

Detection of Interstitial Oxygen Molecules in SiO₂ Glass by a Direct Photoexcitation of the Infrared Luminescence of Singlet O₂

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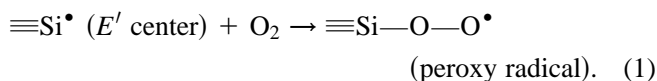
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The presence of interstitial oxygen molecules in glassy SiO₂ has been demonstrated directly by 1064.1 nm ($\nu'' = 0$) \rightarrow ($\nu' = 1$) excitation of the forbidden O₂ molecule ${}^1\Delta_g(\nu' = 0) \rightarrow {}^3\Sigma_g^-(\nu'' = 0)$ luminescence transition at 1272 nm in Suprasil W1 fused silica. The interstitial O₂ molecules, introduced into glass network during the synthesis process, are destroyed by vacuum ultraviolet or neutron irradiation. Mobile O atoms may play an important role in radiation processes in SiO₂. The directly photoexcited luminescence of O₂ could be used to detect the presence of O₂ in other solid state matrices as well. [S0031-9007(96)01024-1]

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The creation and annealing processes of point defects in glassy silicon dioxide (*g*-SiO₂) are studied due to the outstanding role this material plays in glass physics, optics, and communications applications. While the early studies of defect creation concentrated on purely electronic processes, in the recent decade it has become increasingly evident that radiolytic ionic mechanisms are relevant [1]. A distinct group among them is formed by mechanisms, involving gas molecules (e.g., H₂, O₂, Cl₂), dissolved into the relatively sparse *g*-SiO₂ network of corner-shared SiO₄ tetrahedrons.

Particular attention has been paid to the possible reactions, involving interstitial oxygen O₂ molecules. They can be introduced into glass network during the synthesis (oxidizing environment) or by a later diffusion via treating in O₂. Edwards and Fowler [2] suggested that the conversion between the two basic intrinsic paramagnetic defects in silica, the *E'* center and peroxy radical, occurring during the thermal annealing, is due to O₂ diffusion:



This mechanism was subsequently confirmed by the finding that the annealing behavior of the *E'* centers and peroxy radicals is dependent on the amount of O₂, diffused into *g*-SiO₂ [3]. Zhang *et al.* [4] proved recently that the reaction (1) is reversible, and that the peroxy radicals can be converted back to *E'* centers by reirradiation. Tsai and Griscom [5] have presented EPR-based evidence that interstitial O₂ is radiolytically created in *g*-SiO₂ by a two-photon absorption of 6.4 eV ArF laser light and that O₂ may contribute to the radiation-induced near-infrared attenuation in Ge-doped silica optical fibers [6]. Imagawa *et al.* [7] have shown that the annealing of a diamagnetic intrinsic defect in *g*-SiO₂, the $\equiv\text{Si}\cdot\text{Si}\cdot$ "wrong bond," is caused by a reaction with diffusing O₂ molecules. The presence of O₂ in *g*-SiO₂ is thought to be responsible for the redshift of the vacuum-ultraviolet

optical absorption edge [8], and for "anomalous" reactions of oxygen rich *g*-SiO₂ with hydrogen [9].

A common problem with verifying all of the numerous proposed O₂-based defect mechanisms is the absence of reliable spectroscopic techniques to detect selectively the interstitial O₂ in *g*-SiO₂. The presence of O₂ is often simply inferred from the stoichiometry balance during the glass synthesis. Up to now the most direct evidence for interstitial O₂ in *g*-SiO₂ is provided by a mass-spectrometric detection of O₂ in outgassing experiments [10]. Relatively straightforward concentration estimates of O₂ have been made as well from the broad, structureless excess absorption in the vacuum-ultraviolet optical absorption edge region (7.5 to 8 eV) [8], which may correspond to the Schuman-Runge bands of free O₂ molecules in the gaseous state. However, a number of different intrinsic and extrinsic defects in *g*-SiO₂ give rise to absorption into that spectral region, and the specific contribution of O₂ is often difficult to separate.

The O₂ in gaseous state exhibits a characteristic infrared luminescence band (the so-called "atmospheric infrared system") at 1268.3 nm which corresponds to the forbidden "band origin" ($\nu' = 0$) \rightarrow ($\nu'' = 0$) transition from the first electronic excited state ($a^1\Delta_g$) to ($X^3\Sigma_g^-$) ground state [11]. When O₂ molecules are dissolved in different organic solvents or water, the transition rate of this luminescence increases, and the emission peak is typically between 1271 and 1277 nm [12,13].

The purpose of this study was to find out whether this luminescence could be used as a tool to detect the presence and relative concentrations of O₂ molecules dissolved in SiO₂ glass. An encouraging hint has been published recently by Shikama *et al.* [14]; a novel sharp luminescence peak at 1270 nm was observed in fluorine-doped *g*-SiO₂ optical fibers under irradiation in a nuclear reactor. The band was tentatively attributed to fluorine dopant ions [14], however, the nearly exact coincidence of the peak wavelength and halfwidth with those reported

[12,13] for the O₂ luminescence in solutions may indicate its O₂-related origin.

A major hindrance in observing optical transitions between $X^3\Sigma_g^-$ and $a^1\Delta_g$ states of O₂ are the associated extremely small oscillator strengths: 4×10^{-12} for a free molecule [11] and of order 10^{-9} for O₂ in solutions [12]. The transition is both symmetry and spin forbidden. Therefore, the photoexcitation of this luminescence in condensed matrices is usually accomplished by energy transfer from intentionally added luminescence sensitizer molecules [12,13]. However, this approach cannot be used in our case because of the difficulty of doping *g*-SiO₂ with suitable sensitizers, and because it would yield a complex, sensitizer-dependent relation between the relative O₂ content and emission intensity.

The wavelength of the transition from the ground ($X^3\Sigma_g^-, \nu'' = 0$) to the first excited vibronic state of O₂ ($a^1\Delta_g, \nu' = 1$) is between 1066 and 1069 nm in different solutions [12], that is, close to the wavelength of Nd-YAG laser (1064.1 nm). Hence, the luminescence of O₂ could be observed under a *direct* 1064.1 nm photoexcitation, if a sufficiently sensitive detection system is used.

The measurements were performed at room temperature with a Fourier-transform infrared spectrometer (Bruker IFS66) equipped with a Nd-YAG laser-based Raman module (Bruker FRA106) and with an Ar ion laser-based Raman system (Jobin-Yvon T64000). The synthetic *g*-SiO₂ samples investigated are described in Table I. The “Suprasil W1” type silica (samples 1 to 4) contains superstoichiometric oxygen [1,10]. The “KUVI” type silica (samples 5 and 6) is oxygen deficient, as evidenced by the presence of an optical absorption band at 245 nm (peak amplitude 0.1 cm⁻¹), due to oxygen excess defects—twofold-coordinated Si atoms [15]. The Corning 7940 silica (samples 7 and 8) is stoichiometric and contains ≈1000 (ppm SiO₂) bound hydroxyl groups.

The spectra obtained are shown in Fig. 1. The spectral region of Raman shifts between 0 and 1400 cm⁻¹ corresponds to the fundamental phonon modes and is in fair agreement with the previously reported spectra (e.g., [16]). The sharp line at 606 cm⁻¹ (the “D2 line”), which is more prominent in heavily neutron-irradiated samples (spectra 4 and 8), has been assigned to the breathing mode of planar three-membered rings of Si-O bonds [17].

A new feature, unreported in the previous Raman studies, is the band located at Raman shift 1535 cm⁻¹. It is observed only in the oxygen-rich Suprasil W1 type glass, and its intensity is progressively reduced by vacuum ultraviolet or neutron irradiation (Fig. 1, spectra 1 to 4). In samples having strong “1535 cm⁻¹” band, an additional weak band split apart by 1549 cm⁻¹ appears (compare spectra 1 and 5).

The new “1535 cm⁻¹” band is present only when the 1064.1 nm excitation is used (compare spectra 1 and 1a). This excitation wavelength dependence indicates that the band could be caused either by resonance Raman scatter-

TABLE I. Description of the investigated synthetic SiO₂ glass samples. Sample numbers correspond to those in Fig. 1.

Sample no.	Type of SiO ₂ glass	Description	Irradiation history
1 or 1a	Suprasil W1	Dry, ^a Oxygen excess	Pristine
2	Suprasil W1	Dry, ^a Oxygen excess	Vacuum Ultraviolet ^c
3	Suprasil W1	Dry, ^a Oxygen excess	10 ¹⁸ n/cm ²
4	Suprasil W1	Dry, ^a Oxygen excess	10 ¹⁹ n/cm ²
5	KUVI (VAD)	Dry, ^a Oxygen deficient	Pristine
6	KUVI (VAD)	Dry, ^a Oxygen deficient	10 ¹⁸ n/cm ²
7	Corning 7940	Wet ^b	Pristine
8	Corning 7940	Wet ^b	10 ²⁰ n/cm ²

^aBound hydroxyl ($\equiv\text{Si}-\text{O}-\text{H}$) content <5 ppm.

^bHydroxyl content. ≈1000 ppm.

^cIrradiated by unfiltered light of a deuterium lamp with a silica window (short wavelength cutoff at 7.6 eV).

ing or by luminescence. The usual techniques employed to resolve this problem, the anti-Stokes spectrum- or time-resolved measurements, were unavailable on our system. The resonance Raman scenario is, however, contradicted by the absence of significant optical absorption bands in *g*-SiO₂ at 1064.1 nm and by the wrong sign of anharmonicity; the frequency of the “basic line” (1535 cm⁻¹) is *less* than its distance to the “overtone” (1549 cm⁻¹, spectrum 1 in Fig. 1).

On the other hand, the *absolute* wavelength of the “1535 cm⁻¹” band, 1272.2 nm, falls within the narrow spectral range between 1271 and 1277 nm, where the luminescence band of singlet oxygen molecules in various liquid matrices is placed [12,13]. Moreover, the distance to the satellite line, 1549 cm⁻¹ (Fig. 1), nearly coincides with the O₂ molecule ground state vibration quantum in the gas phase (1555 cm⁻¹ [11,18]) or in solutions (1549 cm⁻¹ [13], 1546 cm⁻¹ [18]).

Therefore, we conclude that the peak at the absolute wavelength 1272.2 nm is not a Raman line and is rather caused by the forbidden $a^1\Delta_g(\nu' = 0) \rightarrow X^3\Sigma_g^-(\nu'' = 0)$ luminescence emission transition of interstitial oxygen molecules in *g*-SiO₂. The weak satellite line is the first vibronic sideband corresponding to the $a^1\Delta_g(\nu' = 0) \rightarrow X^3\Sigma_g^-(\nu'' = 1)$ transition. The excitation occurs evidently in the first vibronic sideband of the absorption

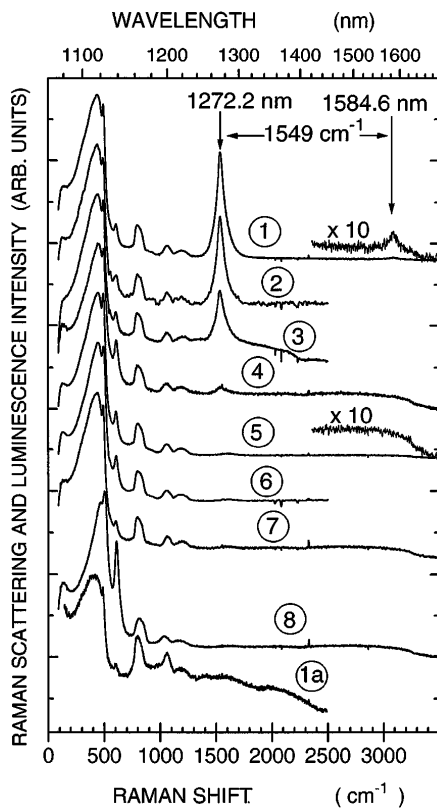


FIG. 1. Raman scattering and photoluminescence spectra of glassy SiO_2 , obtained at room temperature with 1064.1 nm excitation (spectra 1 to 8) and 514.5 nm excitation (spectrum 1a). The absolute wavelengths for spectra 1 to 8 are indicated at the top x axis. Curve numbering corresponds to the sample numbers in Table I. The intensities of all spectra are normalized against the fundamental 440 cm^{-1} Raman band, and the base lines are shifted. The spectral resolution is 8 cm^{-1} for curves 2,6 and 2 cm^{-1} for the other spectra.

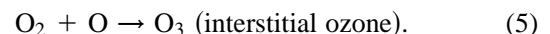
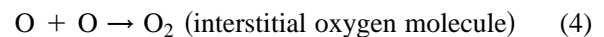
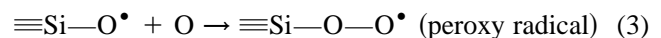
spectrum: $X^3\Sigma_g^-(\nu'' = 0) \rightarrow a^1\Delta_g(\nu' = 1)$. To our knowledge this is the first reported case of a direct infrared photoexcitation of singlet oxygen luminescence.

The intensity of the directly excited O_2 luminescence relative to the intensity of the fundamental Raman band at 490 cm^{-1} may be used as a tool to determine the absolute concentration of O_2 in $g\text{-SiO}_2$. An absolute calibration was not possible in the present study, since the exact concentration of dissolved O_2 in our Suprasil W1 samples was not known. It is thought that this type of $g\text{-SiO}_2$ contains $\approx 10^{18}$ (O_2 molecules)/ cm^3 [4,8].

It must be noted, however, that due to the strictly forbidden nature of the transitions between $a^1\Delta_g$ and $X^3\Sigma_g^-$ states the O_2 luminescence photoexcitation transition probability as well as the emission quantum yield and lifetime are all dependent on interactions with the matrix. The quantum yield for luminescence of O_2 dissolved in different solvents may vary more than 100 times (between 10^{-4} and 10^{-7}) [12]. It may be hoped that these (presently yet unknown) parameters are fairly constant within a single matrix, glassy SiO_2 , and the luminescence

intensity is thus proportional to the concentration of O_2 . Caution must be exercised in special cases, like heavily doped or neutron-irradiated samples, where the average environment of the O_2 molecule may become different from that in the pristine sample.

As seen from Fig. 1, the luminescence of O_2 is observed only in Suprasil W1 type silica (spectra 1–4). This agrees well with the conclusions of other researchers [1,3,4,9,10] that this particular type of $g\text{-SiO}_2$ may contain a large amount of dissolved O_2 . The interstitial O_2 molecules are destroyed by neutron irradiation (spectra 1, 3, and 4); the oxygen atoms or molecules are evidently built-in into the intrinsic radiation defects by reactions with radiation-induced dangling bonds. Since at the irradiation temperatures (300 to 400 K) the atomic oxygen is much more mobile than O_2 molecules, the motion of radiolytic atomic oxygen may be the dominant mechanism for destroying O_2 and creating oxygen-excess intrinsic defects—peroxy radicals and nonbridging oxygen hole centers (NBOHC's). Apart from reaction (1), several other channels involving motion of atomic O may be important:



It has been suggested previously [5] that reaction (4), the formation of radiation-induced interstitial oxygen molecules, occurs under ArF excimer laser irradiation. As evident from Fig. 1 (spectra 5 to 8), no detectable oxygen luminescence peak is induced by high-dose neutron irradiation in glasses, which initially do not contain dissolved O_2 [19]. This may indicate that under neutron irradiation reaction channels (2) and (3) are relatively much more probable than channel (4). Indeed, all the irradiated samples (2,3,4,6,8) show strong red luminescence band around 1.9 eV, which is caused by NBOHC's [20]. However, this does not necessarily contradict the paper [5], since under ultraviolet or γ irradiation fewer dangling bonds are created and reaction (4) may become more competitive with reactions (2) and (3). An additional evidence for reaction (4) has been found recently by Hosono [21], using electronegative ion (fluorine) implantation in SiO_2 .

The formation of interstitial ozone in $g\text{-SiO}_2$ under irradiation [reaction (5)] was first suggested by Awazu and Kawazoe [8]. The 4.8 eV radiation-induced optical absorption band in $g\text{-SiO}_2$, formerly attributed to NBOHC's (see [1,20] for a review), was reassigned to O_3 molecules [8]. By confirming the presence of O_2 molecules and their participation in radiation processes (Fig. 1, spectra 1–4), the present work proves that reaction (5) may indeed take place. On the other hand, the absence of

radiation-induced O_2 in neutron-irradiated samples (spectra 6 and 8) in concentrations above $\approx 10^{16} \text{ cm}^{-3}$ [19] indicates that the concentration of O_3 should be below at least this value. In the same time, the sample 8 shows 4.8 eV optical absorption band of amplitude $\approx 20 \text{ cm}^{-1}$. Assuming oscillator strength $f = 0.25$ [22], Smakula's equation yields center concentration $\approx 10^{18} \text{ cm}^{-3}$. This is in accord with our past [20] and recent [23] conclusion that the dominant cause of the 4.8 eV absorption band in most irradiated silicas is not ozone but rather NBOHC. The contribution of the interstitial O_3 to the absorption in that region may be limited to specific conditions: ultraviolet (ArF or F_2) laser irradiation of oxygen-excess $g\text{-SiO}_2$.

To summarize, the luminescence of O_2 may be used to verify a number of presently discussed models for defect processes in glassy SiO_2 . Because of the spatial resolution ("micro-Raman") capability of the spectrometer used, this luminescence provides as well a convenient tool for studying O_2 diffusion and silicon oxidation processes in microelectronics. Since the basic distinguishing features of this emission, the peak position at $\approx 1270 \text{ nm}$ and the vibrational sideband at $\approx 1585 \text{ nm}$, are almost independent from the surrounding matrix, this luminescence could be used to detect the presence of interstitial O_2 in various other solid state matrices as well.

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