# Correlation of the 5.0- and 7.6-eV absorption bands in SiO<sub>2</sub> with oxygen vacancy

Ryoichi Tohmon, Hiroyasu Mizuno, and Yoshimichi Ohki

Department of Electrical Engineering, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169, Japan

Kotoku Sasagane

Department of Chemistry, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169, Japan

Kaya Nagasawa

Department of Electrical Engineering, Sagami Institute of Technology, 1-1-25 Tsujido-nishi-kaigan, Fujisawa, Kanagawa 251, Japan

Yoshimasa Hama

Science and Engineering Research Laboratory, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169, Japan (Received 5 April 1988; revised manuscript received 30 August 1988)

Various uv and vacuum-uv optical-absorption bands found in as-manufactured high-purity  $SiO_2$  glass were studied. Two types of absorption bands were found near 5.0 eV, one of which is attributed to the oxygen vacancy ( $\equiv Si \_ Si \equiv$ ). The absorption band at 7.6 eV is also found to be caused by the same oxygen vacancy. Observation of the decay lifetime of photoluminescence and calculations using the *ab initio* molecular-orbital program show that the 7.6-eV band is caused by a singlet-to-singlet transition, while the 5.0-eV band is caused by a singlet-to-triplet transition.

## I. INTRODUCTION

Despite the years of attention given to point defects in amorphous  $SiO_2$  (*a*- $SiO_2$ ), many aspects of their behavior are still not understood since electron spin resonance (ESR), which is one of the most powerful tools used for detection of defects, is limited to the characterization of paramagnetic defects. Hence, although paramagnetic defects such as E' center, peroxy radicals, and nonbridging oxygen hole center (NBOHC) have been identified with specific defect structures through ESR, the structure and properties of nonparamagnetic defects are less well understood (for a recent review, see Ref. 1).

The characterization of nonparamagnetic defects is important not only because they are of intrinsic interest, for instance being the cause of optical absorption in opticalwave guides, but also because they serve as precursors of paramagnetic defects. In order to eliminate these paramagnetic defects, which are the major obstacle in using  $a-SiO_2$  in radiation environments, it is necessary to identify their precursors and growth mechanisms. This can be done only when the properties of the nonparamagnetic precursors are fully understood.

One of the oldest known nonparamagnetic defects in  $a-SiO_2$  is the defect which causes the 5.0-eV (245-nm) optical absorption band, known as the  $B_2$  band.<sup>2-4</sup> The general conclusion has been that this band is due to some form of oxygen deficiency in the SiO<sub>2</sub> network. However, the exact structure of the defect is still an open question. Skuja *et al.*<sup>3</sup> and Arnold<sup>4</sup> proposed twofold coordinated silicon (-O-Si-O-) and oxygen vacancy,  $\equiv Si-Si \equiv$  (where  $\equiv Si$  represents a silicon atom bonded to three separate oxygens), respectively, as models for

the defect responsible for the  $B_2$  band. Nagasawa *et al.* reported<sup>5</sup> that E' center created by fiber drawing is observed only in samples which exhibit the  $B_2$  band. Based on this observation,  $\equiv$  Si—Si $\equiv$  was proposed as the oxygen deficiency responsible for the  $B_2$  band.

On the other hand, O'Reilly<sup>5</sup> reported that calculations of local electronic structures showed the  $\sigma \rightarrow \sigma^*$  transition of an unstrained  $\equiv$  Si-Si  $\equiv$  bond to be 7.6 eV. From this result, Griscom<sup>1</sup> suggested that excitation at the site of a  $\equiv$  Si=Si $\equiv$  bond is responsible for the optical-absorption band at 7.4 eV in unirradiated or neutron-irradiated silica. Imai et al.7 observed vacuumuv absorption spectrum in as-manufactured silica glass and found the 7.6-eV band in a number of glasses but no corresponding paramagnetic defect. They suggested that this band is caused by a nonparamagnetic oxygendeficient defect, thus experimentally supporting Griscom's model. However, it is still not clear what relation the 7.6-eV band has with the 5.0-eV band, since both of these absorption bands has been identified with the  $\equiv$  Si—Si $\equiv$  oxygen vacancy.

Another unresolved question is the nature of the photoluminescence excited by the  $B_2$  band. It is well known that type-I and -II silica glasses have emission peaks in the visible to ultraviolet region, but the peak positions are not always clear because the values cited in the literature are not in complete agreement. Manufacturing method, thermal history, irradiation, and temperature at which the observations were made all have an effect on the position and intensity of the emission peaks.<sup>3,8,9</sup>

The purpose of this paper is to show that there are two types of absorption bands at 5.0 eV and that the non-paramagnetic  $\equiv$  Si $\equiv$  Si $\equiv$  oxygen vacancy is responsible for both the 7.6 eV band and one of the two 5.0 eV bands. Results of optical-absorption, photoluminescence, and

ESR measurements of high-purity silica glass, along with the results of *ab initio* molecular-orbital calculations, are presented.

#### **II. EXPERIMENTAL PROCEDURE**

The pure silica glass samples used in the experiment are listed in Table I. The dimensions of the samples were (1) rod, right cylindrical in shape with a diameter of 10 or 15 mm and a length of 40-45 mm; (2) disk, 10 or 15 mm in diameter, 1 mm thick; and (3) plate, 0.6-0.8 mm thick, area of 3 cm<sup>2</sup>. All samples were mirror polished at both ends for optical-absorption measurements and the side surfaces of the rod samples were polished in flame for photoluminescence measurements. The OH content was estimated from the OH vibrational absorption at 3600 cm<sup>-1</sup>, and the chlorine content was measured by radioactivation analysis. Although the OH and chlorine content shown in Table I is somewhat different from those listed in Ref. 5, the discrepancy is believed to arise from the fact that the OH and chlorine content of Ref. 5 was measured using samples drawn into fibers, while the measurement of Table I was made on bulk samples.

All optical measurements were made at room temperature. The optical absorption in the range 200-800 nm was measured using a Shimadzu UV-160 double-beam spectrometer. Optical absorption in the range 140-240 nm was measured using a Hinteregger hydrogen discharge lamp and a Nikon/McPherson 225 monochromator in vacuum. All absorption spectra are shown in optical density (OD/cm). Photoluminescence (PL) spectrum with steady-state excitation was measured using two crossed monochromators and a 200-W deuterium lamp as the light source, as shown in Fig. 1(a). The pulsed emission apparatus for luminescent lifetime measurement is shown in Fig. 1(b). The optical chopper, with a two-slot blade, operated at 140 Hz.

Heat treatment was performed either in pressurized (7.3 atm) oxygen gas or in pressurized (7.5 atm) helium gas for 12 h at 500 °C. Implantation of He<sup>+</sup> ions at room



FIG. 1. Schematic diagram of the apparatus for the measurement of photoluminescence. (a) Spectral measurement under steady-state excitation. (b) Luminescent lifetime measurement.

temperature into the plate samples was made at an ion energy of 3.2 MeV with a total dose of 50  $\mu$ C. The ions were accelerated by a Pelletron Accelerator model 5SDH.

		Cl	 OH				7.6-eV
Sample	Manufacturing	content	content	В	2 band	PL	band
name	method	(ppm)	(ppm)	Туре	(OD/cm)	band	(OD/cm)
SFF	soot	Х	X	α	0.007 00	A	24
S1F	soot	0.3	X	α	0.024 80	A	29
SF1	soot	X	270	β	0.004 08	В	X
SFF-β	soot	X	6.0	β	0.022 80	В	X
DF8	direct	Х	1000	X	X	X	X
D17	direct	76	700	X	X	X	X
P3F	$Ar + O_2$ plasma	370	0.5	X	X	X	X
PRF 1.5%	Ar plasma	4300	0.8	α	0.115 00	A	>> 30
PRF 5%	Ar plasma	670	3.0	α	0.072 00	A	> 30
PRF 15%	Ar plasma	410	3.3	α	0.044 50	A	6
PRF-WF	Ar plasma	3900	0.3	α	0.070 00	A	>> 30
P2F-B	$O_2$ plasma	600	5.0	α	0.050 00	A	10
P81	$O_2$ plasma	770	100	X	X	X	X
P42	Ar plasma	450	250	X	X	X	X
P65	Ar plasma	560	500	X	X	X	X

TABLE I. Sample list. X not detected.

#### **III. CALCULATION METHODS**

In order to obtain the theoretical excitation energies of  $\equiv$  Si—Si  $\equiv$  bond, *ab initio* molecular-orbital calculation was carried out using the cluster (HO)<sub>3</sub>Si—Si(OH)<sub>3</sub>. All calculations were made at the Computer Center, University of Tokyo. The optimal configurations of the cluster, that is, the bond lengths and angles at which the molecules have the lowest total energy, were obtained using GAUSSIAN 80H (GAUSSIAN 80: HITAC version). The total energy of the excited states were obtained using a modified GAUSSIAN 76: IBM version.<sup>10</sup> The latter program is capable of performing calculations based on the SE-CI (single-electron-excitation-configuration-interaction) method. The highest-19 occupied and the lowest-13 unoccupied Hartree-Fock orbitals were taken into account in the SE-CI calculations.

Figure 2 shows the cluster model used for the calculations. Two tetrahedra, each consisting of one silicon atom and three oxygen atoms, are joined together at the oxygen vacancy site X. The two tetrahedra were twisted against each other by 60°. Each oxygen was terminated by a hydrogen placed in the X-G-O plane, at a distance of 1.0 Å from the respective oxygen. Here, G represents the center of gravity of the tetrahedra, and the distance between G and each oxygen was kept constant throughout the calculations at 1.6 Å, the normal distance between silicon and oxygen in silica glass. The angle Si-X-Si was also kept constant at 144°, the average Si—O—Si bonding angle in silica glass, <sup>11</sup> unless stated otherwise.

It was assumed that the two silicon atoms neighboring the oxygen vacancy can move fairly easily, holding symmetry with respect to X. Oxygen atoms, on the other hand, were assumed to be fixed and immobile in the glass network. With these assumptions, the calculations were carried out in the following manner. First, at a given X-G distance, the position of the silicon atom and the angle H-O-G were optimized to obtain the most stable configuration for that X-G distance. Second, the total energy of the configuration, namely the energy at the ground state, was obtained using the restricted Hartree-Fock method and STO-3G (Slater-type-orbital, three-Gaussian-function) basis set. Third, the total energy at the excited singlet state and excited triplet state for the same configuration was calculated using the modified Gaussian 76 program described above. The procedure was then repeated for various X-G distances within the range between 1.0 and 1.8 Å.

# **IV. RESULTS AND DISCUSSION**

### A. Two types of the 5.0-eV optical-absorption band

Figure 3 shows the optical-absorption spectra of some representative samples in the 3-6-eV range (about 210-410 nm). As reported in Ref. 5, the 5.0-eV absorption band  $(B_2 \text{ band})$  cannot be observed in the P3F sample, which is an oxygen surplus sample, nor in the DF8 sample which is a high OH sample. In the samples that show the 5.0-eV band (SFF and SF1), there seems to be a slight difference in the peak of the band. This difference is more clearly demonstrated when a Gaussian curve is fitted to the observed spectrum. As shown in Fig. 4, the peak and the half-width values of the SFF sample [Fig. 4(a)] and the SF1 sample [Fig. 4(b)] are clearly different. The 5.0-eV band of the SFF sample is referred to as the " $B_2 \alpha$  band" and that of the SF1 sample the " $B_2 \beta$  band" in this paper. Curve fitting was carried out on all the samples which have the 5.0-eV band, and the results are summarized in Table I under the heading " $B_2$  band." Here,  $\alpha$  and  $\beta$  refers to the  $B_2\alpha$  and  $B_2\beta$  bands, respectively. The 5.0-eV band of all samples examined except the SF1 and SFF- $\beta$  samples showed peak and half-width values similar to the SFF sample, that is the  $B_2 \alpha$  band.

Figures 5(a) and 5(b) show the photoluminescence emission and their excitation spectra of the SFF and the SF1 samples, respectively. In the SFF sample, which has the  $B_2\alpha$  band, a strong emission at 4.42 eV and a very weak emission at 2.74 eV are observed. This photo-



FIG. 2. Model structure for numerical calculation.



FIG. 3. Optical-absorption spectra of various samples. Absorption shown in optical density (OD/cm).





FIG. 4. Optical-absorption spectra: (a) SFF and (b) SF1. Solid line, experimental data; dotted line, fitted Gaussian curve using parameters given at the top of figure; broken line, result of subtracting Gaussian curve from experimental curve.

luminescence emission type is referred to as type A. In the SF1 sample, on the other hand, two relatively strong emissions are observed, one at 3.16 eV and the other at 4.24 eV. This photoluminescence emission type is referred to as type B. The A photoluminescence spectrum shown in Fig. 5(a) is the well-known luminescence band which can be excited by electrons, <sup>12</sup> by 7.6-eV light, <sup>13</sup> or by 5.0-eV light.<sup>3</sup> The B photoluminescence spectrum shown in Fig. 5(b) is the photoluminescence band observed in type-I and -II silica glasses.9 The results of photoluminescence measurements of all samples examined are summarized in Table I under the heading PL band. Here A indicates that the photoluminescence emission spectrum similar to the SFF sample shown in Fig. 5(a) was observed, whereas B indicates that the PL emission spectrum with two strong emissions, such as that of the SF1 sample shown in Fig. 5(b) was observed. As seen in this table, the  $B_2\alpha$  band is always accompanied by the A photoluminescence spectrum, and the  $B_2\beta$  by the *B* photoluminescence spectrum. No photoluminescence in this wavelength region could be detected

FIG. 5. Photoluminescence spectra; (a) SFF and (b) SF1. 1 and 4, emission spectrum under 5.06-eV excitation. 2, excitation spectrum of 4.42-eV PL band (SFF). 3, excitation spectrum of 2.74-eV PL band (SFF). 5, excitation spectrum of 3.16-eV PL band (SF1). 6, excitation spectrum of 4.24-eV PL band (SF1).

in samples with no 5.0-eV absorption band.

Heat treatment further demonstrates the difference between  $B_2\alpha$  and  $B_2\beta$  bands. Oxygen and helium treatments were made at 500 °C on rod samples. Figure 6(a) and 6(b) show the effects of oxygen treatment while Figs. 7(a) and 7(b) show the effect of helium treatment. As shown in Figs. 6(a) and 6(b), the oxygen treatment decreases the  $B_2\alpha$  band of the SFF sample by about 76%, and has almost no effect on the  $B_2\beta$  band of the SF1 sample. Similarly, the helium treatment decreases the  $B_2\alpha$ band of the SFF sample by about 40% and has almost no effect on the  $B_2\beta$  band of the SF1 sample.

On the basis of the difference in absorption peak wavelength, half-width, photoluminescence spectra, and the effects of heat treatment, the  $B_2\alpha$  band and the  $B_2\beta$  band are conclusively shown to be different absorption bands arising from different defects. The defects responsible are most likely nonparamagnetic defects since no ESR signal could be detected within our detection limit in these samples.

It was reported in Ref. 5 that pure silica glass can be



FIG. 6. Effect of oxygen treatment on optical-absorption spectrum: (a) SFF and (b) SF1.

classified into three types, namely the high-OH silica, oxygen-excessive silica (which contains precursors of peroxy radicals), and oxygen-deficient silica (which has the  $B_2$  band). The present results indicate that since there are two types of  $B_2$  band, silica which was considered oxygen deficient must be reclassified into two types, namely, those with the  $B_2\alpha$  band and those with the  $B_2\beta$  band. This makes the classification four types in all. It should be noted that the samples which have the  $B_2\beta$  band contain detectable amount of OH groups (270) ppm in the SF1 sample), and that there are samples that exhibit all the characteristics of what is referred to as high-OH silica that contains less OH group than samples with  $B_2\beta$  band (such as P81 which contain 100 ppm OH). Therefore, the determining factor in this classification is not the absolute OH content but rather some other aspect of the silica, most likely originating from the manufacturing process. Kohketsu et al.<sup>14</sup> recently reported that silica glass sintered under reducing atmosphere shows an absorption band and photoluminescence similar to the  $B_2\beta$ band, and proposed a twofold coordinated silicon ) as the model for this band.



FIG. 7. Effect of helium treatment on optical-absorption spectrum: (a) SFF and (b) SF1.

### B. Relation between the 7.6-eV and the $B_2\alpha$ bands

With the four types of pure silica in mind, optical absorptions in the vacuum-uv region (140-240 nm) were measured. The results are shown in Fig. 8 and summarized in Table I under the heading 7.6-eV band. This



FIG. 8. Vaccum-uv optical-absorption spectra of various samples.

band has been known for quite some time<sup>2</sup> and has been correlated to both the peroxy radicals<sup>15</sup> and  $\equiv$  Si—Si $\equiv$ bonds.<sup>1</sup> No peroxy radicals could be detected within our detection limit in the samples with the 7.6-eV band, confirming the report by Imai *et al.*<sup>7</sup> that this 7.6-eV band is not caused by peroxy radicals. As shown in Table I, the 7.6-eV band and the  $B_2\alpha$  band always appear together in the same sample. This is an indication that the same defect is responsible for both the 7.6-eV band and the  $B_2\alpha$  band.

Gee and Kastner<sup>13,16</sup> observed photoluminescence in unirradiated and neutron irradiated a-SiO<sub>2</sub> with an emission peak at 4.3 eV, and a excitation peak at 7.6 eV. Stathis and Kastner<sup>17</sup> further elaborated on this photoluminescence band by making a more detailed study using a  $F_2$  laser (7.9 eV) as the excitation source and reported emissions at 4.3, 2.7, and 1.9 eV. Meanwhile, Skuja et al.<sup>3</sup> reported an almost identical emission spectrum under 5.0-eV excitation. These reports show that the 4.2, 2.7, and 1.9-eV luminescence can be excited by both the 5.0- and the 7.6-eV bands. The 4.42 and 2.74 eV luminescence shown in Fig. 5(a) (PL type A in Table I) is, in all likelihood, the 4.3 and 2.7 eV luminescence mentioned in these reports. (The 1.9 eV luminescence is beyond our detection cutoff limit of 500 nm.) The samples which have this type of luminescence are the samples with the  $B_2\alpha$  and the 7.6-eV absorption bands.

It is, therefore, proposed here that the 7.6 eV and the  $B_2\alpha$  absorption bands are caused by the same defect on the grounds that (1) the two bands always appear together in the same samples and (2) excitation into these two bands result in an almost identical luminescence spectrum.

#### C. Cause of the 7.6-eV and the $B_2\alpha$ bands

What then causes these two bands? As reported in Ref. 5, drawing-induced E' centers were observed only in oxygen deficient samples. But a puzzle at that time was why some samples considered oxygen deficient did not exhibit drawing-induced E' centers. The answer is that only samples with the  $B_2\alpha$  band have such E' center; samples with the  $B_2\beta$  band do not. Table II shows a digest of the results of ESR measurements taken from Ref. 5 for various as-manufactured fiber samples drawn under the same conditions. The results show that only samples with the 7.6-eV and the  $B_2\alpha$  bands, the SFF and the S1F samples, have the drawing-induced E' centers, suggesting that these samples have precursors which can easily turn into E' centers by the mere act of fiber drawing. One of

the most widely accepted models of the E' center precursor is the oxygen vacancy,  $\equiv Si - Si \equiv .^{18}$  Therefore the ESR results show that samples which have the 7.6-eV and the  $B_2\alpha$  bands, and only these samples, have a large number of  $\equiv Si - Si \equiv$  oxygen vacancies.

Arnold<sup>4</sup> based his proposal that the  $B_2$  band was caused by a  $\equiv$ Si—Si $\equiv$  oxygen vacancy on observations of ion-implanted silica. The reasoning was that inert-gas ion implantation should result in the displacement of network oxygen atoms, producing such  $\equiv$ Si $\equiv$ Si $\equiv$ configurations. If true, and if the 7.6-eV and the  $B_2\alpha$ bands are actually caused by the same defect, then ion implantations should also induce the 7.6-eV absorption band. Figure 9 shows the effects of ion implantation on optical absorption in the vacuum ultraviolet range. As expected, the 7.6-eV band is induced by He<sup>+</sup> ion implantation in all samples examined. These experimental data support the view that the  $\equiv$ Si $\equiv$ Si $\equiv$  configuration is responsible for both the 7.6-eV and the  $B_2\alpha$  bands.

To investigate how two absorption bands can result from the same  $\equiv$  Si—Si $\equiv$  oxygen vacancy, *ab initio* molecular-orbital calculations were carried out. Figure 10 shows the total energy of the  $(HO)_3Si$ —Si $(HO)_3$  cluster as a function of the X-G distance in the ground state, in the excited singlet state, and in the excited triplet state. The figure shows the lowest energy for each of the excited states; many levels of singlet and triplet states exist. The energy of the ground state was then subtracted from the excited states to obtain the excitation energies for each state. The result of the subtraction is shown in Fig. 11. The figure shows that the X-G distance which best fits the experimental data is 1.65 Å, a distance which is very close to the Si-O distance in a normal SiO<sub>2</sub> network, 1.61 A. The calculations show that at this X-G distance, the excitation energy of the ground-to-singlet transition is about 7.6 eV, while the excitation energy of the groundto-triplet state is about 5.0 eV, values which are nearly identical to the experimental values of the absorption bands.

The most stable position of the two silicon atoms at this X-G distance of 1.65 Å is 1.38 Å from the vacancy site X. In other words, the silicons move towards the vacancy site, elongating the Si—O bond to 1.71 Å. This means that while the positions of the neighboring oxygens were assumed in the calculation to be largely unaffected by the existence of an oxygen vacancy, the silicon atoms are pulled together to resemble a Si—Si bond.

These calculation results are in good agreement with those of O'Reilly and Robertson.<sup>6</sup> Although their calculations were performed using an unstrained Si—Si

 TABLE II. Drawing-induced paramagnetic defects (Ref. 5). O, observed, X, not observed.

Sample	E' center	Peroxy radical	NBOHC	Characteristics
DF8	X	X	X	high OH
P3F	X	0	0	$O_2$ surplus
SF1	X	Х	X	$B_2\beta$ band
SFF	0	Х	X	$B_2 \alpha$ and 7.6-eV band
S1F	0	X	X	$B_2 \alpha$ and 7.6-eV band



FIG. 9. Comparison of vacuum-uv optical-absorption spectrum before and after  $He^+$  ion implantation: (a) SFF, (b) SF1, (c) P3F, and (d) DF8.



FIG. 10. Energy values of the oxygen vacancy in the various states.

"wrong" bond, as opposed to the Si—Si bond at an oxygen vacancy site used in the present paper, the two calculations are essentially the same in that they calculate the transition energy of a Si—Si bond. In both cases, the calculations resulted in a transition energy of 7.6 eV.

Figure 12 shows the excitation energies for various Si—X—Si bond angles. The angle was varied from 120° to 180°, the values reported for the Si—O—Si bond angles in SiO<sub>2</sub> glass.<sup>11</sup> As the figure shows, the bond angle has only a slight influence on the excitation energies. This means the oxygen-vacancy defect responsible for the 7.6-eV and the  $B_2\alpha$  band is essentially independent of the angle between the two neighboring tetrahedra.



FIG. 11. Excitation energies for ground-to-singlet (open circle) and ground-to-triplet (open triangle) transitions as a function of X-G distance.



FIG. 12. Excitation energies for ground-to-singlet (circle) and ground-to-triplet (triangle) transitions as function of Si-X-Si angle.

It is thus proposed that (1) the 7.6 eV band and the  $B_2\alpha$  band found in as-manufactured pure silica glass are both due to the same  $\equiv$  Si=Si $\equiv$  oxygen vacancy defect, (2) the 7.6-eV band is due to the ground-to-singlet transition, and (3) the  $B_2\alpha$  band is due to the ground-to-triplet transition. Although a direct ground-to-triplet transition is a forbidden transition, the absorption intensities of the  $B_2\alpha$  band is so small (three or more orders of magnitude weaker than the 7.6-eV band; see Table I) that we feel it is quite possible that such a forbidden transition does occur.

One way to determine the type of transition is to measure the lifetime of the luminescence. The decay time of the luminescence for the SFF sample is shown in Fig. 13. To measure the time it takes the chopper to completely shut off the light from the sample, the monochromator was set to 200 nm, a wavelength at which no luminescence is observed. This enabled us to measure the decay curve of the excitation light [Fig. 13, curve (b)], which was essentially determined by the shut-off time of the chopper. The effective decay time of the chopper (150  $\mu$ sec) was then compared to the observation made at 280 nm, which is the peak wavelength of the emission [Fig. 13, curve (a)]. The difference in the decay times seen between the two curves, about 100  $\mu$ sec, is the decay life-



FIG. 13. Photoluminescence decay time of SFF. Curve (a), decay measured at 280 nm. Curve (b), decay of excitation light (shutter speed of the chopper) shown for comparison.

time of the 4.42-eV photoluminescence, although it is only a very crude estimate.

Stathis and Kastner<sup>17</sup> measured the decay of the luminescence at 4.3 eV excited by 7.9-eV  $F_2$  laser light in Supersil W, and reported that after  $5 \times 10^{-8}$  sec, the luminescence peak disappears. This was taken as an indication that decay of the luminescence is comparable to, or shorter than, the laser pulse width of 10 nsec.

This decay time of less than 10 nsec for the 4.3 eV luminescence excited by the 7.6-eV band is considerably shorter than the decay time of 100  $\mu$ sec for the 4.42 eV luminescence excited by the  $B_2\alpha$  band. The very fast decay of the luminescence excited by the 7.6-eV band would indicate a singlet-to-singlet transition, while the relatively slow decay of the luminescence excited by the  $B_2\alpha$  band indicates that intersystem crossing (ISC) is involved. We believe this ISC takes place during the excitation, resulting in a ground (singlet)-to-triplet transition. Therefore, in the case of the 7.6-eV band, the absorption corresponds to a singlet-to-singlet  $(S_0 \rightarrow S_1)$  transition and the luminescence to a singlet-to-singlet  $(S_1 \rightarrow S_0)$  transition. In the case of the  $B_2\alpha$  band, the absorption corresponds to a singlet-to-triplet  $(S_0 \rightarrow T_1)$  transition and the luminescence probably to a triplet-to-singlet  $(T_1 \rightarrow S_0)$ transition.

Recent results of Imai *et al.*<sup>7</sup> show that irradiation with ArF excimer laser (6.4 eV) can decrease the 5.0-eV band without changing the 7.6-eV band. These results can be explained if a defect other than the oxygen vacancy is also responsible for optical absorption at 5.0 eV. This is possible since their result shows that while the 6.4-eV laser irradiation can reduce the 5.0-eV band, it cannot completely eliminate the band. In other words, the laser irradiation reduces the 5.0-eV band caused by the "other defect," but the 5.0-eV band due to the oxygen vacancy is unchanged. Consideration of such defect can also explain the fact that the intensities of the  $B_2\alpha$  band and those of the 7.6-eV band do not show a strict one-toone relationship (Table I).

#### V. SUMMARY

(1) There are two types of optical-absorption bands near 5.0 eV ( $B_2\alpha$  and  $B_2\beta$ ) in as-manufactured puresilica glass, each with unique peak wavelength, halfwidth, photoluminescence spectra, and reaction to heat treatments.

(2) The 7.6-eV band and the  $B_2\alpha$  band found in these glass are both due to the same  $\equiv$  Si $\equiv$ Si $\equiv$  oxygen vacancy defect.

(3) The 7.6-eV band is caused by a singlet-to-singlet transition at the oxygen vacancy.

(4) The  $B_2\alpha$  band is caused by a singlet-to-triplet transition at the oxygen vacancy.

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