

## Luminescence and defect formation in undensified and densified amorphous SiO<sub>2</sub>

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(Received 7 August 1989; revised manuscript received 23 October 1989)

Luminescence and optical absorption induced by an electron pulse and by a subsequent laser pulse have been studied in densified and undensified amorphous SiO<sub>2</sub> at 77 K. We find that the decay of the optical-absorption change induced by an electron pulse consists of two components: one which decays following a power law within 1 ms and the other which decays much more slowly. The fast component exhibits the spectrum of the self-trapped excitons, while the spectrum of the slow component includes the *E'* band. The *E'* band thus generated is found to decay with a time constant of about 10 h at 77 K and to be annihilated almost completely by warming to room temperature. We also find that optical excitation of the slow component by a 222-nm laser pulse generates a luminescence band having a peak at 2.1 eV, which is identical to the luminescence band due to the self-trapped excitons. It is likely that the defect pair and the self-trapped exciton have the same composition and both are generated as the result of the relaxation of excitons.

### I. INTRODUCTION

Band-to-band excitation of several insulators by ionizing radiation or by photons irradiation with energies above the band gap generates stable lattice defects in many insulating solids. The mechanism of such photolytic defect formation has been a topic of current interest. For alkali halides it is well established that the lowest state of a triplet self-trapped exciton, from which luminescence with a large Stokes shift is emitted, and a Frenkel pair comprising an *F* center and an *H* center at the ground states lie on the same adiabatic potential surface.<sup>1-3</sup> Thus defect formation in alkali halides is considered to be a channel of relaxation of an exciton and its yield is governed by the branching of the deexcitation of an exciton to the *F-H* pair and to the lowest state of the self-trapped exciton.

Even though both luminescence and defect formation are induced in amorphous solids including SiO<sub>2</sub>, the correlation between the luminescence and defect formation (structural change) has not been established. It has been suggested by Mott<sup>4,5</sup> and Street<sup>4,6</sup> that the luminescence with large Stokes shifts is due to the charged pairs formed by the negative-*U* interaction between dangling bonds existing prior to photoexcitation and that defect formation and structural change arise from nonradiative recombination of the self-trapped excitons. According to their suggestion the origin of defect formation is entirely different from that of the luminescence.

It has become increasingly clear that the luminescence in crystalline SiO<sub>2</sub> at 2.8 eV arises from self-trapped excitons. The experimental results that have led to this conclusion include those of the measurements of the excitation spectrum,<sup>7</sup> of optically detected magnetic resonance (ODMR),<sup>8</sup> and of transient volume change.<sup>9</sup> In amorphous SiO<sub>2</sub> (*a*-SiO<sub>2</sub>), a similar luminescence band is known to be induced around 2.1 eV by band-to-band excitation.<sup>10,11</sup> Tanimura *et al.*<sup>11</sup> have shown that the

optical-absorption bands from the initial state of the luminescence of *a*-SiO<sub>2</sub> are very similar to that of the self-trapped excitons in crystalline SiO<sub>2</sub>. They have concluded that the luminescence band around 2.1 eV in *a*-SiO<sub>2</sub> arises from the self-trapped excitons. Formation of stable defects in *a*-SiO<sub>2</sub> by ionizing radiation has been studied by several authors.<sup>12-14</sup> Recently Tsai *et al.*<sup>14</sup> have shown that two-photon absorption in *a*-SiO<sub>2</sub> gives rise to creation of stable *E'* centers (an oxygen vacancy with an electron).

It is known that *a*-SiO<sub>2</sub> is densified by applying hydrostatic pressure,<sup>15</sup> which results in a reduction of the spread of the distribution of the Si—O—Si bond angle between SiO<sub>4</sub> tetrahedrons but only a small effect on the SiO<sub>4</sub> tetrahedral structure.<sup>16,17</sup> Recently Devine *et al.*<sup>18</sup> have shown that densification of *a*-SiO<sub>2</sub> enhances the creation efficiency of the *E'* centers near room temperature and attributed the enhancement to the restriction of the O<sub>2</sub> diffusion in densified samples. The effects of densification on the luminescence of the self-trapped excitons are not yet known. Uses of densified samples may be of help to make clear the correlation between defect formation and luminescence.

The purpose of this paper is to present the experimental studies having been carried out aiming to verify the correlation between the luminescence and defect formation in *a*-SiO<sub>2</sub>. We present the results of the measurements of the luminescence and of the transient optical absorption induced in both undensified and densified *a*-SiO<sub>2</sub> by an electron pulse. We found that the decay of the optical absorption consists of two components, one corresponding to the self-trapped excitons and the other to defect pairs including the *E'* centers. Densification of the sample was found to enhance the yield of the defect pairs. We measured also the luminescence induced by excitation of the *E'* centers composing the pairs and showed that the luminescence due to self-trapped excitons is generated in compensation for the reduction of the *E'*

centers. This result suggests that the formation of a defect pair and of a self-trapped exciton are correlated.

## II. EXPERIMENTAL TECHNIQUE

Samples of  $\alpha$ -SiO<sub>2</sub> used in this investigation were rods of Suprasil W1 3 mm in diameter. One of the samples was compacted by 10% to a density of 2.433 g cm<sup>-3</sup> by applying a hydrostatic pressure. A specimen was held on the cold finger of a conventional cryostat cooled to 77 K and placed in an optical system having the capability of measuring transient optical-absorption change and luminescence induced by a 1-MeV-electron pulse. Electron pulses were generated with a Febetron-type accelerator (Hewlett Packard, Model 43710A). An electron pulse of the maximum fluence was capable of generating more than 10<sup>18</sup> cm<sup>-3</sup> electron-hole pairs. In order to excite further the defects generated by an electron pulse, the specimen was also bombarded repeatedly with a 222-nm (5.58-eV) laser pulse generated from a KrCl excimer laser (Lambda Physik, EMG-203MSC). The intensity of the laser pulse was less than 570 mJ/cm<sup>2</sup>. For measuring transient change in the optical absorption at a fixed wavelength, the light from a discharge lamp (Hamamatsu L2482) was guided through the sample to an optical detection system comprising a monochromator (Jobin Yvon H-20UV) and a photomultiplier (Electronic Measurements, Inc. EMI-6256B). The output signal was detected with an oscilloscope (Iwatsu TS-8123). The spectrum of the optical-absorption change at a given delay time was obtained using a multichannel transient spectrometer comprising a flash lamp (Hamamatsu L2358), of which the duration is 1  $\mu$ s, a monochromator (Jobin Yvon UFS-200), and a multichannel detector (Princeton RY-1024). Another multichannel detecting system comprising a monochromator (Jobin Yvon UFS-200) and a multichannel detector (Princeton D/SIDA-700) was used to obtain luminescence spectra emitted during a limited time interval determined by gate signals. All measurements were carried out at 77 K.

## III. EXPERIMENTAL RESULTS

In Fig. 1, we show the decay curves of (a) the luminescence probed at 470 nm and (b) the transient optical absorption probed at 240 nm, induced by an electron pulse at 77 K, for undensified  $\alpha$ -SiO<sub>2</sub> and those for densified  $\alpha$ -SiO<sub>2</sub> in Fig. 2. The decay of the luminescence follows a power law for a delay less than 1 ms and an exponential decay later, as reported already.<sup>10</sup> It is clear from the figure that the luminescence decay is little affected by densification. The decay of the transient optical absorption in both samples consists of two components: one which decays fast, following a power law within 1 ms and the other which decays much more slowly. We call the former the *F* component and the latter the *S* component. A comparison of the optical-absorption decays for two samples suggests that the *S* component is enhanced by densification. This presumption is substantiated later. The decay of the *S* component was found to be influenced by changing the intensity of the probe light, indicating that bleaching is induced. We measured the decay of the

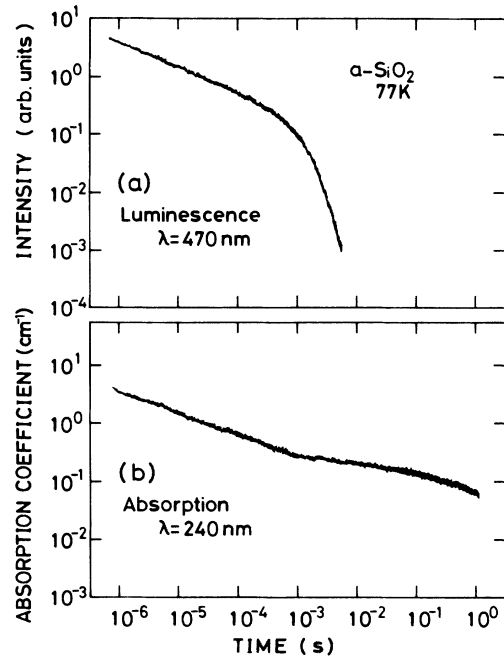


FIG. 1. (a) Decay curves of the luminescence monitored at 440 nm and (b) the optical-absorption change monitored at 240 nm, induced by irradiation with an electron pulse at 77 K, in undensified  $\alpha$ -SiO<sub>2</sub>.

*S* component at 77 K for the densified sample using a single-pulse light from a flash lamp as the probe, by which method the effect of optical bleaching is eliminated. The result is shown in Fig. 3. It is clear that the *S* component decays with a time constant of about 10 h. We found also that the optical absorption at 215 nm

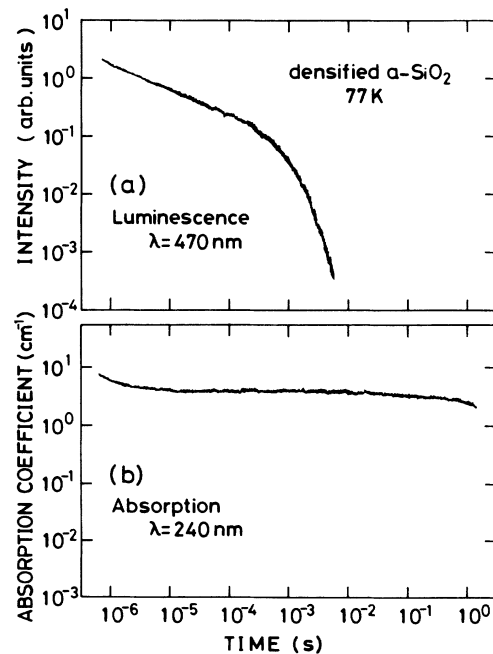


FIG. 2. (a) Decay curves of the luminescence monitored at 440 nm and (b) the optical-absorption change monitored at 240 nm, induced by irradiation with an electron pulse at 77 K, in 10% densified  $\alpha$ -SiO<sub>2</sub>.

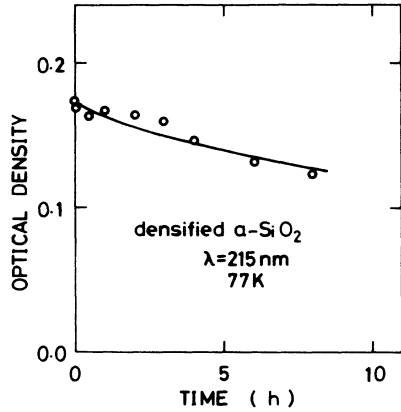


FIG. 3. Decay of the slow component of the optical-absorption change induced by irradiation with an electron pulse in densified  $a\text{-SiO}_2$  at 77 K.

disappears almost completely by raising the temperature to room temperature.

We show in Figs. 4(a) and 4(b), respectively, the spectra of the luminescence around 2.1 eV emitted from the undensified and densified  $a\text{-SiO}_2$  during a period from 500  $\mu\text{s}$  to 1.5 ms after an electron pulse. The luminescence

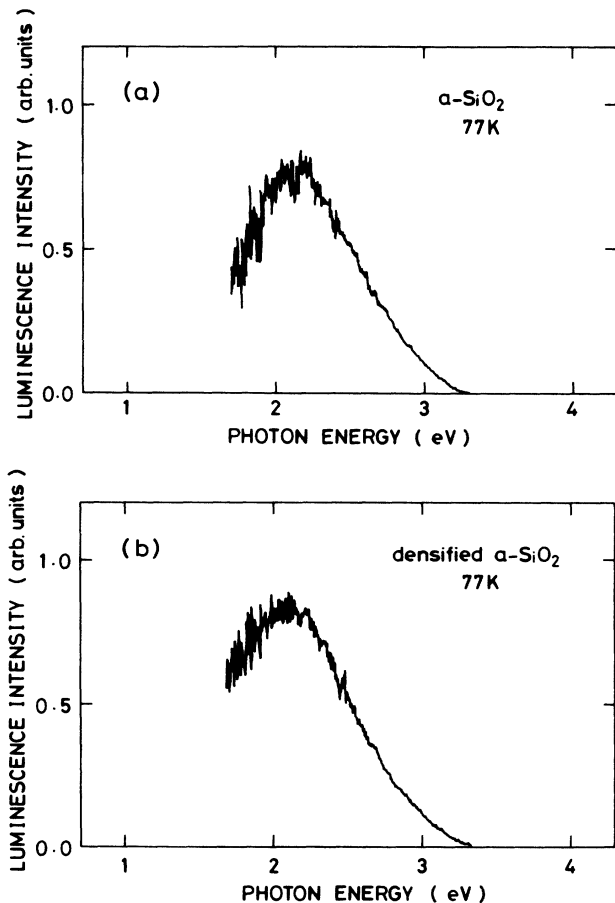


FIG. 4. Luminescence spectra of (a) undensified and (b) 10% densified  $a\text{-SiO}_2$  induced by irradiation with an electron pulse at 77 K.

spectrum of the densified sample is similar to that of the undensified sample. It exhibits also a blue shift with increasing delay time, as observed previously<sup>11</sup> for undensified samples. Thus it is clear that densification does not modify the nature of the luminescence emitted.

We show in Fig. 5 the optical-absorption spectrum measured 2  $\mu\text{s}$  and 500 ms after an electron pulse for the undensified sample [Fig. 5(a)] and that measured 4  $\mu\text{s}$  and 100 ms for the densified sample [Fig. 5(b)]. For the undensified sample the spectrum at 2  $\mu\text{s}$  has peaks at 5.4 and 4.2 eV. The transient optical-absorption spectra exhibiting similar two-peak structures in amorphous and crystalline  $\text{SiO}_2$  have been attributed to the self-trapped excitons.<sup>11,12,19</sup> On the other hand, the spectrum measured 100 ms after an electron pulse has a peak near 5.8 eV and a tail extending to 4.0 eV. The peak energy agrees with that of the  $E'$  band.<sup>12</sup> For the densified sample the spectrum at 4  $\mu\text{s}$  has a peak at 5.5 eV and the spectrum at 100 ms shows a peak at nearly 5.8 eV. The spectrum at 100 ms is similar to that at 500 ms for the

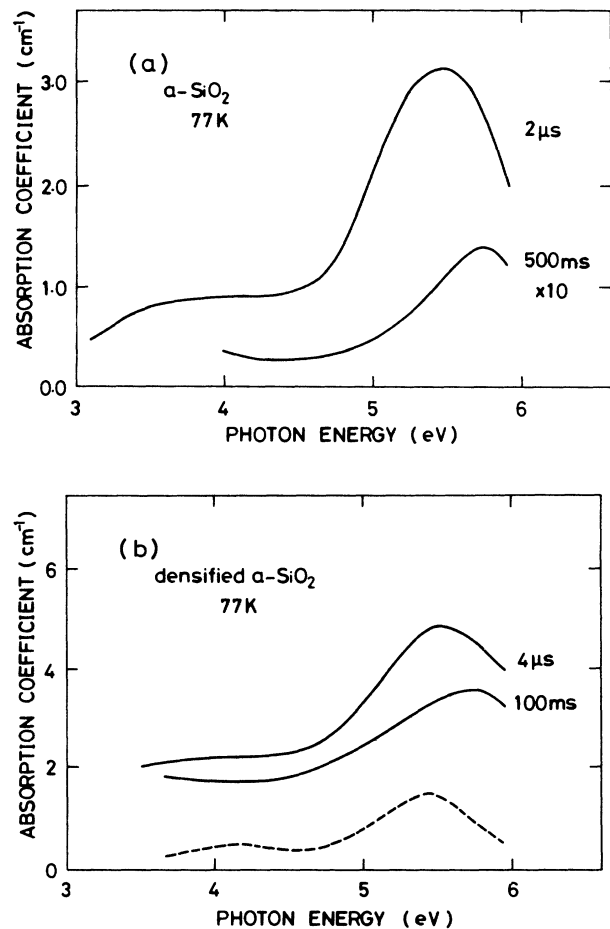


FIG. 5. The spectrum of the optical-absorption change of (a) undensified and (b) 10% densified  $a\text{-SiO}_2$  induced by irradiation with an electron pulse at 77 K. (a) includes the spectra 2  $\mu\text{s}$  and 500 ms after the electron pulse and (b) includes those 4  $\mu\text{s}$  and 100 ms after the electron pulse and the difference (dashed curve) between the spectra for 4  $\mu\text{s}$  and 100 ms.

undensified sample, with enhanced magnitude. This result confirms the description immediately after Figs. 1 and 2 that the  $S$  component is enhanced by densification. The spectrum at  $4 \mu\text{s}$  for the densified sample is seemingly different from that at  $2 \mu\text{s}$  for the undensified sample, which can be attributed to the overlap with the  $S$  component. The dotted curve shown in Fig. 5(b) is the result of the subtraction of the spectrum at 100 ms from that at  $4 \mu\text{s}$ . It is clear that the component that decays between 4 and 100  $\mu\text{s}$  shows two peaks at 5.4 and 4.2 eV, which are characteristics for the self-trapped excitons.

The results of the measurements of both the luminescence and the optical absorption indicate that irradiation with an electron pulse generates the self-trapped excitons in undensified and densified samples. The absolute value of the luminescence intensities from different samples cannot be compared directly, but the results of Figs. 1 and 2, of which the ordinates indicate the output of the detector by the same unit, show that the luminescence intensities for undensified and densified samples are nearly the same, only slightly reduced by densification. The subtraction of the optical-absorption coefficient for the  $S$  component from the  $F$  component leads to the same conclusion.

We have shown that irradiation of  $a\text{-SiO}_2$  at 77 K produces the transient  $E'$  centers ( $S$  component) besides the self-trapped excitons. Since the  $E'$  centers generated at room temperature are stable,<sup>13</sup> the observed transient nature is not the characteristics of the  $E'$  centers but of the complementary partners (CP's) which can annihilate the  $E'$  centers.<sup>13</sup> If the  $E'$  centers are generated as the result of deexcitation of excitons, the CP's are the oxygen interstitials ( $\text{O}_i^-$ ), while if the generation of the  $E'$  centers is related to native defects or impurities, the CP's are defect or impurity related. If the former is the case, as in alkali halides, photoexcitation of the self-trapped excitons will generate the  $E'$ -CP pairs and vice versa.<sup>20</sup>

In order to investigate whether the CP's are oxygen interstitials, we carried out the following experiment. In this experiment, a specimen is irradiated with an electron pulse at time  $t_e$  and subsequently with a 222-nm (5.58-eV) laser pulse at  $t_l$  and the consequent optical-absorption change at 215 nm (the  $E'$  band maximum) and luminescence at 440 nm were measured. The separation between  $t_e$  and  $t_l$  was long enough for the  $F$  component to be annihilated. Typical results obtained for the densified samples are shown in Fig. 6. It is clear that the laser pulse at  $t_l$  eliminates partially the  $E'$  band produced by an electron pulse and increases the luminescence intensity around 440 nm. The correlation between the reduction of the optical absorption at 215 nm and the increase of the luminescence intensity at 470 nm is shown in Fig. 7. In obtaining this correlation, the separation between  $t_e$  and  $t_l$  was changed with keeping the intensity of the laser pulse fixed. The figure includes the results obtained for the undensified and densified samples. The spectrum of the luminescence induced by a laser pulse after an electron pulse  $t_e$  at 77 K is shown by curve (b) in Fig. 8. In the figure the luminescence spectrum due to the self-trapped excitons is also shown [curve (a)]. The spectrum induced by the laser pulse subsequent to an electron pulse

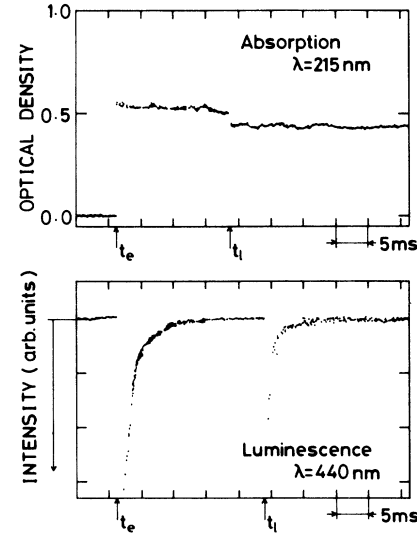


FIG. 6. Response of the optical absorption monitored at 215 nm (upper) and of the luminescence monitored at 470 nm (lower) of the densified  $a\text{-SiO}_2$  irradiation with an electron pulse at  $t_e$  and with a subsequent 222-nm laser pulse at  $t_l$ .

has two peaks at 2.1 and 1.95 eV. We found that the 1.95-eV band was induced when irradiated with a laser pulse alone. Subtracting the 1.95-eV band, it is clear that the 2.1-eV band, which is produced by an electron pulse, is also induced by a laser pulse if incident after irradiation by an electron pulse. Thus it is clear that the  $S$  component (due to the  $E'$ -CP pairs) is converted to the  $F$  component (due to the self-trapped excitons) by photoexcitation with the same conversion ratio, irrespective of densification.

The  $E'$  centers generated at room temperature have a stability much higher than that produced at liquid-

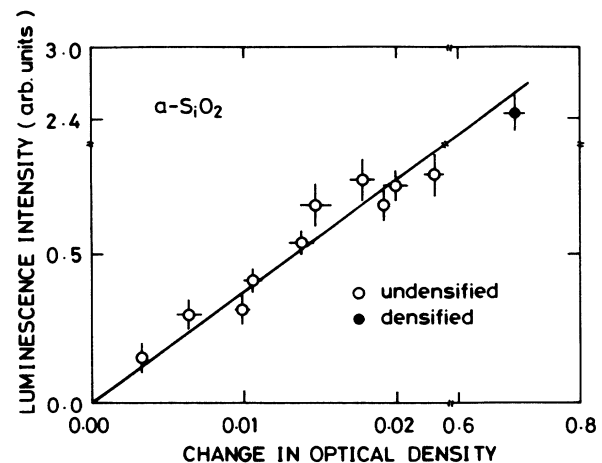


FIG. 7. The relation between the decrement of the optical density monitored at 215 nm and the increment of the luminescence intensity monitored at 470 nm, induced by irradiation with a 222-nm laser pulse of  $a\text{-SiO}_2$  preirradiation with an electron pulse.

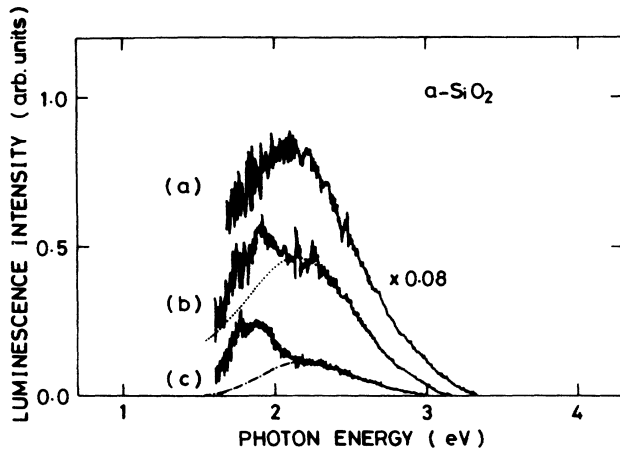


FIG. 8. Luminescence spectra induced (a) by irradiation with an electron pulse of a densified  $a\text{-SiO}_2$  sample at 77 K, (b) by irradiation with a 222-nm laser pulse at 77 K of the densified sample preirradiated with an electron pulse at 77 K, and (c) by irradiation with a 222-nm laser pulse at 77 K of the densified sample preirradiated at room temperature. For (b) the delay time between the laser pulse and the electron pulse is 100 ms. For (c) the specimen was kept for 2 h after irradiation at room temperature with an electron pulse and cooled to 77 K.

nitrogen temperature, indicating that the  $E'$ -CP distance is larger. The luminescence spectrum induced by a laser pulse for the sample preirradiated with an electron pulse at room temperature is also shown by curve (c) in Fig. 8. In this experiment, we took the  $E'$  band height of the sample before the laser pulse nearly the same as that of the sample used for obtaining curve (b). It is clear that the 2.1-eV band for the sample preirradiated at room temperature is much weaker than that of the sample preirradiated at 77 K. We found also that the laser-induced reduction of the  $S$  component is smaller than that for the sample preirradiated at 77 K. Thus the conversion from the  $E'$ -CP pairs to the self-trapped excitons is remarkable when the pairs are generated at low temperatures. This result suggests that the conversion ratio depends on the structure of the  $E'$ -CP pairs: those with shorter distance can be converted more efficiently. The result that the  $E'$ -CP pairs can be converted to the self-trapped excitons suggests strongly that the CP's are oxygen interstitials ( $\text{O}_i^-$ ).<sup>21</sup>

#### IV. DISCUSSION

We found that irradiation with an electron pulse of  $a\text{-SiO}_2$  generates optical-absorption changes of the fast ( $F$ ) and slow ( $S$ ) components. The decay characteristics as well as the spectrum for the  $F$  component were found not to be influenced by densification. The  $S$  component which decays slowly over 10 h is found to be enhanced by densification. We also found that excitation of the  $S$  component by 222-nm laser generates the  $F$  component.

The  $F$  component has been ascribed to the self-trapped excitons and its nonexponential decay to multiplicity of

the structure of the self-trapped excitons in  $a\text{-SiO}_2$ .<sup>10,11</sup> Thus the absence of the effects of densification shows that the structures of the self-trapped excitons are not influenced by densification. According to studies of Raman scattering<sup>16</sup> and NMR (Ref. 17) on the structural changes induced by densification, the mean value of the distribution of the Si—O bond length in a  $\text{SiO}_4$  tetrahedron is not changed by densification, although that of the Si—O—Si bridging bond angle between the  $\text{SiO}_4$  tetrahedra is largely reduced. Thus it is likely that the nature of the self-trapped excitons is governed by the structure of a  $\text{SiO}_4$  tetrahedron. A self-trapped exciton has the composition of the perfect lattice by its nature, and includes an  $\text{O}_2$  molecule according to the ODMR study by Hayes *et al.*<sup>8</sup> Furthermore, since it exhibits an optical-absorption band similar to the  $E'$  band, a self-trapped exciton is considered to be a interstitial-vacancy pair, of which the interstitial takes the form of an  $\text{O}_2$  molecule. The present results support an earlier suggestion that the interstitial-vacancy pair is confined to a  $\text{SiO}_4$  tetrahedron.

The  $S$  component, on the other hand, is more likely due to pairs comprising an  $E'$  center and an  $\text{O}_i^-$  ion located in different  $\text{SiO}_4$  tetrahedrons. Thus the formation yield may be governed by the Si—O—Si bridging-bond angle. Thus the results that the yield of the  $S$  component is enhanced by densification can be easily understood. Devine *et al.*<sup>18</sup> have observed the effects of densification in the creation of the  $E'$  centers at room temperature, where only pairs with larger separation are stable, and found that the yield of the stable  $E'$  centers in densified samples is larger than that in the undensified sample by 2 orders of magnitude. Only a 1-order-of-magnitude enhancement was observed at 77 K. The smaller magnitude of the enhancement for the production of the  $E'$  centers at liquid-nitrogen (77 K) temperature over that at room temperature may arise from the difference between the interstitial-vacancy distance. The enhancement is considered to be due to the restriction of oxygen diffusion, as suggested by Devine *et al.*<sup>18</sup>

The results of the present investigation indicate that irradiation with an electron pulse of  $a\text{-SiO}_2$  generates  $E'$ - $\text{O}_i^-$  pairs as well as self-trapped excitons, which are considered to be isomer to each other. In view of the dependence on the effects of the yields of each of the two products on densification, it is likely that the self-trapped exciton is confined to a  $\text{SiO}_4$  tetrahedron and the pairs comprise an interstitial and a vacancy occupied in different tetrahedrons. The results of the present investigation demonstrate the correlation between the luminescence and the defect formation and give some insight into the mechanisms of their generation. Since a defect pair and the initial state of the luminescence (self-trapped exciton) are isomer and appear to be located on the same adiabatic potential surface, it is very likely that the origin of their generation is the same. We have concluded previously that the luminescence in  $a\text{-SiO}_2$  is due to the self-trapped excitons<sup>11</sup> but not correlated to the negative- $U$  pairs of dangling bonds as suggested by Mott.<sup>5</sup> Present experimental results suggest strongly that defect formation is also related to the self-trapped excitons, as suggested by Street.<sup>6</sup> It is of interest to investigate more

closely the causes of luminescence and the self-trapped excitons in other amorphous materials.

#### ACKNOWLEDGMENTS

The authors are grateful to Dr. R. A. B. Devine, Center National d'Etudes des Télécommunications in Grenoble, France, for providing the densified and

undensified samples and for valuable discussions. They are grateful also to Katsumi Tanimura and Mladen Georgiev for valuable discussions. They also wish to thank H. Matsuoka for the collaboration in constructing experimental apparatus. The work was supported in part by a Grant-in-Aid for Specially Promoted Research from the Ministry of Education, Culture and Science of Japan.

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<sup>19</sup>C. Itoh, K. Tanimura, and N. Itoh, *J. Phys. C* **21**, 4693 (1988).  
<sup>20</sup>In the reaction from an  $E'$ -CP pair to a self-trapped exciton, if the excited state of an  $E'$  center is not bound, the electron ionized will recombine with a self-trapped hole, recently found by Griscom [see D. L. Griscom, *Phys. Rev. B* **40**, 4224 (1989)]. If it is the case, the conversion cannot give any information on the complementary partner. It is known, however, that the excited state of an  $E'$  center is bound [see G. H. Sigel, *J. Non-Cryst. Solids* **13**, 372 (1973)].  
<sup>21</sup>The complementary partner of an  $E'$  center is an  $O_i^-$  interstitial ( $O_i^-$ ) ion. Neither a peroxy radical comprising an interstitial oxygen ion ( $O_i^+$ ) nor a peroxy linkage comprising an interstitial atom ( $O_i^0$ ) can be the complementary partner of an  $E'$  center. The so-called self-trapped hole recently found by Griscom (see Ref. 20) can be the complementary partner of an  $E'$  center if it includes an interstitial oxygen ion ( $O_i^-$ ) but cannot be if it is simply a trapped hole on the perfect amorphous  $SiO_2$  network.