Fig. 2) can be regarded as a probe of ongoing generation of NBOHC defects. Given the order of magnitude of the absorption coefficient of silica at 11 eV, $\alpha_0 \sim 10^6 \text{ cm}^{-1}$,²⁹ the penetration depth can be roughly estimated as the length after which the incoming 11 eV beam is 10-fold attenuated: $d_0 = 2.3\alpha_0^{-1} = 23 \text{ nm}$. This estimate should be considered as very approximate, also because of the possible occurrence of effects unaccounted for, such as the finite thickness of the polished layer being comparable with α_0^{-1} .

Strong evidences have been reported in literature suggesting that the band-to-band transition threshold of silica is located at $E_g \sim 11 \text{ eV}$, and that absorption at $E \leq E_g$ is basically excitonic, rather than being due to production of free charges across the gap.^{1,27} According to this interpretation, nonradiative decay of excitons must be assumed here as the fundamental mechanism leading to NBOHC generation upon illumination with 11 eV light. Existing data indicate that only a minor portion of excitons undergoes self-trapping (as indicated by the ~ 0.01 quantum yield of STE luminescence in silica), so as to become immobile at low temperatures and

eventually decay by emitting the observed 2.5 eV band.^{1,27,30} Most of the generated excitations remain free excitons (FE) until their energy is lost nonradiatively. Our data thus confirm generation of point defects as one of the nonradiative decay mechanisms of FE, although other nonluminescent defects (possibly E' centers) may be formed along with the NBOHC centers. The hypothesis of a NBOHC generation mechanism mediated by excitons could justify the outcome evidenced by Fig. 2: the intensity of the 1.9 and 2.5 eV signals depend on excitation energy in a similar way, both featuring the same threshold energy at 8.7 eV and their ratio weakly depending on E_{exc} . Moreover, as visible in Fig. 3, the temperature dependence of the 1.9 eV band as measured upon 11 eV excitation is quite different from that observed under ordinary 4.8 or 6 eV excitation. This indicates the involvement of temperature-dependent nonradiative processes playing a role before the excited NBOHC defect is ultimately generated. On the other side, the temperature dependence of the 1.9 eV emission excited at 11 eV is in close agreement with that of the STE signal at 2.5 eV. Also this finding qualitatively suggests a link between excitons and NBOHC generation, possibly the fact that STE luminescence and the generation of excited NBOHCs are both driven by FE. Nevertheless, a more detailed understanding of radiative and nonradiative channels determining the temperature dependency of the two emissions would be needed to verify the validity of this scheme. It has been argued that in amorphous SiO₂ the mobility of FEs at low temperatures is much lower than in crystalline SiO₂, and limited below the penetration depth of above-edge exciting light.²⁷ Here, this implies that the generation of NBOHC by 11 eV radiation takes place only in the thin region of depth d_0 below the surface accessible by the 11 eV photons. Data in Fig. 2 demonstrate that the threshold for photogeneration of NBOHC is ~ 9 eV. In the particular case in which NBOHC is induced in the sample by photons between 9 and 10 eV, the value of d_0 is expected to be higher than 23 nm, as the absorption coefficient of silica grows from $\sim 10^5$ to $\sim 10^6$ cm⁻¹ in this spectral region.²⁹ With this in mind, we will use d_0 calculated at 11 eV as a reference value in the rest of the discussion, which is devoted to discussing in further detail the generation mechanism of the defect.

Nonradiative decay of excitons has already been proposed in literature as a leading mechanism for defect generation, especially when excitons arise from two-photon absorption of laser light.^{16,17,19,21,36} The observation (Fig. 3) of thermal quenching of STE luminescence since the lowest measurement temperature indicates significant nonradiative decay of excitons already at 10 K, this being consistent with the formation of permanent defects at this temperature. When the exposure to 11 eV photons is carried out on the irradiated W_β sample (Fig. 1), a remarkably similar signal is measured. However, when exciting at 4.8 eV, the signal in W_β is about nine times higher than in W_0 . This can be explained as follows: in the initially defect-free W_0 sample, 11 eV photons create a distribution of defects concentrated in a d_0 deep volume, which are responsible of the signal measured upon 4.8 eV excitation. In W_β , these thin depth defects are generated as well, with very similar concentration and spatial distribution. Nevertheless, such a distribution of defects is su-

perimposed to the pre-existing bulk NBOHCs pre-induced in W_β by β irradiation, and uniformly distributed in the whole $d_\beta=0.5$ mm thickness. As a consequence, in the W_β sample the pre-existing bulk defects overwhelmingly contribute to the signal excited at 4.8 eV, while the similarity between the signals excited at 11 eV in the two samples indicates that the generation process of NBOHC in the d_0 deep volume occurs with the same efficiency in the two samples independently of the pre-existing defects in W_β .

To make this argument quantitative, we note that the emission signal measured upon excitation at photon energy E with intensity $I(E)$ is given by:

$$S(E) = yI(E)(1 - e^{-\alpha(E)d})\eta(E), \quad (1)$$

where $\alpha(E)$ is the absorption coefficient, $\eta(E)$ the PL quantum yield, y is a geometrical factor expressing the collecting efficiency of emitted photons, while $I(E)$ will be omitted hereafter since all emission spectra were scaled for excitation intensity. When exciting at 4.8 eV, for sake of simplicity Eq. (1) can be approximated by $S(4.8 \text{ eV}) \cong y\alpha(4.8 \text{ eV})d\eta(4.8 \text{ eV})$ within a 21% accuracy.⁴¹ The absorption coefficient is related to defect concentration by: $\alpha(4.8 \text{ eV}) = \sigma(4.8 \text{ eV}) \times [\text{NBOHC}]$, where the absorption cross section can be calculated from the oscillator strength $f=0.04$ to be $\sigma(4.8 \text{ eV}) = 5.5 \times 10^{-18} \text{ cm}^{-2}$.⁴² We can estimate the order of magnitude of the local concentration of NBOHC induced by synchrotron radiation in the d_0 deep volume, by comparing the detected intensity $S(4.8 \text{ eV})$ in the two samples. This quantity can be expressed by Eq. (1), setting d for each sample to be the depth in which defects probed by 4.8 eV excitation are distributed: $d=d_0=23$ nm for W_0 and $d=d_\beta=0.5$ mm for W_β . In this way we obtain:

$$\begin{aligned} \frac{S(4.8 \text{ eV}, W_0)}{S(4.8 \text{ eV}, W_\beta)} &\cong \frac{y\alpha(4.8 \text{ eV}, W_0)d_0\eta(4.8 \text{ eV})}{y\alpha(4.8 \text{ eV}, W_\beta)d_\beta\eta(4.8 \text{ eV})} \\ &= \frac{d_0[\text{NBOHC}]_{W_0}}{d_\beta[\text{NBOHC}]_{W_\beta}}. \end{aligned} \quad (2)$$

The leftmost side of Eq. (2) equals 1/9 from data in the inset of Fig. 1. Substituting also $[\text{NBOHC}]_{W_\beta} = 1.2 \times 10^{18} \text{ cm}^{-3}$, we get $[\text{NBOHC}]_{W_0} \sim 3 \times 10^{21} \text{ cm}^{-3}$. This is a very high value corresponding to about 1/10 of the concentration of tetrahedra in the silica matrix and to a mean NBOHC-NBOHC distance as low as 0.7 nm. This very approximate estimate has to be taken as an upper limit for NBOHC concentration. However, it clearly points to a picture in which the thin SiO₂ layer is so highly damaged by synchrotron radiation that the local concentration of induced defects is orders of magnitude higher than that induced by high doses (10⁶ kGy) of β radiation. It is worth noting that the local defect density ($\sim 10^{21} \text{ cm}^{-3}$) found in the subsurface layer is orders of magnitude higher than ever reported for silica irradiation experiments and may play an important role in a variety of processes such as synchrotron-induced surface

evaporation and light-stimulated desorption.³⁷ We also note that the concentration of NBOHC formed in W_0 per unit surface can be calculated as $d_0[\text{NBOHC}]_{W_0} \sim 7 \times 10^{15} \text{ cm}^{-2}$, comparable with the total number of photons received per unit surface by the sample during a typical exposure time ($\sim 10^2 \text{ s}$) in a measurement upon above-gap light. This suggests defect formation upon synchrotron irradiation to be very efficient (virtually approaching one defect per absorbed photon).

We finally discuss the precursor of NBOHC defects. Two generation processes are widely accepted in literature: (a) breaking of the oxygen-hydrogen bond on Si—OH precursor sites and (b) rupture of Si—O—Si bonds leading to the correlated formation of NBOHCs and E' centers.^{18,38,39} Given the very high estimated local concentration of formed defects (compare with $[\text{Si—OH}] = 2.8 \times 10^{19} \text{ cm}^{-3}$ in W_0 prior to the experiment), and since most of the incoming 11 eV photons are absorbed on ordinary matrix sites giving rise to excitonic transitions, one could simply conclude that NBOHCs are not generated in the thin layer by transformation of pre-existing Si—OH precursors, but they are rather formed out from initially undefected matrix sites. This model is consistent with data obtained (inset of Fig. 2) on the dry SiO_2 sample D_0 . Since the Si—OH concentration in D_0 is ~ 350 times lower than in W_0 , the detection in D_0 of a signal ~ 4 times smaller than in W_0 appears to confirm that the main contribution to induced NBOHC defects arises from breakage of Si—O—Si bonds.⁴³ So high a concentration of formed NBOHCs also suggests that in the subsurface layer most of the Si—O—Si sites are potential precursors for NBOHC generation. This is different from what is known for bulk silica, where it is generally assumed that only strained Si—O—Si bonds are efficient precursors for defect formation.¹

It is worth noting, however, that the local concentration of Si—OH impurities near the surface of the samples is not expected to be necessarily the same as in the bulk material. In particular, the Si—OH concentration on the surface, or in a thin layer below the surface, could be higher than in the bulk, and even comparable for dry and wet materials. For instance, studies on finely divided and/or porous silica systems have pointed out that the surface concentration of OH groups can be equal to that of silicon atoms.⁴⁰ So high a concentration is never found in the bulk of any SiO_2 material. If this occurs, our results would still be consistent with generation of NBOHC occurring by breaking of Si—OH precursors.

While present data do not allow to discern conclusively between the two possibilities, some indications can be drawn by optical absorption, laser-excited photoluminescence and electron spin resonance (ESR) measurements performed *ex situ*, i.e., after conclusion of the experimental session with synchrotron radiation, and removing the sample from the high vacuum sample chamber. We were not able to detect any appreciable variation within 10^{-2} optical densities of the absorption spectrum of W_0 and W_β samples after exposure to synchrotron radiation. In contrast, NBOHCs were detected in the W_0 sample by PL excited by 4.8 eV laser at room temperature, in a concentration $[\text{NBOHC}]_{ex\ situ} = 4 \times 10^{20} \text{ cm}^{-3}$, about 7.5 times lower than estimated above during synchro-

tron measurements. We believe the reduction to be due to passivation of near-surface defects by gaseous species, either present in the specimen and starting to diffuse when the temperature is raised (e.g., hydrogen produced together with NBOHC by OH breaking), or coming from ambient air when the sample is removed from vacuum. We remark that the value $[\text{NBOHC}]_{ex\ situ}$ corresponds to an optical attenuation of $\alpha * d_0 = 5 \times 10^{-3}$ on the peak of the 4.8 eV band that is smaller than our detection limit in absorption measurement. In regard to ESR measurements, we did not detect the signal of E' centers within our detection limit of roughly 10^{12} spins. This provides a clue to understand the generation mechanism of NBOHC. In fact, rupture of Si—O—Si bonds would be expected to generate NBOHC and E' centers in the same concentration, inconsistent with the ESR results, since a concentration of $[\text{NBOHC}]_{ex\ situ} = 4 \times 10^{20} \text{ cm}^{-3}$ corresponds to an absolute number 2×10^{13} of defects, based on the width d_0 of the damaged layer and on the area of the irradiated spot. This result suggests generation from near-surface Si—OH to be the prevalent formation mechanism of NBOHC by above-gap light, as opposed to generation from Si—O—Si bonds. While Si—O—Si breaking is generally regarded in literature as a natural outcome of nonradiative exciton decay, it is not obvious the mechanism by which Si—OH can be broken by nonradiative decay of excitons formed by absorption of above-gap light. The exciton needs to be trapped on a Si—OH impurity and decay by spending its energy in the breakage of the O—H bond. The details of this process remain open at the moment.

V. CONCLUSIONS

We demonstrated that the exposure of amorphous SiO_2 to above-edge synchrotron light at low temperature causes the formation of a remarkably high concentration of NBOHC defects in a thin layer extended for few 10^{-8} m below the surface. At the same time, we provide direct evidence that the 1.9 eV emission of NBOHC is triggered by above-edge illumination. We interpret both findings by proposing that nonradiative decay of excitons induced by absorption of VUV light leads to the generation of NBOHC in the emitting excited electronic state. After generation, NBOHCs can be detected by observing their characteristic 1.9 eV emission upon 4.8 eV excitation. The combined result of ESR, synchrotron, and laser-excited PL measurements suggests exciton-driven breakage of near-surface Si—OH groups to be the leading generation mechanism of NBOHCs.

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- ⁴¹The absorption coefficient at 4.8 eV in W_β was measured to be 8 cm^{-1} , slightly higher than expected (6.6 cm^{-1}) from the known cross section of NBOHC, due to minor contributions associated to other defects. This value of α yields an attenuation of $\alpha(4.8 \text{ eV})d_\beta \sim 0.4$. With this value, one gets $[1 - \exp(-\alpha d)] \sim 0.33$. Since $0.4/0.33 = 1.21$, one can estimate the approximation of low absorption for W_β to be correct within 21%, acceptable for the present purposes. All the more so, this is true for W_0 , since data in the inset of Fig. 1 imply the attenuation of W_0 at 4.8 eV to be 9 times smaller.
- ⁴²The f value of the 4.8 eV absorption band is proportional to that (1.9×10^{-4}) of the 2.0 eV band,¹⁴ experimentally derived from the radiative decay constant of the 1.9 eV luminescence, the proportionality coefficient being the ratio between the absorption band integrals (~ 200).¹¹
- ⁴³The small reduction in intensity from W_0 to D_0 may be due to some factor unaccounted for in data analysis. In particular, we expect the unchecked status of the surface to be critical in determining the intensity of this PL signal arising from such a thin layer. Two materials manufactured by different techniques are not expected to be identical as concerns surface roughness, this potentially leading to fluctuations in signal intensity.