Structures and generation mechanisms of paramagnetic centers and absorption bands responsible for Ge-doped SiO_2 optical-fiber gratings

Makoto Fujimaki, Tomofumi Watanabe, Tetsuya Katoh, Toshiaki Kasahara, Nahoko Miyazaki, and Yoshimichi Ohki
Department of Electrical, Electronics, and Computer Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169, Japan

Hiroyuki Nishikawa
Department of Electrical Engineering, Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji, Tokyo 192-03, Japan
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Paramagnetic centers and absorption bands induced by ultraviolet photons in Ge-doped SiO_2 glass are investigated. Four kinds of samples with different Ge contents were exposed to ultraviolet photons from a KrF excimer laser (5.0 eV), a XeCl excimer lamp (4.0 eV), and a KrCl excimer lamp (5.6 eV). Irradiation with the KrF excimer laser induces two paramagnetic centers, named Ge(1) and Ge(2), in proportion with a decrease in the absorption at 5.1 eV and with an increase in absorption at 4.5 and 5.8 eV. The total density of the induced paramagnetic centers is linearly proportional to each induced change of the three absorption components and their proportionality constants are independent of the Ge content of the samples. The 4.0-eV photons from the XeCl excimer lamp induce only a Ge E' center, while the 5.6-eV photons from the KrCl excimer lamp induce a Ge(1) besides a Ge E' center. From these results, Ge(1) and Ge(2) are, respectively, assigned to the Ge electron center (GEC) and the positively charged Ge oxygen-deficient center $(\mathrm{GODC})^+$, which donated an electron to the GEC. The oscillator strength of the GODC for the absorption at 5.1 eV was found to be 0.1. From this, it is considered that the GODC that acts as the electron donor is the Ge lone pair center (GLPC). Thermally stimulated luminescence (TSL) is also examined in Ge-doped SiO_2 glass that was exposed to photons from the KrF excimer laser. The TSL spectrum is very similar to the photoluminescence spectrum that is known to be due to the GLPC's. It was found that the absorption, which was induced by the KrF excimer laser photons, decreases during the TSL measurement and that this decrement of the absorption is proportional to the TSL intensity. As mentioned above, the electrons that are to be trapped to generate the GEC's are released from the GLPC's during the photon irradiation. Then, in its reverse reaction, these electrons are thermally detrapped from the GEC's to regenerate the GLPC's, and the TSL is caused by an electronic de-excitation in such formed GLPC's. To conclude, the TSL phenomenon further validates the assumption that the GLPC is the electron donor to generate the GEC's. [S0163-1829(98)05407-1]

I. INTRODUCTION

Ultraviolet (uv) photosensitivity of Ge-doped SiO_2 glass is attracting much attention especially for Bragg gratings,[1] where the photorefractive index change caused by the uv-induced absorption[2–8] is utilized.[9,10] Two structural changes responsible for the absorption change have been reported. One is the generation of Ge E' center ($\equiv Ge^{\bullet}$, where symbols "$\equiv$" and "$^{\bullet}$" denote bonds with three separate oxygens and an unpaired electron, respectively) accompanied by the decrease of absorption near 5.1 eV due to Ge oxygen-deficient center (GODC) and the emergence of absorption near 6.4 eV. Although there are two kinds of GODC's, it has been reported that the GODC responsible for this structural change is the neutral oxygen vacancy (NOV; $\equiv Ge—T\equiv$, where T is either Ge or Si).[2] The other change is the generation of the Ge electron center (GEC), where an electron is trapped at a fourfold coordinated Ge.[4,5,11,12] The generation of Ge E' center is fairly well understood, but the generation of the GEC is not fully understood. Although it has been known that GEC's are induced by strong uv photons from a KrF or a XeCl excimer laser through a two-photon process,[4,5] the structure of the electron donor to generate the GEC is still debated among two types of GODC's (Refs. 5 and 12) and the bridging oxygen.[4] If this puzzle can be solved, the mechanism of the generation of the GEC should be clarified. As a result, it will become possible to increase the photosensitivity of Ge-doped SiO_2 glass, thus enabling fabrication of Bragg gratings with a much higher efficiency.

Besides the NOV, the Ge lone-pair center (GLPC; $-\dot{\underset{\bullet\bullet}{Ge}}-$ where "$\bullet\ \bullet$" denotes a lone electron pair), which also has a large absorption at 5.1 eV,[2,13,14] has been reported as the other type of the GODC's. Absorbing around 5.1-eV photons, the GLPC shows two photoluminescence (PL) bands at 4.3 and 3.1 eV. These two PL bands are due to the electronic transition to the ground state (S_0) from the lowest excited singlet state (S_1) and that from the lowest excited triplet state (T_1) at the GLPC, respectively.[14] It has been reported that the intensity of the 3.1-eV PL decreases with the occurrence of the uv-induced structural change.[7,15] Therefore, it is important to investigate the 3.1-eV PL in order to understand the mechanism of the structural change induced by uv-photon irradiation.

In the present research, we have measured the induced paramagnetic species and optical-absorption change in four different Ge-doped SiO_2 glasses upon irradiation of uv photons from three different photon sources. Furthermore, we report that thermally stimulated luminescence (TSL), which

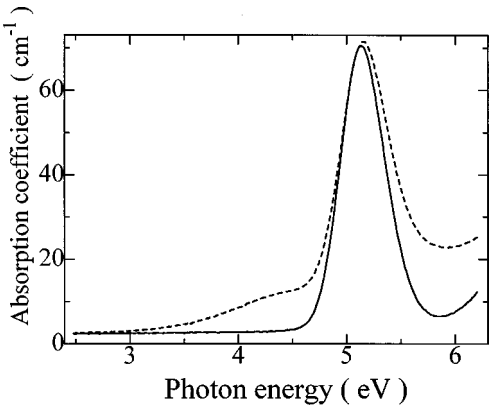

FIG. 1. Absorption spectra of sample *A* before (solid line) and after (dotted line) the irradiation of 20 shots of 5.0-eV photons from the KrF excimer laser.

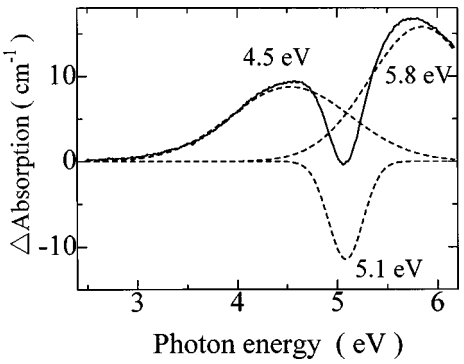

FIG. 2. Absorption spectrum induced by the irradiation of 20 shots of 5.0-eV photons from the KrF excimer laser in sample *A* (solid line). Dotted lines are three spectral components with Gaussian line shapes whose peak positions and FWHM's are shown in Table I.

is believed to be due to the same origin of the 3.1-eV PL, appears in the oxygen-deficient Ge-doped SiO_2 glass irradiated by strong 5.0-eV photons, and we examine the correlation between the TSL and the uv-induced paramagnetic centers. Based on these experimental results, we propose a model of the photochemical reaction occurring in the generation of the GEC's.

II. EXPERIMENT

Four Ge-doped SiO_2 glasses, *A*, *B*, *C*, and *D* with Ge contents of 1.0, 1.4, 6.9, and 9.2 mol %, respectively, were prepared by the vapor-phase axial deposition method. They were cut and polished into plates 0.3 mm thick. A KrF excimer laser (248 nm=5.0 eV, 80 mJ/cm^2 pulse, pulse duration of 20 ns), a XeCl excimer lamp [308 nm=4.0 eV, 10 mW/cm^2, full width at half maximum (FWHM) of 0.03 eV], and a KrCl excimer lamp (222 nm=5.6 eV, 7 mW/cm^2, FWHM of 0.05 eV) are used as irradiation photon sources. The absorption spectra from the visible to uv region were measured by a Shimadzu UV 160 spectrophotometer. The induced paramagnetic centers were detected by electron spin resonance (ESR) with a JEOL RE-2XE spectrometer at the *X*-band frequency, and their concentration was evaluated by comparing the double-integrated intensity of the first-derivative spectrum with that of the signal from a standard diphenylpicrylhydrazyl sample of a known weight (the accuracy of the standard is believed to be $\pm 20\%$).

For the PL and TSL measurements, the KrF excimer laser was used as the photon source. To measure the PL or TSL spectrum at a defined temperature, the PL or TSL dispersed by a monochromator (Jobin Yvon, HR320) was observed by a multichannel detector (Princeton, RY1024). To measure the change in the TSL intensity with temperature, the dispersed TSL was detected by a photomultiplier while heating the sample at a rate of 3–8 °C/min. The laser photon irradiation, the absorption measurement, and the ESR measurement were done at room temperature.

III. RESULTS

A. Photoinduced absorption and paramagnetic centers

The solid line in Fig. 1 shows the original absorption spectrum of sample *A*. The absorption at 5.1 eV, which really consists of two different absorption components due to the two types of GODC's, NOV, and GLPC,[2,13,14] is observed in the spectrum. This absorption is observed in all the samples. This means that all the samples are of the oxygen-deficient type. The dotted line in Fig. 1 is the absorption spectrum of sample *A* after a 20-shot irradiation of photons from the KrF excimer laser. The photoinduced absorption spectrum obtained by subtracting the solid line from the dotted line is shown in Fig. 2. The induced spectrum is divided into one negative and two positive Gaussian components with peak positions and FWHM's shown in Table I. Laser irradiation of the other samples also induced similar absorption changes.

The ESR spectrum induced in sample *A* by the 20-shot irradiation of photons from the KrF excimer laser is shown in Fig. 3. Two signals named Ge(1) and Ge(2) (Refs. 8, 11, and 12) are observed, although there still remain debatable points on the assignment of their structures. In Ref. 11, Ge(1) and Ge(2) are assigned to two kinds of GEC's. Namely, Ge(1) is assigned to the GEC of which all the next-nearest four neighbors are silicons (referred to as the NNS in the present paper), while Ge(2) is assigned to the GEC which has one Ge atom at the next-nearest neighbors (NNG). On the other hand, in Ref. 12, they are, respectively, assigned to the GEC and the hole center of the GODC, which donated an electron to GEC. The total density of the induced paramagnetic centers shown in Fig. 3, i.e., the sum of Ge(1) and Ge(2), is 7.1×10^{17} cm^{-3}. Similar ESR spectra were observed in all the other samples after similar irradiation by laser photons.

Figure 4 shows the correlation between the intensity of each Gaussian absorption component and the total induced density of the paramagnetic centers for the four samples upon the irradiation of photons up to 20 shots from the KrF excimer laser. A good proportionality with a sample-independent slope is seen between the intensity of each component and the density of the induced paramagnetic centers.

Figure 5 shows the ESR spectra induced in sample *A* after 50-h irradiation of photons from the two excimer lamps. The spectrum (a) is for 4.0-eV photons from the XeCl excimer lamp and (b) is for 5.6-eV photons from the KrCl excimer lamp. Spectra (a′) and (b′) represent the expansion of spec-

TABLE I. Peak positions and values of FWHM of the three absorption components.

Peak position (eV)	FWHM (eV)
4.5	1.3
5.1	0.4
5.8	1.2

tra (a) and (b) in the region surrounded by the dotted box, respectively. Spectrum (a) is recognized as the signal of Ge E' centers with a density of 5.7×10^{15} cm^{-3}, while spectrum (b) is divided into the signal of Ge E' centers ($\sim7.1\times10^{15}$ cm^{-3}) and that of Ge(1) ($\sim3.5\times10^{15}$ cm^{-3}). The signal of Ge(2) is not seen in the two spectra, even if the measurements were done under increased sensitivity. For all the other samples, a similar ESR spectrum was observed if the irradiation condition was similar. Contrary to the fact that ESR signals were thus induced, no change was observed in the absorption spectrum by the irradiation of photons from either of the two lamps in any of the four samples. This is because the number of paramagnetic centers induced by the irradiation, which is two orders of magnitude smaller than that induced by 20-shot irradiation of KrF excimer laser photons, is too small.

B. PL and TSL

Sample *B* was used for the PL and TSL measurements. To measure the TSL spectrum, the sample, which had been irradiated by the KrF excimer laser photons at room temperature and kept at room temperature for a few minutes, was put on a hot plate whose temperature was set to be 300 °C. The absorption similar to that shown in Fig. 2 and paramagnetic centers, Ge(1) and Ge(2), were observed after the irradiation. The solid line in Fig. 6 shows the TSL spectrum obtained. No TSL was observed without the laser photon irradiation. The dotted line in Fig. 6 shows the PL spectrum, which occurs with the irradiation of the KrF excimer laser photons.

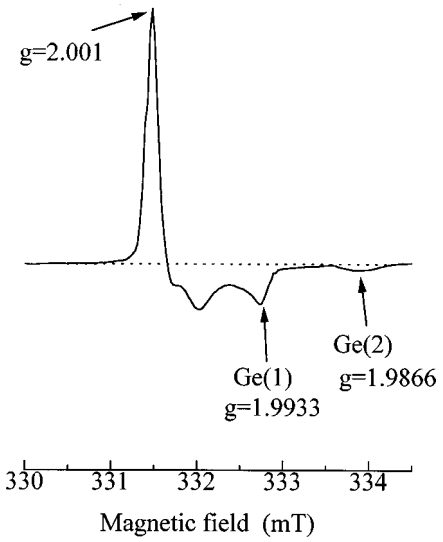

FIG. 3. ESR spectrum induced by the irradiation of 20 shots of 5.0-eV photons from the KrF excimer laser in sample *A*. Two ESR signals, named Ge(1) and Ge(2), are observed.

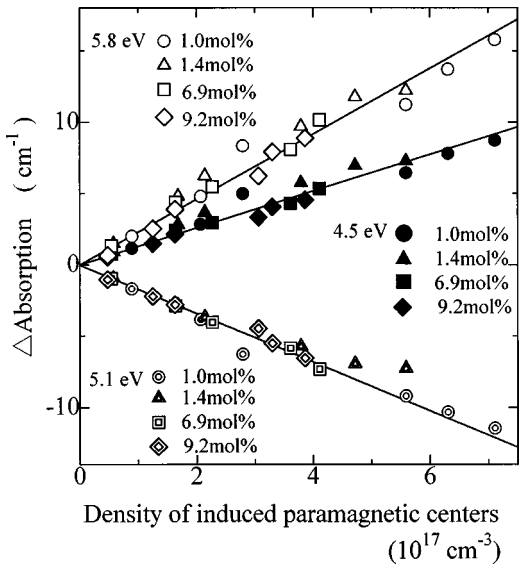

FIG. 4. Correlations between the intensities of the three absorption bands at 4.5, 5.1, and 5.8 eV and the total density of the paramagnetic centers in the four samples induced by the irradiation of photons of 5.0 eV up to 20 shots of the KrF excimer laser.

This 3.1-eV PL is due to the electronic transition from T_1 state to S_0 state at GLPC.[14] The TSL spectrum is very similar to the 3.1-eV PL spectrum. Figure 7 shows the change in the TSL intensity monitored at 3.1 eV while heating the sample after the irradiation of six laser pulses at room temperature. The TSL intensity reaches maximum around 220 °C and becomes almost zero around 300 °C. There is no difference among the TSL spectra at different temperatures

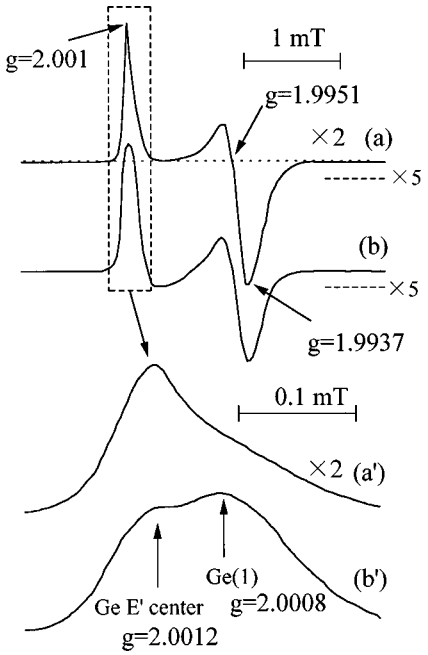

FIG. 5. ESR spectra induced in sample *A* by 4.0-eV photons from the XeCl excimer lamp (a) and by 5.6-eV photons from the KrCl excimer lamp (b). Broken lines are the signals observed under increased sensitivity of five magnifications. Spectra (a′) and (b′) represent the expansion of spectra (a) and (b) in the region surrounded by the dotted box, respectively.

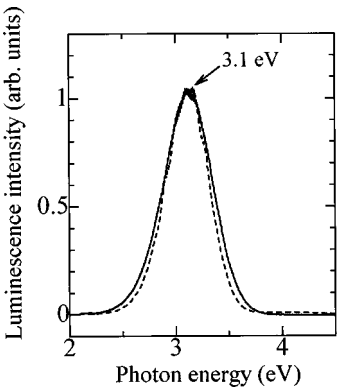

FIG. 6. TSL spectrum observed at 300 °C (solid line) and PL spectrum due to the GLPC (dotted line).

as shown in the inset, where normalized spectra at 100 °C (a), 200 °C (b), and 300 °C (c) are shown. The solid and the dotted lines in Fig. 8 show the spectra obtained by subtracting the absorption spectrum observed before the laser-photon irradiation from those observed before and after the TSL measurement shown in Fig. 7, respectively. From this figure, it is obvious that the photoinduced absorption seen before the TSL measurement almost disappears after the TSL measurement. Samples with different intensities of the photoinduced absorption were prepared by changing the number of irradiated pulses. With these samples, measurements similar to those shown in Figs. 7 and 8 were done, and correlation between the thermally decreased intensity of the absorption during the TSL measurement and the total TSL intensity calculated by integrating the observed TSL curve with the measurement time is investigated. Figure 9 shows the result, where the decreased absorption is divided into the three Gaussian components shown in Table I. A good linear proportionality is observed between the total TSL intensity and the decrement or the increment of each absorption component. Since the increment of the 5.1-eV absorption means the recovery of this absorption that had been decreased by the laser irradiation, the TSL and the regeneration of the defect responsible for the 5.1-eV absorption are induced by a thermal process that bleaches the photoinduced defects responsible for the absorptions at 4.5 and 5.8 eV.

A sample was loaded with H_2 at a pressure of 170 atm for two weeks at room temperature and then irradiated with six

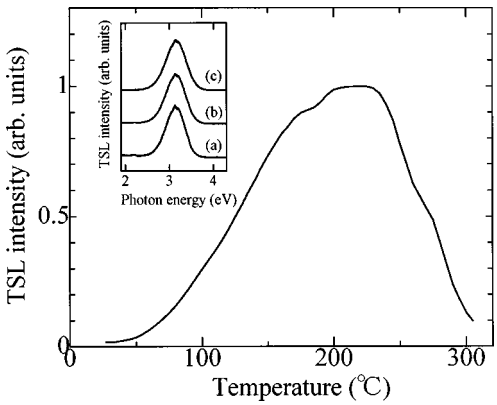

FIG. 7. Change in the TSL intensity, monitored at 3.1 eV, while heating the sample. The inset shows normalized TSL spectra observed at 100 °C (a), 200 °C (b), and 300 °C (c).

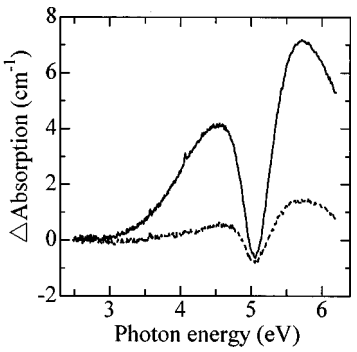

FIG. 8. Differential absorption spectra obtained by subtracting the absorption spectrum before the laser photon irradiation from those before (solid line) and after (dotted line) the TSL measurement shown in Fig. 7.

laser pulses. The ESR spectrum observed in this sample is shown in Fig. 10. Only Ge(1) (2.1×10^{17} cm^{-3}) is observed, and Ge(2) is not. Even though the laser irradiation condition is the same as that for the non-H_2-loaded sample, showing the TSL, the TSL was hardly observed in the H_2-loaded sample; about three orders of magnitude smaller than the non-H_2-loaded sample.

IV. DISCUSSION

A. Generation mechanism of GEC

First, the absorption bands, the ESR signals, and the structures that are being discussed are tabulated in Table II for convenience. By the irradiation of photons from the KrF excimer laser, the absorption change shown in Fig. 2 is induced, and the paramagnetic centers named Ge(1) and Ge(2) are generated. As there is a good proportionality between the intensity of the decreased absorption at 5.1 eV and the total density of the induced paramagnetic centers, it is natural to consider that some defect that has absorption at 5.1 eV strongly contributes to the generation of the paramagnetic centers. Since there is no absorption around 5 eV in oxygen-rich Ge-doped SiO_2 glass,[13,16,17] the defect should be either of the two types of GODC's. As mentioned above, there are two assumptions concerning the correspondence of the de-

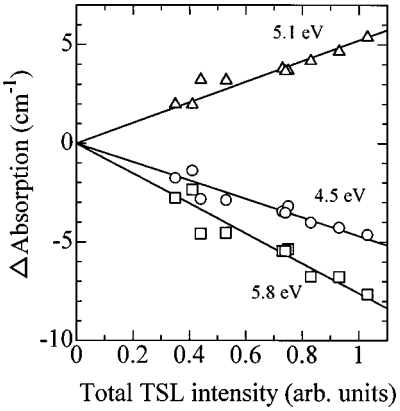

FIG. 9. Correlation between the total TSL intensity and the thermally breached intensity of the laser photon-induced absorption during the TSL measurement. The increment of the 5.1-eV absorption means the recovery of this absorption, which was decreased by the photon irradiation.

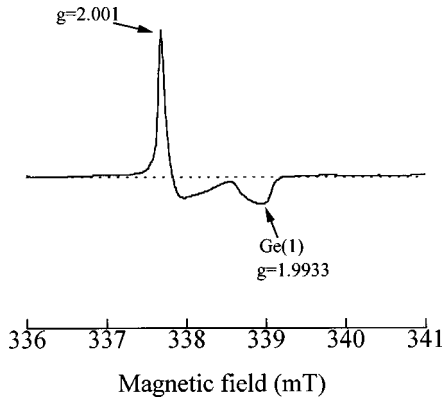

FIG. 10. ESR spectrum of the paramagnetic centers induced in the H_2-loaded sample by the laser irradiation.

fect structure of the GEC to the ESR signals Ge(1) and Ge(2).[11,12] Whichever assumption we may stand on, the GEC is an electron trapped center at a fourfold coordinated Ge. This indicates that the GODC should be the electron donor. Therefore, the following photochemical reaction is proposed:

$$\underset{\substack{\text{(fourfold coordinated Ge)}\\ \text{GEC}\\ \text{Ge(1) and Ge(2)}\\ \text{Ge(1)}}}{GeO_4} + \underset{\substack{\text{(positively charged GODC)}\\ \text{(in Ref. 11)}\\ \text{Ge(2)}\\ \text{(in Ref. 12)}}}{\text{GODC at 5.1 eV}} \longrightarrow (GeO_4)^{e^-} + (GODC)^+ . \quad (1)$$

The bottom two lines of the right term show the ESR signals that should be assigned. Of course, there may exist electrons that are released from the GODC but are not trapped at any fourfold coordinated Ge. Therefore, the following relation between the number of GEC's and that of electrons (e^-) are established:

$$\text{GEC}:e^- = y:1-y, \quad 0<y\leq 1. \quad (2)$$

The ratio y should be higher in the sample with a higher content of Ge, since fourfold coordinated Ge should exist more and the probability that the electrons are trapped should be higher in such a sample. The only one exception occurs when $y=1$. Namely, if all the electrons released from the GODC's are trapped, y is unity and becomes independent of the sample. In Fig. 4, it is clearly shown that the linear relationship between the decreased intensity of the 5.1-eV absorption and the total density of the induced paramagnetic centers, Ge(1) and Ge(2), does not depend on the sample. This means that the value of y is unity. Therefore, it is concluded that the number of induced GEC's is equal to the number of induced $(GODC)^+$'s in the present samples.

TABLE II. Absorptions, ESR signals, and structures being discussed. Note that the side-to-side correspondence is not indicated.

Absorption	ESR signal	Structure	
4.5 eV	Ge(1)	GEC	(1) NNS
			(2) NNG
5.8 eV	Ge(2)	$(GODC)^+$	(1) $(GLPC)^+$
			(2) $(NOV)^+$
5.1 eV		GODC	(1) GLPC
			(2) NOV

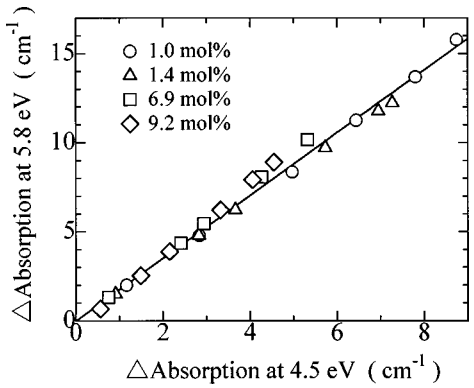

FIG. 11. Correlation between the 4.5- and the 5.8-eV absorption bands in the four samples.

The induced absorption bands at 4.5 and 5.8 eV are also proportional to the induced paramagnetic centers as shown in Fig. 4. Here, according to Ref. 11, let us first assume that Ge(1) and Ge(2) are the two kinds of GEC's, i.e., NNS and NNG, respectively. In this case, the abscissa in Fig. 4 represents the total density of GEC's. From the good proportionality shown in Fig. 4, these absorption bands and GEC's should correlate with each other. Figure 11 shows that the ratio between the induced absorption intensities at 4.5 and at 5.8 eV is constant throughout all four samples examined. Since the probability of the existence of Ge atoms at the next-nearest neighbors should be higher in the sample with a higher content of Ge, NNG should be induced more in such a sample. Therefore, if the two absorptions at 4.5 and 5.8 eV are, respectively, assigned to NNS and NNG as was assumed in Ref. 18, the intensity ratio of the induced absorption at 5.8 eV to that at 4.5 eV should be higher in the sample with a higher content of Ge. This contradicts the result shown in Fig. 11. Therefore, the above assignment that the two absorptions at 4.5 and 5.8 eV are, respectively, due to NNS and NNG is unlikely to be correct. The reverse assignment that NNS to the 5.8-eV absorption and NNG to the 4.5-eV absorption is also unlikely for the same reason. Next, since the difference in g value between the two ESR signals Ge(1) and Ge(2) means that their excited states are different, NNS and NNG should have different absorptions.[19] Therefore, it is difficult to consider that both NNS and NNG have either of the two absorption bands at 4.5 and 5.8 eV or both. To conclude, the only one remaining possibility is that either the NNS or NNG has both absorptions, provided that the two GEC's, NNS and NNG, have different ESR signals.

As discussed in relation to Eq. (1), it is highly probable that two paramagnetic centers, the GEC and $(GODC)^+$, are induced when the sample is exposed to the KrF excimer laser photons. Therefore, if the GEC is distinguishable by the number of neighboring Ge atoms, there must exist at least three kinds of ESR signals in the irradiated sample. Provided that Ge(1) and Ge(2) were, respectively, assigned to NNS and NNG, there would be no ESR signal to be assigned to the $(GODC)^+$. The model that the paramagnetic centers Ge(1) and Ge(2) should be, respectively, assigned to the GEC and $(GODC)^+$ (Ref. 12) seems to be more probable. In this model, the two GEC's (NNS and NNG) would have to be indistinguishable by ESR. Then, the above-mentioned assignment of the absorptions at 4.5 and 5.8 eV has to be modified. Since, as mentioned above, the induced density of

the GEC is considered to be equal to that of the $(GODC)^+$, the linear proportionality between the induced absorption intensities at 4.5 and 5.8 eV shown in Fig. 11 is explainable by assuming that one of the two absorptions is due to the GEC whose ESR signal is Ge(1) and the other is due to the $(GODC)^+$ whose ESR signal is Ge(2). Therefore, the two absorptions are considered to be, respectively, due to the GEC and $(GODC)^+$, even though which absorption is due to which defect cannot be determined. However, there still remains the possibility that both absorptions at 4.5 and 5.8 eV are due to either the GEC or the $(GODC)^+$. More analyses about the assignment of the absorptions at 4.5 and 5.8 eV will continue in a future paper.

So far it has been concluded that the induced paramagnetic centers consist of the GEC and $(GODC)^+$. Because the number of the induced GEC is considered to be equal to the number of the induced $(GODC)^+$, and also because the accurate separation of the two signals is very difficult, the density of $(GODC)^+$ is estimated to be half of the total density of the two signals. This $(GODC)^+$ density induced by the irradiation should be equal to the decreased density of the GODC. From the intensity and the FWHM of the decreased 5.1-eV absorption band due to the GODC and the decreased density of GODC, the oscillator strength (f) of the GODC for the 5.1-eV absorption is calculated by the following Smakula's formula:[20]

$$Nf = 0.87 \times 10^{17} n \alpha \omega / (n^2+2)^2, \tag{3}$$

where n is the refractive index of glass, α (cm^{-1}) the absorption coefficient at the peak of the absorption band, ω (eV) the FWHM, and N (cm^{-3}) the defect concentration. From Eq. (3), we obtained f of ~ 0.1. From the above contention, it is concluded that the electron donor to generate GEC is the GODC, which has absorption at 5.1 eV with the oscillator strength of 0.1. For the absorption at 5.1 eV, two types of GODC's, NOV and GLPC, have been assigned.[2] Although it is known that NOV is converted to the Ge E' center by the irradiation of uv photons and that electrons are released during this reaction,[2,21] the released electrons do not generate a GEC.[2] Furthermore, the oscillator strength of a NOV for the 5.1-eV (in Ref. 2, 5.06 eV) absorption has been reported to be 0.4,[2] which is far larger than the calculated value in the present study. On the contrary, the oscillator strength of the GLPC for the 5.1 eV (in Ref. 2, 5.16 eV) absorption is reported to be 0.1,[2] which agrees quite well with the present result. These two important facts that it is Ge E' center and not GEC which is induced from NOV and that the oscillator strength of NOV is 0.4 were also confirmed for all the present samples by similar experiments to those reported in Ref. 2 using a Hg/Xe lamp. Furthermore, it has been reported Ge E' centers are induced from NOV through a one-photon process of 5-eV photons, and that GEC's are induced through a two-photon process of 5-eV photons.[4,5] From these reports and our results, it is concluded that the electron donor to generate GEC is not a NOV but a GLPC. This in turn advances the aforementioned assignment of Ge(2) to the conclusion that Ge(2) should be assigned to $(GLPC)^+$.

As shown in Fig. 5, the irradiation of 4.0-eV photons from the XeCl excimer lamp induces only Ge E' centers, and the generation of GEC's is not observed. On the other hand, 5.6-eV photons from the KrCl excimer lamp induce the ESR signal of Ge(1), which should be assigned to a GEC as mentioned above, besides Ge E' centers. It has been also reported that the irradiation of photons from a Hg/Xe lamp induces only Ge E' centers[2] and that the irradiation of strong 4.0-eV photons from a XeCl excimer laser induces GEC's as well as Ge E' centers.[4] From these results, we can estimate the threshold photon energy to induce the GEC. A two-photon process easily occurs in the case of the XeCl excimer laser, while it never occurs in the case of the Hg/Xe or the two excimer lamps. Therefore, the above results, together with the above-mentioned fact that the generation of GEC is not observed in the case of a one-photon process of 5-eV photons, indicate that the threshold photon energy of the ionization of, or the electron release from, the GLPC to generate the GEC is higher than 5.0 eV and lower than 5.6 eV. The authors have revealed that the absorption beginning from a position slightly below 6 eV seen in Fig. 1 is caused by the electronic transition from the ground state of the GLPC to the conduction band.[17] It is reasonable to assume that the ionization of the GLPC is caused by exciting electrons into the edge of the conduction band and that the transfer of electrons to generate the GEC is done through the conduction band, at least for the case of the KrCl excimer lamp. To the authors' knowledge, the lowest reported photon energy to induce the GEC was 8.0 eV through a two-photon process of the photons from a XeCl excimer laser.[4] By the present study, the threshold energy is found to be much lower.

From Fig. 5, another important fact is deduced. While Ge(1) and Ge E' center were induced by the KrCl excimer lamp, Ge(2) was not. This might contradict the conclusion that Ge(1) ($=$GEC) and Ge(2) [$=(GLPC)^+$] are induced in the same number. The Ge E' centers are mainly generated from NOV's by releasing electrons.[2,21] The released electrons would neutralize the $(GLPC)^+$'s, which otherwise should have been observed in the same number as GEC's. Furthermore, these facts strongly support the model that Ge(2) is not the NNG but the $(GLPC)^+$. If Ge(1) and Ge(2) should, respectively, correspond to the NNS and NNG, the above-mentioned results would never be observed.

B. TSL

It is obvious that the TSL is due to a photoinduced structural change, since it is not observed without the laser irradiation. Furthermore, since the two spectral shapes shown in Fig. 6 are almost the same and since no other PL bands have been reported around 3.1 eV, it can be concluded that the TSL is due to the electronic transition from T_1 state to S_0 state at the GLPC as in the case of the 3.1-eV PL. Then, we can assume that electrons first trapped at a certain defect are thermally detrapped and move to T_1 state of the GLPC. Therefore, the total TSL intensity should be proportional to the number of electrons thermally supplied to the GLPC's. Since, as shown in Fig. 9, the total TSL intensity is proportional to the thermally bleached intensity of each photoinduced absorption component shown in Fig. 2, it is considered that the TSL is induced by the thermally bleaching process of the GEC's, namely, the reverse reaction of Eq. (1).

The present results on TSL give strong validation to the model that the electron donor to generate the GEC's is the GLPC. As mentioned above, the reverse reaction of Eq. (1) causes the TSL. That is to say, the electrons thermally detrapped from the GEC's are supplied to positively charged electron donors and that the subsequent electronic transition in the neutral electron donors shows the TSL. On the other hand, the TSL should be due to the electronic transition at the GLPC as mentioned above. Therefore, if we suppose that the electron donor is the bridging oxygen,[4] the TSL phenomenon cannot be explained. The only possibility that can explain TSL is that the electron donor must be the GLPC. The electrons thermally detrapped from the GEC's are captured by the $(\mathrm{GLPC})^+$'s, and the neutralized GLPC's are then deexcited by moving down the electrons to S_0 state via T_1 state, through which the TSL occurs. The fact that the 5.1-eV absorption that is considered to be due to the GLPC (Ref. 2) increases proportionally with the total TSL intensity strongly indicates that the regeneration of the GLPC causes the TSL.

As shown in Fig. 10, Ge(2) is not induced in the H_2-loaded sample by the laser irradiation. Since both Ge(1) and Ge(2) are observed in the non-H_2-loaded sample, Ge(2) should be due to a defect whose generation is suppressed by hydrogen or a defect that is generated but soon becomes a different structure by reacting with hydrogen. This result also supports that Ge(1) and Ge(2) are assigned to the GEC and $(\mathrm{GLPC})^+$, respectively. The disappearance of Ge(2) in the H_2-loaded sample indicates that the $(\mathrm{GLPC})^+$ is terminated by hydrogen. Therefore, the TSL should not be observed in this sample. This is really the case in the present research.

V. CONCLUSIONS

The generation mechanism of the GEC in Ge-doped SiO_2 glass has been investigated through absorption and ESR measurements with three different photon sources. It was found that clear proportionalities, which do not depend on the Ge content in the sample, exist between the generation of paramagnetic centers [Ge(1) and Ge(2)], the decrease in the 5.1-eV absorption, the increase in the 4.5-eV absorption, and the increase in the 5.8-eV absorption. It was also found that the 5.6-eV photons from the KrCl excimer lamp induce the GEC. Furthermore, TSL with quite a similar spectrum as that of the PL due to the GLPC's appears in the sample that was irradiated by the KrF excimer laser. From these experimental results, the following facts are clarified. (1) By the laser irradiation, electrons are released from the GLPC's and the GEC's are generated. The reverse reaction can be induced thermally, where electrons are detrapped from the GEC's and are supplied to the $(\mathrm{GLPC})^+$'s. The electrons are further deactivated to S_0 state of the GLPC via T_1 state, and this process causes the TSL. (2) The ESR signals Ge(1) and Ge(2) are assigned to the GEC and a hole trapped at the GLPC, respectively. (3) The threshold photon energy to generate the GEC is between 5.0 and 5.6 eV.

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