

Visible to vacuum-UV range optical absorption of oxygen dangling bonds in amorphous SiO<sub>2</sub>Linards Skuja,<sup>1,\*</sup> Koichi Kajihara,<sup>2</sup> Masahiro Hirano,<sup>3</sup> and Hideo Hosono<sup>3,4</sup><sup>1</sup> Institute of Solid State Physics, University of Latvia, Kengaraga iela 8, LV1063 Riga, Latvia<sup>2</sup> Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji 192-0397, Japan<sup>3</sup> Frontier Collaborative Research Center, Mail Box S2-13, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan<sup>4</sup> Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan  
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Synthetic silica glass with an optical absorption spectrum dominated by oxygen dangling bonds (nonbridging oxygen hole centers, or NBOHCs) and having negligible (<1%) contribution from the usually copresent Si dangling bonds (E'-centers), was prepared by room temperature ultraviolet photobleaching of high SiOH content ("wet") silica, irradiated by F<sub>2</sub> laser (7.9 eV) at  $T = 80$  K. This allowed us to obtain the up-to-now controversial optical absorption spectrum of NBOHC in the ultraviolet and vacuum-ultraviolet (UV-VUV) region of the spectrum and to show that it is semicontinuous from 4 to 7.8 eV and cannot be represented by a pair of distinct Gaussian bands. Since NBOHC is one of the main UV-VUV range optical absorbers in silica, its spectral shape provides a tool to disentangle contributions of different color centers to optical losses in this spectral region.

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## I. INTRODUCTION

Amorphous silicon dioxide (a-SiO<sub>2</sub>) in the form of silica glass or oxide films, has one of the largest band gaps (~9 eV) among all known noncrystalline materials. It is the most important glassy optical material used in windows, lenses, and optical fibers for ultraviolet (UV), deep ultraviolet (DUV = 5–6.5 eV), and vacuum-ultraviolet (VUV > 6.5 eV) applications or for transmitting high-power laser pulses. In high-purity silica, optical absorption (OA) of point defects is often the main factor, limiting the practically achievable UV transmittance (see, e.g., Refs. 1 and 2 for an overview). This material remains relatively transparent for photon energies  $\hbar\omega < 4$  eV, even after a strong particle, ionizing, or UV irradiation. Intense radiation-induced UV OA bands start to appear at  $\hbar\omega > 4$  eV, in effect forming a continuum up to silica fundamental absorption edge ~8 eV. The three strongest OA peaks that can be discerned in this region are located at 4.8, 5.8, and 7.6 eV.

The 7.6-eV OA band is prominent in oxygen-deficient silicas and can be introduced by irradiation.<sup>3</sup> It is assigned to neutral diamagnetic O vacancy,<sup>4</sup> which also can be treated as an abnormal Si-Si bond ( $\equiv \text{Si-Si} \equiv$ ) in a SiO<sub>2</sub> glass network. The 5.8-eV OA band is present in practically all types of irradiated a-SiO<sub>2</sub> and is due to the "E'-center" family<sup>5,6</sup>—paramagnetic silicon dangling bonds, either in a form of relaxed, paramagnetic O vacancies ( $\equiv \text{Si}^\bullet \cdots \text{Si} \equiv$ ) or in a form of an isolated Si dangling bond ( $\equiv \text{Si}^\bullet$ ), projecting into a local void of the glass structure. They give rise to characteristic electron paramagnetic resonance (EPR) signals, which correlate well with the amplitude of the 5.8-eV OA band.<sup>6</sup>

The 4.8-eV OA band and its accompanying OA band at 2.0 eV of ~50 times lower amplitude are usually the main causes of absorption in irradiated a-SiO<sub>2</sub> in the photon range from 1.8 to 5 eV. They are assigned to oxygen dangling bonds ( $\equiv \text{Si} - \text{O}^\bullet$ ).<sup>7,8</sup> The related photoluminescence (PL) band at 1.9 eV is the only one among defects in a-SiO<sub>2</sub> that shows a

distinct zero-phonon line. Its energy dispersion was recently used to study the degree of disorder around oxygen dangling bonds in the bulk SiO<sub>2</sub> glass and on surfaces of porous SiO<sub>2</sub>.<sup>9</sup>

The bulk of the structural information on oxygen dangling bonds is provided by EPR studies,<sup>5,10</sup> which also coined their widely used name, NBOHCs (nonbridging oxygen hole centers). The unpaired spin was found to reside in an oxygen 2p-like orbital, giving a broad EPR signal with  $g_1 = 1.9999$ ,  $g_2 = 2.0095$ , and  $g_3 \approx 2.08$  (strongly distributed). Hyperfine/superhyperfine couplings to <sup>17</sup>O nuclei<sup>10</sup> and <sup>29</sup>Si nuclei<sup>11</sup> were confirmed. However, the relationship between the optical and the EPR signals of NBOHCs is not always reliable,<sup>8</sup> due to NBOHCs nearly degenerate ground state and the presence of EPR-silent varieties of centers in some types of a-SiO<sub>2</sub>. Silicon and oxygen dangling bonds have been observed and studied in detail on the surfaces of a-SiO<sub>2</sub> (see reviews in Refs. 12 and 13).

Apart from the three major UV OA bands at 4.8, 5.8, and 7.6 eV in irradiated a-SiO<sub>2</sub>, there are additional ones related to, e.g., interstitial ozone (4.8 eV), divalent Si (5.04 eV, B<sub>2</sub>-band), peroxy radicals (5.2–5.4 eV, PORs),<sup>14</sup> and interstitial Cl<sub>2</sub> (3.8 eV).<sup>8</sup> It has been demonstrated that oxygen excess-related OA must be present at 5.8 eV in O<sup>+</sup>-implanted silica.<sup>15</sup> However, these bands are typically minor and/or limited to specific off-stoichiometric samples.

Because of an overlap of multiple unresolved OA bands, the origins of the OA in energy range 5.5–7.5 eV are much less understood than OA at lower photon energies. Apart from fundamental interest, this spectral range is technologically important, in particular due to ArF excimer laser (6.4 eV) applications. Previous work has shown that NBOHC strongly contributes to this spectral region with an additional OA band, represented by a Gaussian peak at 6.8 eV and a full width at half maximum (FWHM) of 1.8 eV.<sup>16</sup> However, its exact spectral shape and its intensity relative to the 4.8-eV OA band of NBOHC remain somewhat uncertain, since the reported<sup>16</sup> OA spectrum may have some contribution from the 5.8-eV band

of  $E'$ -centers. Moreover, calculations predict<sup>17</sup> additional OA bands of  $E'$ -centers at higher energies whose exact parameters have not been experimentally obtained. The true shape of the NBOHC OA spectrum thus depends mainly on the correct subtraction of the  $E'$ -center contribution. Further controversy was raised by subsequent measurements<sup>18</sup> in a  $\gamma$ -irradiated sample with strong 5.8- and 7.6-eV OA bands. They indeed showed a shoulder at 6.7 eV in the OA spectra. However, the photoluminescence excitation (PLE) spectrum of NBOHC PL at 1.9 eV, which, when corrected for absorption effects, is likely to follow the OA spectrum, shows bands at 4.85 eV (FWHM = 0.95 eV) and 6.35 eV (FWHM = 1.7 eV).<sup>18</sup> While the 4.8-eV PLE band is in a good agreement with the OA spectrum and previous PLE data,<sup>2,7</sup> the high-energy PLE band is significantly shifted from the peak position of the 6.8-eV OA band reported earlier.<sup>16</sup>

The controversy on the nature and shape of the basic DUV OA bands introduces large uncertainties in the Gaussian decompositions of complex absorption spectra of a-SiO<sub>2</sub>, performed in numerous works. The aim of this paper was to obtain more accurate data on DUV/VUV OA of oxygen dangling bonds (NBOHCs) in a-SiO<sub>2</sub> by using samples whose concentration of other interfering absorption centers is as low as possible. We obtained silica glass samples, which—highly unusually—contain only paramagnetic oxygen dangling bonds and practically no silicon dangling bonds. In addition, a way to account for the interference from irradiation-induced changes in VUV absorption of silanol (SiOH) groups was found.

## II. EXPERIMENTAL DETAILS

Synthetic “UV grade” wet a-SiO<sub>2</sub> samples (Tosoh Quartz, type ES) with a thickness of 1 or 2 mm that have two optically polished surfaces were studied. The SiOH group content was determined from Fourier transform infrared (IR) OA spectra to be  $1.0 \times 10^{20} \text{ cm}^{-3}$ . Samples were irradiated in a cryostat that had “excimer grade” CaF<sub>2</sub> windows in oil-free vacuum  $\approx 10^{-6}$  Torr at  $T = 80 \text{ K}$  by 157-nm F<sub>2</sub> laser (Lambda Physik LPF210, 20-ns pulses of the power density 20–25 mJ/cm<sup>2</sup>/pulse) at 5-Hz repetition frequency. After irradiation, samples were warmed to 295 K and etched with diluted (1%) hydrofluoric acid for 30 s to remove any traces of surface contamination. Part of the F<sub>2</sub> laser-irradiated samples was photobleached by visible-ultraviolet (VIS-UV) radiation from a 300-W xenon lamp, with the IR portion of the spectrum reduced by a reflective interference “heat” filter. Changes in the VIS-UV OA spectra (Hitachi U4000, resolution 1 nm), VUV absorption (JASCO VU201M, resolution 0.6 nm), Fourier transform IR OA spectra (Perkin-Elmer Spectrum One, resolution 2 cm<sup>-1</sup>), and EPR spectra (Bruker EMX X-band continuous wave) were measured. For a separate group of samples, VIS-UV OA spectra were measured directly in the cryostat in the following sequence: at 80 K (1) before and (2) immediately after F<sub>2</sub> laser irradiation at different doses, (3) after warming to 295 K, and (4) after repeatedly cooling down to 80 K. To separate the radiation-induced effects, spectra taken before irradiation were subtracted in all cases. It was verified that the additional absorption induced by the laser in cryostat CaF<sub>2</sub> windows was negligible.

The EPR spectra of the F<sub>2</sub> laser-irradiated and photobleached sample were taken in two modes, optimized to detect different types of centers. Mode I ( $E'$ -center mode) was at room temperature, with low microwave power (0.4–5  $\mu\text{W}$ ) and small modulation amplitude (0.02–0.05 mT) suited to detecting narrow, easily saturating signals. Mode II (NBOHC/POR mode) had  $T = 77 \text{ K}$ , high power (1–10 mW), and large field modulation amplitude (0.05–0.2 mT) suited to detecting broad, nonsaturating signals and to separating them from the usually ubiquitous  $E'$ -type center signals.

## III. RESULTS

In Fig. 1, spectrum A shows VIS-UV range OA induced by 8 J/cm<sup>2</sup> F<sub>2</sub> laser irradiation<sup>19</sup> at 80 K, measured after warming the sample to room temperature. It contains distinct OA bands at 1.96, 4.8, and 5.8 eV (a more exact spectral shape of the weak 1.96-eV band is shown in inset to Fig. 5). These bands remain stable at room temperature. No measurable amplitude change (<1%) was detected after several months. Irradiation for 2 h by UV light from a Xe lamp filtered by a 340-nm UV cutoff filter did not affect the absorption bands. However, a following 2-h-long irradiation with unfiltered light caused a moderate (1.765 times) decrease of the intensities of 1.96- and 4.8-eV OA bands and complete vanishing of the 5.8-eV band (Fig. 1, spectrum B; note the scaling coefficient).

There were no EPR signals in the sample prior to F<sub>2</sub> laser irradiation. The mode I spectrum taken on the laser-irradiated sample before UV bleaching (Fig. 2, spectrum A) revealed a strong signal of a subtype of  $E'$ -centers, known as  $E'(\text{OH})$ -centers,<sup>20</sup> distinguished by proton superhyperfine splitting. The spectrum taken in mode II revealed a characteristic signal

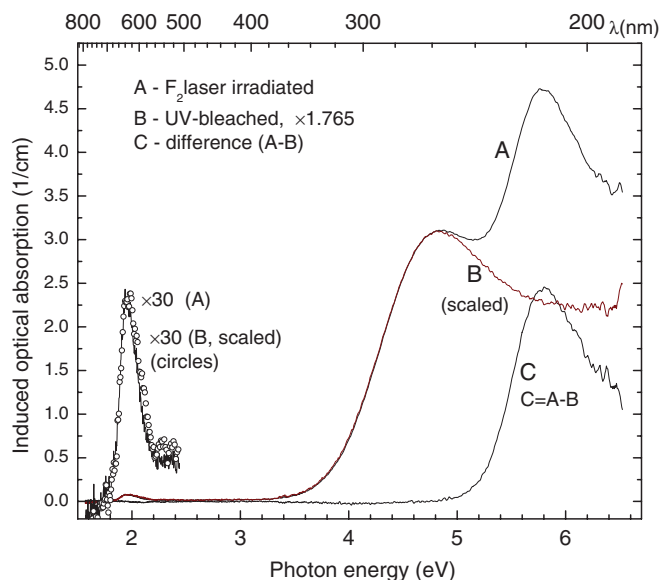


FIG. 1. (Color online) OA of wet silica glass, irradiated at  $T = 80 \text{ K}$  by F<sub>2</sub> laser fluence of 8 J/cm<sup>2</sup>, measured after warming to  $T = 295 \text{ K}$  (spectrum A) and after subsequent photobleaching by UV light at room temperature (spectrum B). Spectrum B represents the as-measured data multiplied by 1.765 to match the 4.3- to 4.7-eV region of spectrum A. Spectrum C is the difference between spectra A and B.

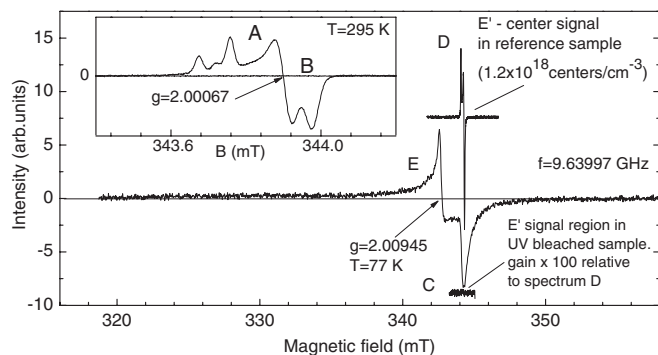


FIG. 2. EPR spectra of the  $F_2$  laser-irradiated and photobleached  $a$ - $SiO_2$  sample described in Fig. 1. Spectra A and B (inset) were taken at  $T = 295$  K and microwave power of  $1 \mu W$  before (A) and after (B) UV photobleaching. Spectrum B is redrawn with a 100 times gain (spectrum C) and compared to the spectrum of a reference sample (spectrum D) to show the negligible concentration ( $< 3 \times 10^{14} \text{ cm}^{-3}$ ) of  $E'$ -centers remaining after photobleaching. Spectrum E, characteristic of NBOHCs, was recorded at 77 K and microwave power of 1 mW after photobleaching. Spectrum recorded in this mode before photobleaching (not shown), had an identical shape and  $\sim 1.5$  times higher intensity.

assigned to NBOHCs.<sup>5</sup> Its shape (not shown) was identical to the shape of spectrum E in Fig. 2.

After UV bleaching, the  $E'(\text{OH})$ -type signal vanished (Fig. 2 inset, spectrum B). At a 100 times gain, a very weak trace of the  $E'$ -center-like signal was detected hardly above the noise level at  $g = 2.0006$  (Fig. 2, spectrum C). By comparison to the spectrum of a reference sample of neutron-irradiated dry  $a$ - $SiO_2$  (Fig. 2, spectrum D), the absolute concentration of  $E'$ -centers remaining after UV bleaching was estimated as  $3 \times 10^{14} \text{ cm}^{-3}$ . In contrast, the mode II spectrum of the UV-bleached sample (Fig. 2, spectrum E) still showed the same broad signal, associated with NBOHC, which was only  $\sim 1.5$  times less intense than the signal before UV bleaching. No other EPR signals were detected.

The spectral shape of room temperature-stable VIS-UV OA remaining after UV bleaching (Fig. 1, spectrum B, replotted in Fig. 3, spectrum D) was very close to the OA spectra taken at 80 K immediately after  $F_2$  laser irradiation without warming the sample (Fig. 3, spectra E–G). The shapes of the induced low-temperature OA spectra remained nearly the same in the investigated irradiation dose range from 0.8 to 95  $J/cm^2$  (Fig. 3, spectra E–G), while their amplitude increased 15 times.

When comparing OA spectra, measured at 80 K and 295 K, one must take into account the differences in shape caused by temperature-dependent populations of the local vibrational states of the electronic ground state. To assess the significance of this effect, the top panel of Fig. 3 compares OA spectra measured at 295 K (spectrum A) and at 80 K (spectrum B) for an  $F_2$  laser-irradiated sample, which has stable concentrations of NBOHC (4.8-eV OA band) and  $E'$ -centers (5.8-eV OA band). By fitting the peak region and the low-energy wing of the 4.8-eV band with a Gaussian function, it can be estimated that cooling to 80 K causes a  $\sim 4\%$  increase of the 4.8-eV OA band amplitude and a 4% decrease of its FWHM.

The top panel of Fig. 4 shows changes to the IR absorption of SiOH groups in laser-irradiated and UV-bleached  $a$ - $SiO_2$ .

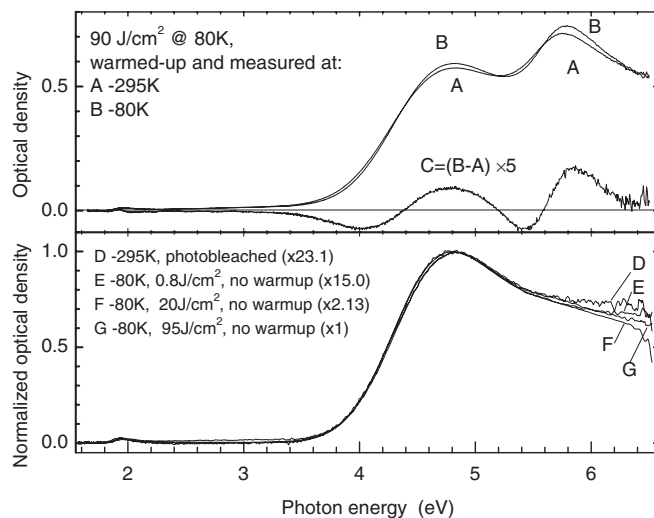


FIG. 3. Comparison of the shape of the stable OA band remaining in the  $F_2$  laser-irradiated (80 K,  $8 J/cm^2$ ) sample after photobleaching with UV light (spectrum D, lower panel). Shapes of the metastable bands induced by  $F_2$  laser irradiation at  $T = 80$  K with doses of 0.8  $J/cm^2$  (spectrum E), 20  $J/cm^2$  (spectrum F), and 95  $J/cm^2$  (spectrum G) and measured at 80 K, without warming. Spectra D–G are all independently normalized to 1. The top panel shows the difference (spectrum C) between the shapes of the OA measured at 295 K (spectrum A) and 80 K (spectrum B) in a sample with a temperature-independent concentration of absorbing centers.

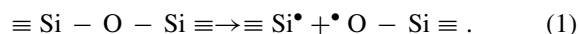
While they are very small, their pattern is similar to the previously reported results:<sup>21,22</sup> increase in the  $3600\text{-cm}^{-1}$  region assigned to H-bonded SiOH groups and decrease in the  $3700\text{-cm}^{-1}$  region corresponding to “free” (i.e., not H-bonded) SiOH groups. The band at  $2235 \text{ cm}^{-1}$  shows generation of SiH (hydride) groups. The point scatter at  $3700 \text{ cm}^{-1}$  in the difference spectrum C and the feature marked by asterisk at  $2270 \text{ cm}^{-1}$  are due to absorption lines of air humidity and  $CO_2$  in the measurement chamber.

The bottom panel of Fig. 4 shows the corresponding VUV OA spectra before (spectrum A) and after (spectrum B) irradiation, as well as irradiation-induced changes (spectrum C). The high-energy part of the difference spectrum C is negative, indicating a photobleaching of species that absorb in the VUV absorption edge region.

## IV. DISCUSSION

### A. Oxygen dangling bonds without copresence of $E'$ -centers

The most unusual feature in the reported experimental data is the presence of NBOHCs in the silica glass sample without any significant co-presence of  $E'$ -centers (Figs. 1 and 2). Discovered<sup>23</sup> long ago and described in fine detail,<sup>5</sup>  $E'$ -centers are nearly universally present in irradiated samples of  $a$ - $SiO_2$ . Whenever paramagnetic defects were detected in  $a$ - $SiO_2$ ,  $E'$ -centers were always among them. This situation has two main causes. The first is the omnipresence of defect precursors in  $a$ - $SiO_2$ —strained Si–O bonds, which allow for creation of pairs of  $E'$ -centers and NBOHCs by the “intrinsic” mechanism:





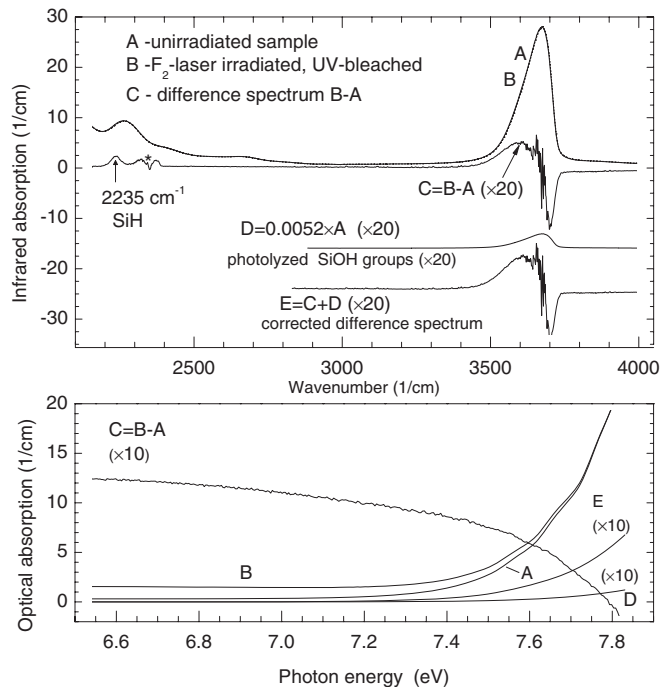


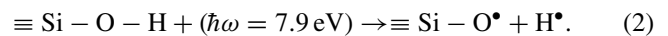
FIG. 4. Correlated changes in IR (top panel) and VUV (bottom panel) absorption spectra of wet silica glass (a-SiO<sub>2</sub>) due to F<sub>2</sub> laser irradiation and UV bleaching. Co-related spectra are denoted by the same letter in both panels: pristine sample (spectrum A), F<sub>2</sub> laser-irradiated and UV-bleached sample (spectrum B), and difference sample (spectrum C). The data scatter in the 3600- to 3700-cm<sup>-1</sup> region is due to humidity in air. Spectrum D represents the decrease of both IR and VUV absorption due to photolysis of SiOH groups. Their number was estimated from the concentration of created SiH groups (top panel, band at 2235 cm<sup>-1</sup>). Spectrum E shows the changes to IR absorption (top) and the related decrease of VUV absorption (bottom) caused by formation of H-bonded SiOH groups. The true VUV absorption spectrum of laser-induced color centers, corrected for the changes in overlapping SiOH absorption, equals C + D + E (see Fig. 5, spectrum A).

The second cause for the ubiquity of E'-centers is their relationship to oxygen vacancies. In terms of stoichiometry, an O vacancy is an equivalent of two Si dangling bonds. O vacancies in glassy SiO<sub>2</sub> are created in a Frenkel process during irradiation<sup>3</sup> or by thermal treatment during sample synthesis. The latter process is more probable in “dry” (low SiOH content) a-SiO<sub>2</sub>, which has a tendency to O deficiency. In such glasses, E'-centers often occur without the complementary [Eq. (1)] NBOHCs; however, the opposite situation, NBOHCs without E'-centers, is highly unusual.

The universal presence of E'-centers and their strong OA band at 5.8 eV with FWHM reported between 0.6<sup>24</sup> and 0.8 eV has been an obstacle to better understanding of optical properties of other defects in the DUV (5.5–6.5 eV) and VUV spectral ranges. The lowest-energy UV OA band of NBOHC is routinely represented by a Gaussian function with a peak at 4.8 eV and FWHM of 1.05 eV. However, the estimate of its FWHM is based only on the fitting to the low-energy side and peak region, since the high-energy side is always overlapped by the E'-center band.<sup>25</sup>

In past studies, the standard treatment of the composite UV-VUV OA spectra of irradiated a-SiO<sub>2</sub> has been to resolve them into the (usually dominant) 4.8- and 5.8-eV Gaussian bands. In addition, in the case of oxygen-deficient a-SiO<sub>2</sub>, two more OA bands at 5.0 eV (weak) and 7.6 eV (strong) due to divalent silicon and O vacancy, respectively, can be added. However, this treatment is insufficient to explain OA in the region between 5 and 7.6 eV. This uncertainty is an obstacle to further understanding of defects in a-SiO<sub>2</sub>. A number of defects that are still not well characterized, like the silicon-oxygen double bond ≡Si=O (silanone group) (proved to exist as a surface center)<sup>12</sup> or peroxy bridge (≡Si-O-O-Si≡ bond),<sup>26</sup> are all expected to have absorption bands in the 5.5- to 7.2-eV range.

At first glance, NBOHCs alone, without the copresence of E'-centers, could be easily produced from extrinsic precursors, hydroxyl OH groups bonded to the glass network (SiOH):



Indeed, silanol groups are abundant, up to 10<sup>20</sup> SiOH/cm<sup>-3</sup> in wet a-SiO<sub>2</sub>, and they are efficiently photolyzed by 7.9-eV photons from F<sub>2</sub> laser (quantum yield ≈0.2).<sup>27</sup> The resulting interstitial atomic hydrogen H<sup>0</sup> is nearly immobile at T = 80 K and has no absorption bands in the transparency region of a-SiO<sub>2</sub>. However, OA and EPR measurements, performed *after* the irradiated sample has been warmed to room temperature, consistently show that a substantial number of E'-centers have been coproduced as well.<sup>20</sup> Therefore, in our previous paper<sup>16</sup> seeking to establish the DUV/VUV OA spectrum of NBOHC by measurements at 80 K, a significant contribution by the 5.8-eV OA band of E'-centers was assumed. This conjecture was then supported (see, however, later caveats) by a separate experiment in which a fairly large number of E'-centers were detected by EPR in the sample, irradiated at 80 K, and measured without warming to 295 K.

In contrast to that previous study, E'-centers practically do not contribute to the absorption spectrum of the UV-bleached sample (Fig. 1, spectrum B), since EPR data indicate that only 3 × 10<sup>14</sup> cm<sup>-3</sup> E'-centers remain. The amplitude of the corresponding OA peak at 5.8 eV (cross section 2.5 × 10<sup>-17</sup> cm<sup>2</sup>)<sup>6</sup> is then less than 0.01 cm<sup>-1</sup>.

## B. Are other UV-absorbing centers present?

The concentration of NBOHCs in a UV-bleached sample is 7.8 × 10<sup>17</sup> cm<sup>-3</sup>, as estimated from the amplitude and the absorption cross section (σ = 2.25 × 10<sup>-18</sup> cm<sup>2</sup>; see Sec. IV.D) of the 4.8-eV band (Fig. 1, spectrum B). It is more than 10<sup>3</sup> times higher than the concentration of E'-centers. This raises a possibility that spectrum B of Fig. 1 (and its extension in the VUV part, Fig. 5, spectrum A) could represent a *pure* OA spectrum of NBOHCs. Indeed, no other paramagnetic centers apart from NBOHCs and E'-centers were detected in the sample. IR absorption spectra of a-SiO<sub>2</sub>, irradiated by F<sub>2</sub> laser at 80 K, typically show growth of hydride (≡SiH) groups,<sup>20</sup> but ≡SiH has no absorption bands in the visible to VUV transparency region of a-SiO<sub>2</sub>.<sup>28,29</sup> However, a presence of some types of less-well-characterized diamagnetic centers absorbing in UV region cannot be excluded without further proof. Interstitial oxygen (peroxy bridge) is expected to absorb

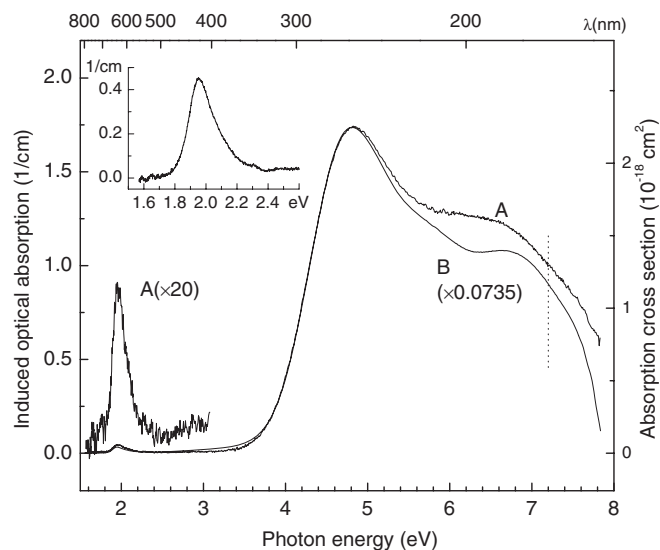
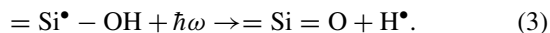


FIG. 5. Joint visible to VUV range OA (spectrum A) of wet silica glass, containing dominant concentrations of NBOHCs, negligible amounts of  $E'$ -centers, and no other paramagnetic defects. Spectrum B is a scaled-down OA spectrum from Ref. 16. The vertical dashed line at 7.2 eV marks the energies above which the corrections for the destruction of hydroxyl groups and formation of additional hydrogen bonding become significant (see Fig. 4). The inset shows a more accurate shape of the 1.96-eV absorption band measured in the sample, irradiated by a higher dose (95 J/cm<sup>2</sup>) of 7.9-eV photons. We suggest that spectrum A represents the current best available approximation to the VIS-UV to VUV absorption spectrum of NBOHC in a-SiO<sub>2</sub>.

in the 7-eV region.<sup>26</sup> There are several oxygen-related defects, including silanone group = Si = O (oxygen double bond) and dioxasilirane group, which have been shown to exist as surface defects in SiO<sub>2</sub> and have wide absorption bands in the 5- to 6-eV region.<sup>12,13</sup> Such defects in principle also could contribute to the absorption spectrum in the bulk a-SiO<sub>2</sub>.

In this aspect, the most troublesome could be interference from silanone groups, because they have been observed to appear on SiO<sub>2</sub> surfaces during UV bleaching of surface  $E'(\text{OH})$ -centers, i.e., the same subtype of  $E'$ -centers that were in the present work samples before UV photobleaching (Fig. 2, spectrum A). The proposed photolysis reaction for their creation is<sup>30</sup>



Silanone groups on SiO<sub>2</sub> surfaces are associated with a wide (FWHM = 0.9 eV) OA peak at 5.65 eV with a peak absorption cross section  $\sigma \approx 3 \times 10^{-18}$  cm<sup>2</sup>,<sup>13</sup> which is ~8 times smaller than  $\sigma$  for the 5.8-eV OA band of  $E'$ -centers ( $\sim 2.5 \times 10^{-17}$  cm<sup>2</sup>). If UV photobleaching of  $E'(\text{OH})$ -centers observed in the present samples occurs by a similar reaction, and if OA of bulk silanone groups has parameters similar to those of surface silanone groups, then they could contribute an OA band with an amplitude of  $\sim 0.3$  cm<sup>-1</sup> to the absorption spectrum after UV photobleaching (Fig. 1, spectrum B), which could correspond to ~20% of the absorption amplitude at 5.6 eV (see, however, the later discussion). Mobile atomic hydrogen, released by the reaction in Eq. (3), could additionally contribute to the decay

of absorption by recombining with NBOHC and  $E'$ -centers to create hydroxyl and silicon hydride groups.

In this way, silanone groups produced by Eq. (3) could give a small yet significant contribution to the absorption spectrum B in Fig. 1. The question of whether that spectrum is almost solely due to NBOHCs can be answered by comparing it to OA spectra of wet a-SiO<sub>2</sub>, measured at 80 K directly after F<sub>2</sub> laser irradiation at 80 K (Fig. 3). SiOH groups are by far the main absorbing species of 7.9-eV laser photons in wet a-SiO<sub>2</sub>, and their photolysis quantum yield is high (0.2).<sup>27</sup> Therefore, their photolysis and creation of NBOHCs and atomic hydrogen [Eq. (2)] should be the dominant process under F<sub>2</sub> laser irradiation conditions, at least at the initial stage. Creation of a significant number of other defects must involve some secondary reactions, which can become significant only after the primary reaction products accumulate and the primary reaction [Eq. (2)] starts to saturate. However, the shape of the induced absorption spectra at 80 K does not change when the irradiation dose is increased more than 100 times (Fig. 3, spectra E–G). Moreover, the shape of all these spectra is very close to that of the OA spectrum of the UV-bleached sample, measured at 295 K (Fig. 3, spectrum D, replotted from Fig. 1, spectrum B), which has negligible contribution from  $E'$ -centers. Spectra A and B in Fig. 3 illustrate that the effect of different measurement temperatures (80/295 K) on OA shape and intensity is relatively small; therefore, the comparison of spectra, measured at 295 K (Fig. 3, spectrum D) and 80 K (Fig. 3, spectra E–G) is meaningful.

These results show that the OA spectrum depicted in spectrum B of Fig. 1 or spectrum D of Fig. 3 represents a nearly pure NBOHC absorption spectrum, particularly in the energy region up to the 5.8 eV, only after which a small deviation between its shape and the low- $T$  spectra (Fig. 3, spectra E–G) appears. These findings also reduce the possibility that silanone groups could significantly contribute to OA spectra of Fig. 3 in the 5.6-eV region, since their creation, always in a constant proportion to NBOHCs, is required to explain the invariant shape of OA spectra induced by different irradiation doses (Fig. 3, spectra E–G) at 80 K and after UV bleaching at 295 K (Fig. 3, spectrum D). As a corollary, Eq. (3) is not the dominant mechanism explaining the photobleaching of  $E'(\text{OH})$ -centers, since would imply that ~20% of OA at 5.6 eV in spectrum B of Fig. 1 is caused by silanone groups.

### C. Absorption in the VUV region

Analysis of the VUV part of absorption is complicated, because the increase of absorption due to the laser-induced defect centers is accompanied by a decrease of VUV absorption of SiOH groups. This decrease has two causes: (1) transformation of SiOH groups to the H-bonded configuration<sup>22,31</sup> and (2) their photolysis by F<sub>2</sub> laser photons [Eq. (2)].

Figure 4 shows the effect of laser irradiation and UV bleaching on the VUV absorption spectra (bottom panel, spectra A–C) and the corresponding changes in the IR OA spectra (top panel, spectra A–C). The high-energy side of the induced VUV OA spectrum C clearly shows the SiOH bleaching effect. Its size must be determined to obtain the pure NBOHC absorption spectrum.

The contributions to SiOH OA bleaching due the SiOH photolysis and due to their conversion to H-bonded SiOH can be evaluated separately. The starting point is the concentration  $K$  of irradiation-induced SiH groups, which can be determined as  $K = 5.28 \times 10^{17}$  centers per cubic centimeter from the amplitude of their IR absorption band at  $2235 \text{ cm}^{-1}$  ( $0.090 \text{ cm}^{-1}$ , Fig. 4, spectrum C) and peak absorption cross section  $\sigma = 1.7 \times 10^{-19} \text{ cm}^2$ .<sup>32-34</sup> Assuming that the source of hydrogen necessary for creating SiH groups is the photolysis of SiOH groups [Eq. (2)], an equal number  $K$  of SiOH groups is destroyed.<sup>35</sup> Their contribution to the bleaching of the VUV OA spectrum (Fig. 4, bottom panel, spectrum D) can be estimated as  $K\sigma$  using the published<sup>36</sup> VUV OA cross-section spectrum  $\sigma$  of SiOH groups in a-SiO<sub>2</sub>. The size of the related bleaching of IR absorption spectra (top panel, spectrum D) was estimated by scaling the SiOH IR spectrum of a pristine sample that has  $R$  SiOH groups by the ratio  $K/R (=0.0052)$ .

In Fig. 4, the sum of the IR difference spectrum (top panel, spectrum C) and the contribution due to photolysis of SiOH groups (top panel, spectrum D) gives the difference spectrum (top panel, spectrum E), which represents the changes in IR absorption, caused purely by the effect of the formation of H-bonded SiOH groups. The quantitative relationship between changes of this type in IR absorption and corresponding changes in VUV absorption  $\alpha_{\text{VUV}}$  has been established in Ref. 22:

$$\alpha_{\text{VUV}} = \alpha_{3680}(ax + b + cx^{-1}), \quad (4)$$

where  $\alpha_{3680}$  and  $\alpha_{3620}$  are IR absorption coefficients at 3680 and 3620  $\text{cm}^{-1}$ , respectively,  $x = \alpha_{3620}/\alpha_{3680}$ , and the polynomial coefficients  $a$ ,  $b$ , and  $c$  are tabulated<sup>22</sup> for different photon energies in the VUV range. The value of  $\alpha_{3680}$  is practically not changed by irradiation (isobestic point). Denoting the difference between  $x$  for pristine and  $x$  for irradiated samples as  $\Delta x = x_{\text{pristine}} - x_{\text{irrad.}}$  and taking into account that in our case  $\Delta x \ll x$ , the difference between VUV OA spectra of pristine and those of irradiated samples is obtained from Eq. (4) as

$$\alpha_{\text{VUV}}^{\text{pristine}} - \alpha_{\text{VUV}}^{\text{irrad.}} \approx \alpha_{\text{IR}}^{3680} \Delta x (a - cx_{\text{pristine}}^{-2}), \quad (5)$$

where VUV photon energy-dependent coefficients  $a$  and  $c$ <sup>37</sup> are taken from Table 1 of Ref. 22. In the bottom panel of Fig. 4, spectrum E shows the difference VUV spectrum, obtained by Eq. (5) from the IR difference spectrum (Fig. 4, top panel, spectrum E). The true VUV absorption spectrum of laser-induced color centers, corrected for the decrease of the VUV absorption of SiOH groups due to their photolysis and H-bond formation, is given by the sum of VUV spectra (C + D + E) in the bottom panel of Fig. 4 and shown by spectrum A in Fig. 5.

#### D. Visible to VUV absorption spectrum of NBOHC

In Fig. 5, spectrum A shows the broad-range absorption spectrum, obtained by joining spectrum B in Fig. 1 (range = 1.7–6 eV) and the sum of the VUV spectra (C + D + E) in Fig. 4 (range = 6–7.8 eV). Based on the previous discussion, we suggest that this spectrum is almost completely due to NBOHCs.

The absorption cross section  $\sigma$  (right-hand scale of Fig. 5) was obtained in the following way. First,  $\sigma$  for the 1.96 eV

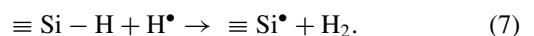
OA band,  $\sigma(1.96)$ , was calculated from the measured spectral shapes of the 1.96 eV OA<sup>38</sup> and 1.91 eV photoluminescence bands, and from the radiative decay constant of this luminescence ( $\tau = 18 \mu\text{s}$ ), using Strickler-Berg equation:<sup>8,39</sup>

$$\frac{1}{\tau} = \frac{n^2}{\pi^2 \hbar^3} \frac{g_l}{g_u} \frac{1}{\langle (\hbar\omega)^{-3} \rangle} \int \frac{\sigma(\hbar\omega)}{\hbar\omega} d(\hbar\omega) = \frac{g_l}{g_u} \frac{n^2}{\langle (\hbar\omega)^{-3} \rangle} \times \int \frac{\sigma(\hbar\omega)}{\hbar\omega} d(\hbar\omega) \times 3.95 \cdot 10^{23} \text{ eV}^{-3} \text{ cm}^{-2} \text{ s}^{-1}, \quad (6)$$

where  $n$  is the refractive index ( $n = 1.46$ );  $g_l = 2$  and  $g_u = 1$  are electronic degeneracy of the lower and upper (excited) states, respectively;<sup>40</sup> and  $\langle (\hbar\omega)^{-3} \rangle$  denotes the average value of  $(\hbar\omega)^{-3}$  weighed over the entire luminescence spectrum  $L(\hbar\omega)$ :  $\langle (\hbar\omega)^{-3} \rangle = \int (\hbar\omega)^{-3} L(\hbar\omega) d(\hbar\omega) / \int L(\hbar\omega) d(\hbar\omega)$ , where  $L(\hbar\omega)$  is plotted in photons per electron volt units. After obtaining  $\sigma(1.96)$ ,  $\sigma$  for the UV-VUV part of the spectrum was obtained by scaling it with the measured ratio between absorption amplitudes at 4.83 and 1.96 eV ( $\approx 52$ ),<sup>38</sup> yielding  $\sigma = 2.25 \times 10^{-18} \text{ cm}^2$  at 4.8 eV.

For comparison with the published data, a scaled-down absorption spectrum from Ref. 16 is also drawn in Fig. 5 (spectrum B). Both spectra A and B agree well up until  $\sim 5.5$  eV; at higher energies, slight differences appear. The principal difference between the present and the previous data is that E'-centers with their absorption band at 5.8 eV are practically absent, as shown by EPR data, and do not contribute to the OA spectrum obtained in the present paper (Fig. 5, spectrum A), whereas in the previous work their absorption was considered<sup>16</sup> to fill in the gap between the suggested Gaussian band of NBOHC at 4.8 eV (FWHM = 1.07 eV) and the one at 6.8 eV (FWHM = 1.76 eV).

The E'-centers, whose OA band at 5.8 eV is prominent at room temperature before UV bleaching (Fig. 1, spectra A and C) are evidently created only during postirradiation warming from 80 to 295 K and are not immediately created by the 80 K F<sub>2</sub> laser irradiation, as previously assumed.<sup>16,41</sup> This follows from the identical UV absorption shapes of the E'-center-free sample containing NBOHCs and of the F<sub>2</sub> laser-irradiated samples at 80 K (Fig. 3). Given the  $\sim 10$  times larger OA cross section of E'-centers relative to that of NBOHCs, the optical data show that the concentration of directly induced E'-centers at 80 K is at least 50 times lower than the concentration of NBOHCs. The most probable creation path of E'-centers during warming to 295 K is by the scavenging of hydrogen from SiH bonds by atomic hydrogen, which becomes mobile above 110 K:



Calculations show that such a reaction is exothermic by 0.55 eV<sup>42</sup> and has an activation energy of less than 0.03 eV. Atomic hydrogen has been demonstrated to create dangling Si bonds (P<sub>b</sub>-centers) on the Si-SiO<sub>2</sub> interface in a similar reaction,<sup>43-46</sup> differing from Eq. (7) only by the three "backbonds" of the silicon atom, which in the P<sub>b</sub>-center are to three silicon atoms instead of three oxygen atoms. In our case, there is evidence that the silicon in the SiH group at the left side of Eq. (7) is backbonded by two bridging oxygen atoms bonding to the glass network, but the third backbond is to an OH group. This conclusion is based on (1) the EPR spectrum of the F<sub>2</sub> laser-induced E'-centers observed at



$T = 295$  K before UV photobleaching (Fig. 2, spectrum A), which is close to that of  $E'(\text{OH})$ -centers,<sup>20</sup> and (2) the  $\sim 15$   $\text{cm}^{-1}$  red-shift of the observed IR OA band ( $2235$   $\text{cm}^{-1}$ , Fig. 4, top panel, spectrum C) as compared to the usually observed SiH peak position ( $2250$   $\text{cm}^{-1}$ ). Red-shift of  $15$   $\text{cm}^{-1}$  due to the substitution of one of the three bridging oxygen atoms around the SiH group by an OH group has been predicted by calculations.<sup>47</sup>

The large total width ( $\sim 4$  eV) of the intense UV-VUV part of the NBOHC absorption spectrum (Fig. 5, spectrum A) is generally consistent with the predictions of calculations,<sup>17,48</sup> assigning this part of the spectrum to transitions from the 2p-like lone pair states of the bridging oxygen atoms within the  $\text{SiO}_2$  valence band to the half-filled 2p nonbonding orbital of the NBOHC, which forms a localized gap state above the valence band edge.

### E. Analytical representation of the spectral shape of NBOHC OA and its accuracy

As past and present results show, NBOHC is a major optical absorber in irradiated a- $\text{SiO}_2$ . Knowledge of its “reference” UV-VUV absorption spectrum allows one to evaluate the lower VUV transparency limit for irradiated silica optics without doing VUV measurements, just relying on the visible/near-UV OA data. Even much lower levels of UV-VUV OA could be indirectly measured, relying on the relative intensity of the associated 1.9-eV PL band.

Another important incentive for obtaining the exact shape of UV-VUV NBOHC absorption is the gaining of the ability to disentangle the complex absorption spectrum of a- $\text{SiO}_2$  in the 5.5–7.5-eV region and determine the properties of other species absorbing in this spectral range.

The low-energy wing of the UV spectrum up to 4.73 eV (Fig. 5, spectrum A) can be represented by a single Gaussian band (Fig. 6, dashed line) with parameters (peak = 4.80 eV, FWHM = 1.10 eV) close to the usually cited ones. However, when considering a wider spectral range toward VUV, we should operate with a spectral shape similar to spectrum A in Fig. 5 as a whole, rather than assume contributions of just one or two separate Gaussian bands. For these purposes, an analytical representation of the NBOHC OA spectrum would be useful so that its shape could be easily reproduced and would be free of experimental noise.

An excellent fit to the entire UV-VUV spectrum is possible by five Gaussian functions with deviations of less than  $0.005$   $\text{cm}^{-1}$  within the 3.5- to 7.7-eV range (Fig. 6, least-square fitted parameters in Table I). This fit is by no means unique, and the component peak positions do not necessarily indicate underlying electronic transitions at these energies. The parameter matrix in Table I merely gives a convenient way to reproduce the measured spectral shape.

If spectrum A in Fig. 5 and its fitting parameters (Fig. 6 and Table I) can serve as a reference for the shape of NBOHC OA, then their accuracy is important. It can be estimated as follows:

(1) *1.7–3.5-eV range*. This range of low absorption is dominated by the visible band at 1.96 eV, usually referred as the “2 eV” band. It is usually not overlapped by other bands, so the main accuracy-limiting factor is its small amplitude. In

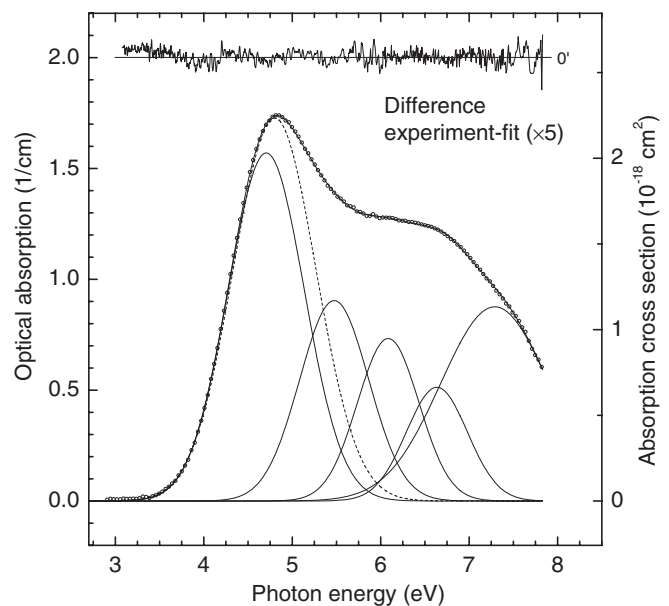


FIG. 6. Spectral shape of UV-VUV range OA of oxygen dangling bonds in a- $\text{SiO}_2$  (circles, replotted from Fig. 5, spectrum A) fitted by a sum of five Gaussian functions (solid lines), whose parameters are given in Table I. They serve merely as a convenient reference representation of the experimental band shape and are not associated with distinct electronic transitions at their respective peak energies. The top spectrum shows a magnified spectrum of the difference between the experimental spectrum and the fit. The dashed line (peak = 4.80 eV, FWHM = 1.10 eV) illustrates the commonly used representation of the low-energy wing by a single Gaussian function.

a sample that has been irradiated by a high dose ( $95$   $\text{J}/\text{cm}^2$ ) of  $\text{F}_2$  laser photons and that has a relatively large ( $0.4$   $\text{cm}^{-1}$ ) 2-eV band, which can be accurately measured (Fig. 5, inset), the ratio between the OA amplitude at 4.83 eV and the one at 1.96 eV is  $52 \pm 2$  at  $T = 295$  K. An exact knowledge of this ratio would enable us to determine the intensity of the UV-VUV part of the spectrum merely by measuring the relative intensity of the 2-eV band. In the present paper, using a less strongly irradiated sample, this ratio is slightly smaller ( $\sim 45$ ) (Figs. 1 and 5). However, the signal is noisy and still within the error margins with the value of 52. A recent study<sup>49</sup> of surface NBOHCs raised the possibility of a modification of this center, distinguished by the substitution of one of the three bridging oxygen atoms connecting the NBOHC to the rest of the glass network by a SiOH group. As compared to the usual NBOHCs, slightly shorter luminescence decay constants have been measured for their PL at 1.9 eV, indicating different oscillator strengths of the respective 2-eV bands, and in this way changes in the ratio between the 2.0- and the 4.8-eV

TABLE I. Parameters of five Gaussian functions, approximating the shape of the UV to VUV OA cross section  $\sigma(\hbar\omega)$  of NBOHCs in silica (see Fig. 6).

Peak position (eV)	4.706	5.474	6.085	6.635	7.29
FWHM (eV)	1.014	0.919	0.818	0.813	1.439
Amplitude ( $10^{-18}$ $\text{cm}^2$ )	4.019	2.314	1.877	1.313	2.243

OA bands are also possible. The extent to which this could affect the bulk NBOHCs in a-SiO<sub>2</sub> remains to be found. The reported PL decay constants for bulk centers range from 15<sup>50</sup> to 20 μs.<sup>8</sup>

(2) *3.5–5.6-eV range*. This range can be considered quite exact, with NBOHC being the only contributing species, as illustrated by the excellent coincidence between spectrum D in Fig. 3 (the same as spectrum A in Fig. 5) and low-*T* spectra E–G in Fig. 3 (see the discussion in Sec. IV.B).

(3) *5.6–7.2-eV range*. We cannot a priori exclude the presence of some additional nonparamagnetic centers, which could contribute to the absorption spectrum in this region alongside NBOHCs. Indeed, spectrum A in Fig. 5 shows higher absorption in this region than spectrum B, which was measured at 80 K in a sample that had ~14 times larger concentrations of NBOHCs and therefore presumably was less prone to interference from other centers. If we consider only the magnitudes of NBOHC concentrations, then spectrum B would seem a safer candidate for a pure NBOHC spectrum in this region. However, unlike the room temperature measurement of spectrum A, spectrum B has been obtained under experimental conditions, which make exact measurements more difficult (low-*T* measurements in the VUV range, problems with a reliable baseline, and problems with keeping the cooled-down sample and cryostat windows free from contamination). A hint to possible problems of this type is that spectrum B in Fig. 5 is already running lower at 5.4 eV, as compared to the other low-*T* spectra (Fig. 3, spectra E–G), which were measured later under a better-controlled baseline and vacuum conditions. Therefore, the current best estimate of the “true” NBOHC spectrum in this spectral region is in the zone confined between spectra A and B in Fig. 5, giving a relative accuracy of ~10%.

(4) *>7.2-eV range*. While every effort has been made to compensate for the irradiation-induced changes of SiOH VUV absorption (Sec. IV.C), the accuracy of the correction depends on many parameters, like error limits of the used SiOH VUV absorption cross sections and the SiH and SiOH IR cross sections (>10%). Since the SiOH VUV absorption in this region becomes much larger than the defect absorption (Fig. 4), additional error can be introduced even by small inhomogeneities in SiOH distribution in the sample. This could yield uncertainty up to ±20% at 7.8 eV.

## V. CONCLUSIONS

The results of this study indicate that the UV-VUV OA spectrum of NBOHCs in a-SiO<sub>2</sub> is wide and semicontinuous, extending from 4 to 8 eV, and cannot be represented by one or two Gaussian bands. Rather, the whole spectral shape depicted in Fig. 6 should be considered as a reference. The finding that NBOHCs strongly absorb at the typical E'-center absorption band energy (5.8 eV) may cause some revision of previous studies, which were often based on Gaussian resolution of the absorption spectrum in 5.8-eV (FWHM ≈ 0.8 eV) and 4.8-eV (FWHM = 1.05 eV) bands of E'-centers and NBOHCs, respectively.

The accuracy of the obtained spectral shape of NBOHC OA (Fig. 6) in many cases may be sufficient for practical estimates of the UV-VUV transparency in a wide spectral region, relying on the measurement of only part of the entire spectrum, e.g., the 1.96-eV visible OA band. However, for research purposes, greater accuracy is desirable, since the subtraction of the NBOHC spectrum would allow us to obtain the OA of other defects in this region. For example, it would give a tool to verify the theoretical predictions<sup>17</sup> of the VUV range OA of silicon dangling bonds and E'-centers.

However, some caveat to the current results should be added. The conclusion about the spectral shape of NBOHC OA for photon energies in the 5- to 6.5-eV region is based on the premises that (1) photolysis of a single SiOH group [Eq. (2)] is the dominant defect creation mechanism in wet a-SiO<sub>2</sub> irradiated by 7.9-eV photons at 80 K, (2) its efficiency at low doses by far exceeds the efficiency of all other competing mechanisms, and (3) created NBOHCs therefore dominate the low-*T* OA spectra (Fig. 3). Concerning paramagnetic defects, this point has been experimentally proved: only the NBOHC EPR signal is detected in a UV-bleached sample, which has an OA spectrum nearly identical to those of the low-*T* spectra (Fig. 3). However, the situation is less clear with a number of diamagnetic defects that are not yet well understood. One example of such defects, a silanone group, was discussed in Sec. IV.B. Generally, if some diamagnetic defect indeed contributes to the shape of low-*T* OA spectra in Fig. 3, to explain their invariant shape, such defects must be always created in a constant proportion to NBOHCs—a possibility that looks improbable but cannot be excluded entirely. Further work is necessary to clarify this point.

\*skuja@latnet.lv

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- <sup>35</sup>The creation of SiH groups is the main process, which stabilizes the mobile hydrogen atoms created by SiOH photolysis [Eq. (2)] and prevents restoration of SiOH groups. The other alternative, a dimerization H<sup>0</sup> + H<sup>0</sup>(H<sub>2</sub>), cannot stabilize hydrogen in the presence of NBOHCs, because H<sub>2</sub> interstitials are mobile at 295 K and are cracked at NBOHC sites.
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- <sup>37</sup>The coefficients *a* and *c* for 7.4–7.9 eV (step 0.1) are (from Ref. 22): *a* = (0.112, 0.155, 0.171, 0.144, 0.2, 0.323) and *c* = (0.0963, 0.172, 0.295, 0.467, 0.831, 1.392). Coefficient *a* for 7.7 eV in Table 1 of Ref. 22 should have the opposite sign (*a* = +0.144).
- <sup>38</sup>Measured using a more strongly irradiated (95 J/cm<sup>2</sup>) sample. The 1.96-eV OA band of this sample is shown in the inset to Fig. 5.
- <sup>39</sup>S. J. Strickler and R. A. Berg, *J. Chem. Phys.* **37**, 814 (1962).
- <sup>40</sup>The ground state of NBOHC is nearly twofold degenerate, yielding *g<sub>l</sub>/g<sub>u</sub>* = 2. This peculiarity of NBOHC has been overlooked in previous PL lifetime-based estimates of *σ*; therefore, the present estimate of *σ* is about two times lower than the commonly assumed value.
- <sup>41</sup>The presence of E'-centers was confirmed in Ref. 16 by EPR measurements performed at 77 K on the sample, which was F<sub>2</sub> laser irradiated at 77 K. In hindsight, this contradictory observation may be explained by inadvertent warming by tens of kelvins during the (experimentally nontrivial) transfer of the sample from the VUV-irradiation setup to the liquid N<sub>2</sub>-filled EPR dewar.
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