Physical Disorder and Optical Properties in the Vacuum Ultraviolet Region of Amorphous SiO$_2$

Hideo Hosono,[1,2] Yoshiaki Ikuta,[1] Takeru Kinoshita,[2] Kouichi Kajihara,[1] and Masahiro Hirano[1]

[1]*Transparent Electro Active Materials, Exploratory Research for Advanced Technology, Japan Science and Technology Corporation, KSP C-1232, Sakato 3-2-1, Takatsu, Kawasaki 213-0012, Japan*
[2]*Materials and Structures Laboratory, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

The optical absorption of point-defect-free SiO$_2$ glass in the vacuum ultraviolet region is primarily controlled by the concentrations of three- and four-membered ring structures composed of heavily strained Si-O-Si bonds. The main channel of color center formation by F$_2$ excimer laser (7.9 eV) irradiation is not Frenkel-defect generation of oxygen via two-photon absorption processes but a pair generation of E' and nonbridging oxygen hole centers by the one-photon excitation of these strained bonds with 7.9 eV photons.

Amorphous (a-)SiO$_2$, a key material in optical fibers, metal-oxide semiconductors, and other optical elements [1,2], contains two types of structural disorder. One is a point defect defined as chemical disorder in perfect SiO$_2$ glass, which is visualized as a continuous network structure of SiO$_4$ tetrahedra joined by corner sharing [2,3]. Thus, point defects include oxygen or silicon vacancies and their interstitials, homobonds, or over- or undercoordinated silicons or oxygens. The second defect is physical disorder, which results from a wide distribution of Si-O-Si bond angle (peak = $\sim$145°, full width at half maximum = $\sim$40°) and the size of (Si-O)n ring structure (dominant $n = \sim5-7$), characterizing a-SiO$_2$ as a polymorph of SiO$_2$ [3]. Although numerous studies have revealed the role of chemical disorder in optical absorption and radiation sensitivity [1,2,4], the effects of the physical disorder, intrinsic to the amorphous state, on the optical properties of the glass have not been clarified to date. Recently, the leading edge of optical lithography in semiconductor technologies is shifting from ArF (193 nm or 6.3 eV) to F$_2$ (157 nm or 7.9 eV) excimer laser [5]. Although a-SiO$_2$ is a promising optical material for F$_2$ laser optics, improvements of optical transparency and radiation toughness to F$_2$ laser pulses are strongly required. It is crucial for the understanding of physical disorder in a-SiO$_2$ as well as overcoming the current material issue to clarify the primary factor controlling optical transparency in vacuum ultraviolet (VUV) and radiation sensitivity to F$_2$ laser light. Here we report that physical disorder of the network structure controls both VUV absorption edge and defect formation by F$_2$ excimer laser irradiation. The VUV absorption edge shifts to a longer wavelength with increased concentrations of strained Si-O-Si bonds such as small ring structures; the direct dissociation of these strained bonds is the main defect formation channel for F$_2$ laser irradiation.

Selection of samples is critical for the present purpose; chemical disorder must be suppressed to clarify the effects of physical disorder. It is essential to reduce the number of Si-Si bonds [6] and SiOH groups [7], which give intense absorption bands peaking at 7.6 eV and $>$7.4 eV, respec-

tively. In addition, the concentration of H$_2$ molecules embedded in the samples must be low to avoid the restoration of induced defects via chemical reactions with H$_2$ [8,9]. Synthetic SiO$_2$ glasses, prepared by vapor phase axial deposition, were used. The SiOH concentration in this glass is $\sim$1 $\times$ 10^{18} cm^{-3}; the H$_2$ concentration is below the detection level ($\sim$10^{16} cm^{-3}) as demonstrated by Raman spectroscopy [10]. No absorption band was resolved in the VUV region. A glass plate (12 $\times$ 16 $\times$ 6 mm thick) was heated at $\sim$900$-$1400 °C in an ambient atmosphere to impart the specimen to a fictive temperature (T_f), a value representing the degree of physical disorder of Si-O-Si network. The durations of heating necessary to attain the thermal equilibrium [11] were 120 h at 900 °C, 30 h at 1100 °C, 1 h at 1200 °C, or 0.1 h at 1400 °C. After heating at the desired temperature, the glass plate was dropped into water to minimize structural relaxation during the cooling process. The annealing temperature is hereafter referred to as T_f, based on the assumption that the structure of a-SiO$_2$ at an annealing temperature of $\sim$900$-$1400 °C is frozen by this quenching method. The resulting plates were then ground to a 10 $\times$ 14 $\times$ 4 mm^3 plate to eliminate surface contamination and polished to optical grade.

Specimens were irradiated at an ambient temperature by an F$_2$ excimer laser (Lambda Physik, LPX 240) in a stainless-steel chamber. The chamber was continuously purged with dry nitrogen to remove VUV-absorbing oxygen gas (residual O$_2$ concentration of $\sim$50 ppm). The power density at the sample position and the repetition frequency of the F$_2$ laser were $\sim$2.5 mJ/cm^2/pulse and 200 Hz, respectively, and the pulse duration was $\sim$10 ns. The measurements of VUV and UV absorption spectra were performed at an ambient temperature with a VUV spectrometer (JASCO, VUV-201) and a conventional spectrophotometer. Raman spectra were measured with a Fourier-transform Raman spectrometer (Nicolet, ESP-960), utilizing an Nd:YAG laser as the excitation source. Electron paramagnetic resonance (EPR) spectra were measured at 300 or 77 K using a Bruker model E-580. The error of spin concentrations, due to integration of the
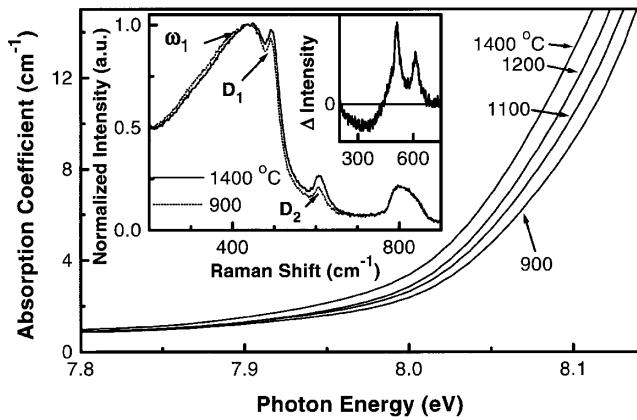
FIG. 1.   VUV absorption spectra of SiO_2 glasses with different T_f. Numbers in the figure denote T_f. The inset details the Raman spectra of specimens with either $T_f = 1400$ or 900 °C together with their difference spectrum.

first derivative spectrum, was $\pm 5\%$ for E' center ($\equiv$Si·, where — denotes an oxygen bond) [12] or $\pm 20\%$ for NBOHC (·O-Si$\equiv$) [12].

VUV absorption spectra of samples with different T_f reveal that the absorption edge [13] shifts continuously toward the low energy side with increasing T_f (Fig. 1) [12]. First, it is necessary to consider the primary factor determining the VUV-absorption edge in defect-free SiO_2 glasses. Although SiOH groups in SiO_2 glass gives absorption >7.4 eV, we could not observe a correlation between the amount of residual SiOH and the F_2 absorption edge shift (the residual OH content was reduced by several percent after heat treatment). In the Raman spectra of samples with different T_f (inset, Fig. 1), two sharp bands, the D_1 (495 cm^{-1}) and D_2 (606 cm^{-1}) bands, resulting from the symmetric breathing modes of four-membered

(D_1) and three-membered (D_2) ring structures in SiO_2 glasses [14,15] are seen. The intensities of these bands, relative to the main band at ~450 cm^{-1}, were enhanced with increasing T_f. For example, the D_1- and D_2-band intensities increase ~1.3 and ~1.6 times, respectively, with increasing T_f from 900 to 1400 °C. The absorption coefficients at 8.0 eV, a measure of the VUV absorption edge, correlate clearly with the intensity of the D_1 or D_2 bands (Fig. 2). These two small (three and four) rings have a planar structure composed of Si-O-Si bond angles of 130.5° for the three-membered ring or 160.5° for the four-membered ring [14]. As the most stable and populated bond angle is ~145° in the six- to seven-membered rings

(a)

(b)
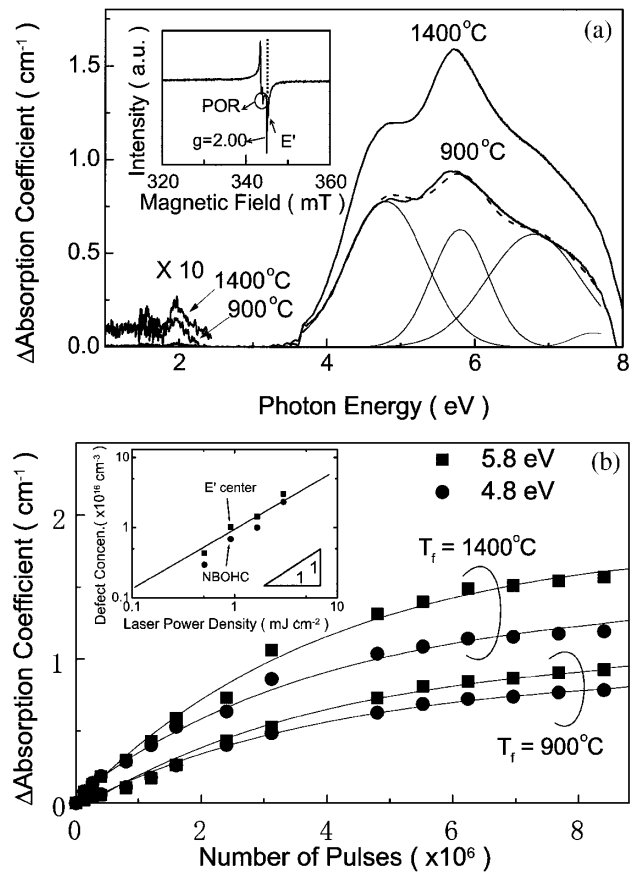
FIG. 3.   Defect formation in SiO_2 glasses with different T_f upon irradiation with F_2 excimer laser pulses. (a) UV absorption induced by irradiation with F_2 laser pulses at room temperature. Irradiation conditions; 2.5 $mJ/cm^2 \times (8.4 \times 10^6)$ pulses at a repetition of 200 Hz ($= 2.1 \times 10^4$ J/cm^2). The inset describes the EPR signals (NBOHC + E' center + trace of POR) induced by F_2 irradiation. The spectra were measured at 77 K. Each optical absorption spectrum was deconvoluted into three-Gaussian components with peaks at 4.8, 5.8, and 6.8 eV. An arrow denotes the 1.9 eV band resulting from NBOHC. (b) Intensities of the 5.8 eV bands (E' center) and the 4.8 eV bands (NBOHC) plotted against the accumulation fluence of the F_2 laser for SiO_2 glasses with $T_f = 1400$ and 900 °C. The curves correspond to fits according to Eq. (1). The inset details the relationship between F_2 laser power density and the intensities of induced optical bands due to E' center (5.8 eV) or NBOHC (4.8 eV). The slope was ~0.9 as evaluated by a least squares fit.
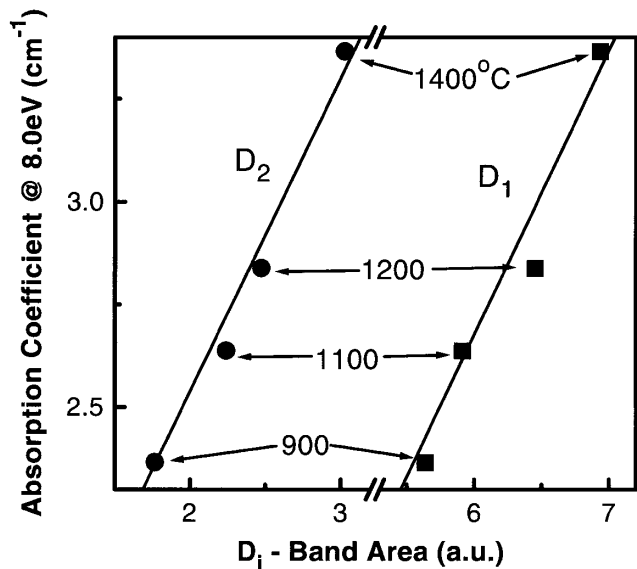

FIG. 2.   The correlation between the absorption coefficient at 155 nm (8 eV) and the intensity of either the D_1 or D_2 band in the Raman spectra of SiO_2 glasses with different T_f. The error in D_i is ~$\pm 10\%$.

of a-SiO$_2$ and α-quartz [16], Si-O-Si bonds in these small ring structures are heavily strained. Thus, it may be considered that the VUV absorption edge of point defect-free, bulk a-SiO$_2$ is controlled by the concentration of strained Si-O-Si bonds.
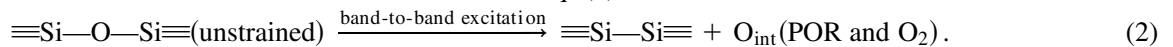
Next, we examine the relation between concentration of strained bonds and defect formation by F$_2$ excimer laser irradiation. Following optical absorption in samples with different T_f (900 or 1400 °C) irradiated with F$_2$ laser pulses, the intensity of induced absorption increases with increasing T_f (Fig. 3a). The intensity of induced absorption in a specimen with $T_f = 1400$ °C is larger by a factor of ~ 1.5 than that of a sample with $T_f = 900$ °C. This value, ~ 1.5, is close to the intensity ratio of D_i ($T_f = 1400$ °C)/D_i ($T_f = 900$ °C), where $i = 1$ or 2. The induced spectral shape, however, remains unchanged, with a weak absorption attributed to NBOHC at 1.9 eV and a broad UV-VUV absorption, deconvoluted into three components attributed to NBOHC (4.8 and 6.4 eV) and E' center (5.8 eV) (Fig. 3a). Irradiation with millions of F$_2$ laser pulses (inset, Fig. 3a) primarily induces the EPR signals of E' centers and NBOHCs; the participation of peroxy radicals (PORs, $\cdot$O-O-Si$\equiv$) [12] is minor ($\sim 1/20$ of NBOHC). This situation does not change upon postirradiation annealing [17]. The concentration of E' centers is similar to that of NBOHC at each F$_2$ laser fluence. The intensities of the 4.8 eV band and the 5.8 eV band increase with increasing pulse number both in specimens with $T_f = 900$ °C and 1400 °C to a saturation level which depends on the specimen T_f (Fig. 3b). The data fit a first order kinetic reaction as described in Eq. (1):

$$\Delta\alpha(n) = \Delta\alpha(\infty)[1 - \exp(kn)], \qquad (1)$$

where $\Delta\alpha$ is the absorption coefficient of an induced optical band, n is the number of irradiated F$_2$ laser pulses, and k is the reaction rate constant. Although the value of k is independent of T_f, $\Delta\alpha_{5.8\ eV}(\infty)$ and $\Delta\alpha_{4.8\ eV}(\infty)$ for a specimen with $T_f = 1400$ °C are larger than those for a sample with $T_f = 900$ °C by a factor of ~ 1.6. The concentrations of induced E' and NBOHC, shown as a function of F$_2$ laser power density (inset, Fig. 3b), are very similar. Both quantities are simply proportional to the laser power density, indicating that E'-NBOHC formation proceeds via one-photon absorption processes.

Defect formation resulting from F$_2$ laser irradiation is discussed in the context of strain bonds. The main defect species created by F$_2$ laser irradiation are comparable concentrations of NBOHC and E' center. This mechanism differs strikingly from the Frenkel-type mechanism expressed in Eq. (2).

$$\equiv\text{Si—O—Si}\equiv(\text{unstrained}) \xrightarrow{\text{band-to-band excitation}} \equiv\text{Si—Si}\equiv + \text{O}_\text{int}(\text{POR and O}_2). \qquad (2)$$

The Frenkel-type mechanism was proved by Tsai and Griscom [18], while studying defect formation induced by electronic excitation via band-to-band excitation in specimens irradiated with ArF excimer laser pulses, and by Hosono *et al.* [19], while examining SiO$_2$ glasses bombarded with 10 MeV H$^+$ ions. The primary defect species in Eq. (2) are oxygen vacancies (such as Si-Si bonds) and oxygen interstitials (PORs or O$_2$ molecules). This is not, however, the major channel for F$_2$ laser irradiation as neither PORs (nor O$_2$) nor $\equiv$Si-Si$\equiv$ were detected as primary defects; pairs of E' and NBOHC are instead created via a one-photon absorption process. This finding leads to an idea that these defects are created from defect precursors, which have an optical absorption at 7.9 eV. The precursors are likely to be the strained Si-O-Si bonds; absorption near 7.9 eV is controlled by the fraction of strained Si-O-Si bonds including three- or four-membered ring structures. This process is distinctly distinguished from the recently observed E' center (and oxygen vacancy) formation via two-photon absorption processes by ArF excimer laser irradiation [20]. Therefore, the primary defect formation mechanism by F$_2$ laser irradiation may be expressed as

$$\equiv\text{Si—O—Si}\equiv(\text{strained}) \xrightarrow{h\nu(7.9\ \text{eV})} \equiv\text{Si}\cdot + \cdot\text{O—Si}\equiv. \qquad (3)$$
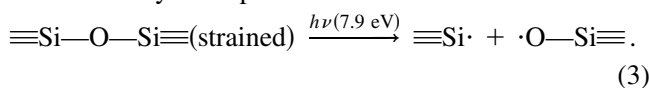
The dependence of the E'-NBOHC defect pair concentrations on laser fluence (Figs. 3a and 3b) substantiates this model; the ratio of the saturated concentration levels of defect pairs in the specimens is close to the concentration ratio of three- or four-membered ring structures. Strained Si-O-Si bonds control an optical absorption at the wavelength of F$_2$ laser light, allowing the mechanism expressed in Eq. (3) to become dominant over the Frenkel-type mechanism. The quantum efficiency (Q.E.) of Eq. (3), estimated from the initial stage of the growth curve (Fig. 3b) using the oscillator strength (0.048) [21] of the 4.8 eV band of the NBOHC, is $\sim 3 \times 10^{-4}$, which is *larger by 2 orders of magnitude* than that ($\sim 5 \times 10^{-6}$) [19] of Eq. (2). The release of bond strain energy by the photon-induced ring opening reaction is considered to lead to much higher Q.E. for the present mechanism. In addition, the present mechanism may explain the persistent question [22] why the EPR signal is distinctly observable for pair generation of E' and NBOHC from a Si-O-Si bond. If the radical pair is created from the same precursor, the radical pair must be separated to a distance where the dipolar broadening effect is negligibly small. The defect formation via a ring opening process of the three- and four-membered ring structures upon F$_2$ laser irradiation leads to a well-separated E'-NBOHC pair.

The significance of the present findings has important ramifications on the use of F-doped SiO$_2$ glasses [23] in VUV excimer laser lithography. Shortening of the exposure wavelength, however, imposes severe requirements upon optical materials. Although amorphous materials are preferable, SiO$_2$ glasses, exclusively used as optical materials in KrF (5.0 eV) and ArF (6.4 eV) lithography, are not currently applicable to F$_2$ laser lithography because of
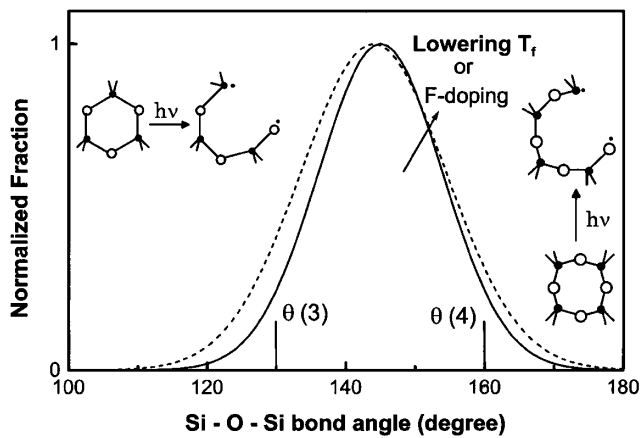
FIG. 4. A schematic model explaining the relation between fictive temperature T_f, degree of physical disorder, and defect creation by F_2 laser irradiation in SiO_2 glasses. When the T_f is decreased, the distribution of Si-O-Si bond angle becomes narrow and the peak position is slightly shifted to a large angle side. The bond angle is 130.5° in the three-membered ring or 160.5° for the four-membered ring. Since heavily strained bonds in these small rings have optical absorption at the wavelength of F_2 laser pulse (7.9 eV), they are converted into a pair of E' center and NBOHC upon irradiation with F_2 laser pulse. If the separation between the paramagnetic centers is very close, the ESR signal should be unobservable due to dipolar broadening [22]. Rupture of the strained bond creates a defect pair separated at a distance which is enough to observe the ESR signal. Doping of fluorine, which is incorporated as Si-F bond, leads to lowering the T_f via reduction of the high temperature viscosity. This effect is the same as thermal annealing treatment to lower the T_f.

insufficient transparency at 7.9 eV. The present study revealed that the presence of strained Si-O-Si bonds controls both the VUV transparency and defect formation resulting from F_2 laser irradiation. Fluorine doping into dry SiO_2 glasses effectively enhances both transmittance at 7.9 eV and radiation toughness for F_2 lasers by narrowing the $\angle$Si-O-Si distribution [23]. As fluorine is incorporated, the formation of Si-F bonds breaks the continuity of the SiO_2 network structure and drastically reduces the high temperature viscosity [24]. As a consequence, the T_f in F-doped SiO_2 is reduced from that of F-free SiO_2, decreasing the fraction of the three- and four-membered ring structures (strained bonds) [25]. F doping may, therefore, be regarded as *chemical annealing,* which does not require a long time to reach a low T_f. This may prove to be a distinct advantage over conventional thermal annealing. Figure 4 schematically summarizes the effect of physical disorder on defect formation by F_2 laser irradiation. The VUV cutoff wavelength of α-quartz is shorter by ~15 nm than that of current F-doped silica in 1-mm-thick samples. The narrowing of $\angle$Si-O-Si distribution will hopefully lead to novel SiO_2 glasses available for use as VUV optical materials.

[1] L. Skuja, J. Non-Cryst. Solids **239**, 16–48 (1998).

[2] D. L. Griscom, J. Ceram. Soc. Jpn. **99**, 923–942 (1991).

[3] A. C. Wright, J. Non-Cryst. Solids **179**, 84–115 (1994).

[4] G. Pacchioni, in *Defects in SiO₂ and Related Dielectrics,* edited by G. Pacchioni, L. Skuja, and D. L. Griscom (Kluwer, Dordrecht, 2000), pp. 161–195.

[5] V. Liberman *et al.,* J. Vac. Sci. Technol. B **17**, 3273 (1999).

[6] H. Hosono, Y. Abe, H. Imagawa, H. Imai, and K. Arai, Phys. Rev. B **44**, 12 043–12 045 (1991).

[7] Y. Morimoto, S. Nozawa, and H. Hosono, Phys. Rev. B **59**, 4066–4073 (1999).

[8] J. E. Shelby, J. Appl. Phys. **50**, 3702-3706 (1979).

[9] D. H. Levy, K. K. Gleason, M. Rothschild, and J. H. C. Sedlacek, J. Appl. Phys. **73**, 2809–2815 (1993).

[10] V. S. Khotimchenko, G. M. Sochivkin, I. I. Novak, and K. N. Kuksenko, Z. Prik. Spektro. **46**, 987–991 (1987).

[11] J. C. Mikkelsen, Jr. and F. L. Galeener, J. Non-Cryst. Solids **37**, 71–84 (1980).

[12] D. L. Griscom, in *Glass Science and Technology,* edited by D. R. Uhlmann and N. J. Kreidl (Academic Press, New York, 1990), Vol. 4B, Chap. 3.

[13] The absorption coefficient of bulk a-SiO₂ (4 mm thick) near 8 eV is $\geq 10^1$ cm⁻¹, which corresponds not to *Urbach tail* [I. T. Godmanis, A. N. Trukhin, and K. Hubner, Phys. Status Solidi (b) **116**, 279 (1983)] but to so-called *weak absorption tail.*

[14] F. L. Galeener, in *The Structure of Non-Crystalline Materials 1982,* edited by P. H. Gaskell, J. M. Parker, and E. A. Davis (Taylor & Francis, London, 1982), pp. 337–359; A. E. Geissberger and F. L. Galeener, Phys. Rev. B **28**, 3266–3270 (1983).

[15] A. Pasquarello and R. Car, Phys. Rev. Lett. **80**, 5145–5147 (1998).

[16] L. W. Hobbs, C. E. Jesurum, and B. Berger, in *Structure and Imperfections in Amorphous and Crystalline Silicon Dioxide,* edited by R. A. B. Devine, J.-P. Duraud, and E. Dooryhee (Wiley, New York, 2000), pp. 3–48.

[17] If O₂ molecules as an oxygen interstitial are created by the irradiation, the POR concentration should be enhanced by annealing following $E' + O_2 =$ POR as reported in Ref. [18]. The formation of O₂ was not detected by fluorescence excited by Nd:YAG laser using an FT-Raman spectrometer. The detection limit by this technique is ~10¹⁶ cm⁻³ [L. Skuja, B. Guttler, D. Schiel, and A. R. Silin, Phys. Rev. B **58**, 14 296 (1998)].

[18] T. E. Tsai and D. L. Griscom, Phys. Rev. Lett. **67**, 2517–2520 (1991).

[19] H. Hosono, H. Kawazoe, and N. Matsunami, Phys. Rev. Lett. **80**, 317–320 (1998); H. Hosono and N. Matsunami, Nucl. Instrum. Methods Phys. Res., Sect. B **141**, 566–574 (1998).

[20] Y. Ikuta, S. Kikugawa, M. Hirano, and H. Hosono, J. Vac. Sci. Technol. B **18**, 2891–2895 (2000).

[21] A. A. Bobyshev and V. A. Radzig, Sov. Phys. Chem. Glass **14**, 501 (1988).

[22] R. A. Silin, L. N. Skuja, and A. N. Trukhin, J. Non-Cryst. Solids **38&39**, 195 (1980).

[23] H. Hosono, M. Mizuguchi, H. Kawazoe, and T. Ogawa, Appl. Phys. Lett. **74**, 2755–2757 (1999).

[24] M. Kyoto, Y. Ohoga, S. Ishikawa, and Y. Ishiguro, J. Mater. Sci. **28**, 2738–2744 (1993).

[25] H. Hosono, M. Mizuguchi, L. Skuja, and T. Ogawa, Opt. Lett. **15**, 1549–1551 (1999).