Structural changes induced by KrF excimer laser photons in H_2-loaded Ge-doped SiO_2 glass

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Photochemical reactions related to the Ge lone-pair center (GLPC) that are induced by KrF excimer laser photons in H_2-loaded Ge-doped SiO_2 glass have been investigated. Without the H_2 loading, the Ge electron center (GEC) and the positively charged GLPC were induced by the laser irradiation. In the H_2-loaded sample, the GEC, the Ge E' center, and the germyl radical (GR) were induced by the irradiation, while the positively charged GLPC was not observed after the irradiation. If the H_2-loaded sample was thermally annealed after the photon irradiation, the concentration of the photo-induced GEC decreased monotonically with an increase in the annealing temperature. On the other hand, the concentration of the GR increased up to the annealing temperature of 160 °C, and it decreased at higher temperatures. Without the pre-irradiation, the induction of the GR was not observed even in the H_2-loaded sample. From these results, it is concluded that the positively charged GLPC is terminated with a hydrogen atom in the H_2-loaded sample and then becomes the GR by trapping an electron thermally released from the GEC. [S0163-1829(99)05631-3]

I. INTRODUCTION

Recently, optical fiber gratings, where periodical refractive-index change is fabricated by ultraviolet (uv) photon irradiation in the core of an optical fiber made of Ge-doped SiO_2 glass,[1] have been expanding their applications to various devices, such as optical filters,[2–6] sensors,[7–10] fiber lasers,[2–4,11] dispersion eliminators,[12,13] and so on. Many trials, e.g., development of special fibers with increased Ge concentration and/or codopants, have been made to increase the refractive index change.[14] However, it is often more desirable to fabricate fiber gratings in standard optical fibers for compatibility with existing systems. Low-temperature H_2 loading is one of the most effective sensitization techniques to increase photo-induced refractive index changes in standard optical fibers. Molecular-hydrogen-loaded Ge-doped SiO_2 optical fibers exhibit markedly increased photo-induced refractive index changes.[15–17] Therefore, it is very important to understand the photo-induced structural changes in H_2-loaded Ge-doped SiO_2 glass for the fabrication of high performance optical fiber gratings.

It has been known that there are two types of Ge oxygen-deficient centers in Ge-doped SiO_2 glass.[18] One is the neutral oxygen vacancy (NOV; $\equiv Ge-T\equiv$, $\equiv$ represents bonds with three separate oxygens and T is either Ge or Si) and the other is the Ge lone-pair center (GLPC; $—\dot{G}\dot{e}—$, ''••'' denotes lone-pair electrons).[18] With uv photon irradiation, the NOV becomes the Ge E' center ($\equiv Ge\bullet + {}^{+}T\equiv$, • denotes an unpaired electron):[18]

$$\mathrm{NOV}\rightarrow \mathrm{Ge}\ \ E'\ \text{center}+e^{-}. \tag{1}$$

By irradiation with uv photons of high-energy density, such as KrF excimer laser photons, the GLPC is ionized and becomes the positively charged GLPC [$(GLPC)^{+}$].[19] The electron released from the GLPC by the irradiation is trapped at fourfold coordinated Ge (abbreviated as GeO_4) and forms the Ge electron center (GEC, GeO_4^{-}):[19]

$$\mathrm{GLPC}+\mathrm{GeO_4}\rightarrow(\mathrm{GLPC})^{+}+\mathrm{GEC}. \tag{2}$$

These uv-induced structural changes are accompanied by the induction of absorption changes in the visible-to-uv region, which in turn causes the refractive index changes through the Kramers-Kronig relation.[20,21]

It has been reported that the Ge E' center and the GEC are also induced by photon irradiation in H_2-loaded Ge-doped SiO_2 glass.[19,22] Not only the NOV but also the GLPC becomes the Ge E' center with a high dose irradiation of uv photons in H_2-loaded Ge-doped SiO_2 glass.[22] In addition to these paramagnetic centers, the germyl radical (GR), which has the structure that H is bonded to the GLPC ($=\dot{G}eH$),[23,24] is induced by uv photon irradiation. These phenomena strongly indicate that the GLPC plays an important role in the photo-induced structural changes. In the present paper, in order to understand structural changes related to the GLPC in H_2-loaded Ge-doped SiO_2 glass, we have investigated paramagnetic centers and absorption bands induced by KrF excimer laser photons and the changes in their behavior by thermal annealing.

II. EXPERIMENTAL DETAILS

A $99SiO_2$:$1GeO_2$ glass rod, prepared by the vapor-phase axial deposition method, was cut into disks having 0.3-mm thickness and polished for optical measurements. Molecular hydrogen loading was performed under a H_2 pressure of 170 atm for two weeks at room temperature. Hereafter, the H_2-loaded and non-H_2-loaded samples are called samples *H* and *N*, respectively. A KrF excimer laser (Lambda Physik, LPX 105i, 248 nm=5.0 eV), with an energy density of 70 mJ/cm^2 per pulse, was used as a photon source. The absorption spectra from the visible-to-uv region were measured by

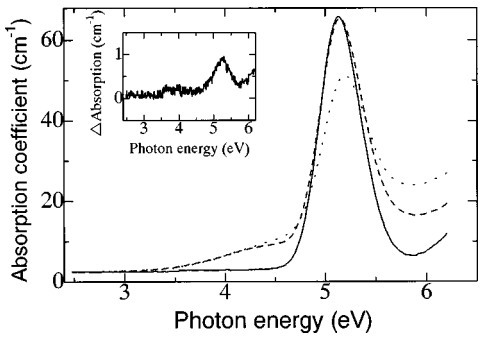

FIG. 1. Absorption spectra before and after the KrF excimer laser photon irradiation. The solid curve denotes the absorption spectrum of the as-received sample *N* before the laser photon irradiation, which overlaps with the spectrum of sample *H* before the irradiation in this scale. The inset shows the difference obtained by subtracting the absorption spectrum of sample *N* from that of sample *H*. The broken and the dotted curves denote the spectra of samples *N* and *H* after the 30-pulse irradiation of the laser photons, respectively.

a Shimadzu UV-3100PC spectrophotometer with wavelength resolution of ~2 nm. The induced paramagnetic centers were detected by electron spin resonance (ESR) with a JEOL JES-PX 1060 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 ±20%). All the photon irradiation and the measurements were done at room temperature.

III. RESULTS

A. Photo-induced structural changes

The solid curve in Fig. 1 indicates the absorption spectrum of the as-received sample, i.e., sample *N* before photon irradiation. Absorption is observed at 5.1 eV, which is known to be composed of the two absorption bands due to the NOV (5.06 eV) and the GLPC (5.16 eV).[18] The inset shows the difference obtained by subtracting the absorption spectrum of sample *N* from that of sample *H*. A slight increase in the 5.1 eV absorption is observed with the H_2 loading. The broken and the dotted curves in Fig. 1, respectively, show the absorption spectra of samples *N* and *H* after 30 laser pulses were irradiated. By subtracting the solid curve from the broken and dotted curves in Fig. 1, the photo-induced absorption changes in samples *N* and *H* were obtained as shown by the solid curves in Figs. 2(a) and 2(b), respectively. It has been reported that photo-induced absorption bands in a Ge-doped SiO_2 glass in the visible-to-uv region are well fitted with Gaussian shapes, and the parameters of the Gaussian components have been well identified.[19,25–29] Therefore, we applied Gaussian decomposition to the obtained spectra. The broken curves in Fig. 2 denote the spectral components obtained by the least-squares fitting with Gaussian shapes. The synthesized line shapes, indicated by the dotted curves, reproduce well the observed absorption spectra. The intensities and the values of the full width at half maximum (FWHM) of these absorption components are shown in Table I. The instrumental errors for the values of

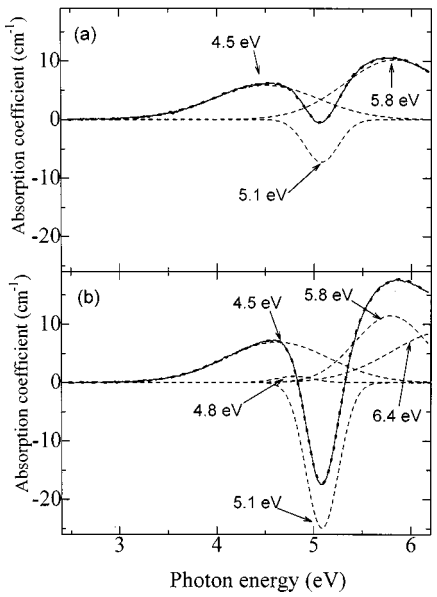

FIG. 2. Solid curves indicate the absorption changes in samples *N* (a) and *H* (b) induced after 30 laser pulses were irradiated. The broken and the dotted curves denote the spectral components obtained by the least-squares fitting with Gaussian shapes and the synthesized line shapes, respectively. Note that the solid and the dotted curves agree quite well with each other.

the peak positions and the FWHM's are within 0.05 eV, and those of the intensities are within 0.2 cm^{-1}. The errors shown in the table are due to the ambiguity of the calculation. As shown in Fig. 2, a decrease in the 5.1-eV absorption and the induction of two absorption bands at 4.5 and 5.8 eV are observed in samples *N* and *H*. In addition to these absorption changes, an absorption band at 6.4 eV, which is considered to be due to the Ge E' center,[25] is observed in sample *H*. A weak absorption band at 4.8 eV, which has not been assigned yet, is also induced in sample *H*.

Figures 3(a) and 3(b) show the ESR spectra induced by the photon irradiation of 30 laser pulses in samples *N* and *H*, respectively. Two signals, named Ge(1) and Ge(2) that are, respectively, assigned to the GEC and the $(GLPC)^+$,[19] are observed in sample *N*. The sum of the concentrations of the GEC and the $(GLPC)^+$ is calculated to be 4.8×10^{17} cm^{-3}. The authors have confirmed that the concentration of GEC and that of $(GLPC)^+$ induced in Ge-doped SiO_2 glass are

TABLE I. Peak positions, intensities, and values of FWHM of the absorption components induced in samples *N* and *H*.

Sample	Peak position (eV)	Intensity (cm^{-1})	FWHM (eV)
	4.5	5.9	1.3
N	5.1	−7.2	0.4
	5.8	10.2	1.2
	4.5	6.9±0.5	1.3±0.1
	4.8±0.1	1.1±0.5	0.4±0.1
H	5.1	−24.8±1.0	0.4
	5.8	11.5±2.0	0.9±0.2 (1.2±0.1)[a]
	6.4±0.15	9.0±3.0	1.2±0.2

[a]The calculated value based on the Gaussian fitting to the result shown in Fig. 5.

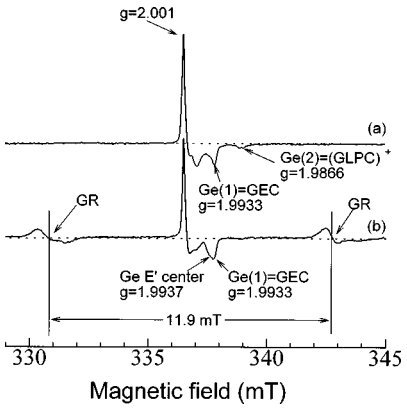

FIG. 3. ESR spectra of samples *N* (a) and *H* (b) induced by the irradiation of 30 pulses of laser photons.

equal when it is irradiated up to a few tens of pulses with the present KrF excimer laser.[19] Therefore, the induced concentration is $2.4\times10^{17}\,\mathrm{cm}^{-3}$ for both GEC, and $(\mathrm{GLPC})^+$. In sample *H*, the ESR signals due to the GEC, Ge E' center, and GR are seen. The concentration of the GEC induced in sample *H* is $2.6\times10^{17}\,\mathrm{cm}^{-3}$, which is quite similar to that induced in sample *N*. The concentrations of the Ge E' center and the GR are 0.6×10^{17} and $2.6\times10^{17}\,\mathrm{cm}^{-3}$, respectively. The fact that the Ge(2) signal is not seen in Fig. 3(b) means that the $(\mathrm{GLPC})^+$ does not exist in sample *H* even after the photon irradiation.

B. Thermal effects on the photo-induced structural changes

The following thermal annealing procedure was applied to sample *H* after 30 pulses of laser photons had been irradiated at room temperature. First, the sample was annealed at 160 °C for 5 min, and the absorption and ESR measurements were done at room temperature. This sequence of annealing and measurements was repeated with a step of 20 °C until the annealing temperature reached 300 °C. Figure 4 shows the ESR results. The circle and square show the concentrations of GEC and GR, respectively. The photo-induced Ge E' center in sample *H* scarcely changed its concentration with the thermal annealing. As seen in this figure, the concentration of GEC decreases monotonically with an increase in the annealing temperature. On the other hand, the concentration of GR increases with the thermal annealing at 160 °C, and then it decreases monotonically. The thermal annealing was also

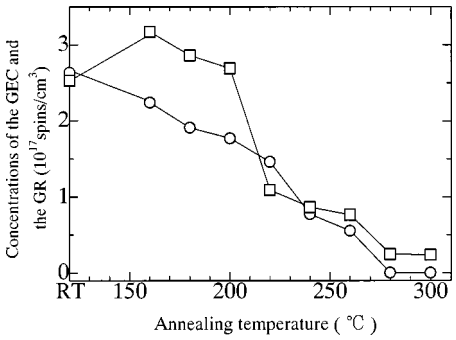

FIG. 4. Changes in the concentrations of the GEC (circles) and the GR (squares) in sample *H* with the thermal annealing following the 30-pulse irradiation of laser photons.

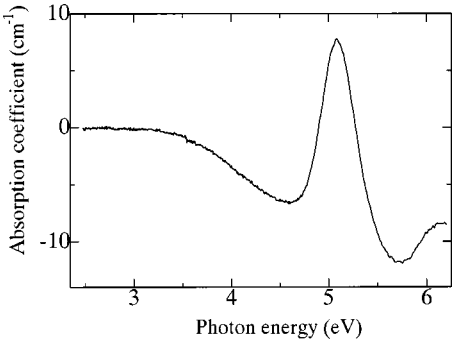

FIG. 5. Differential absorption spectrum of the photon-irradiated sample *H* obtained by subtracting the spectrum before the thermal annealing from the one after the total sequences of thermal annealing.

applied to sample *H* which had not been irradiated with the laser photons. In this case, induction of the GR was not observed. This result indicates that the precursor of thermally induced GR is a defect induced by the irradiation.

Figure 5 shows the differential absorption spectrum of the photon-irradiated sample *H* before and after the total sequences of thermal annealing. The 5.1-eV absorption, which was bleached by the photon irradiation, shows a recovery by the thermal annealing. Decrease in the 4.5 and 5.8 eV bands, which were induced by the photon irradiation, is also observed.

Figure 6 shows the correlation between the decrease in the concentration of GEC ($-\Delta N_{\mathrm{GEC}}$) and the increase in the intensity of 5.1-eV absorption ($\Delta\alpha_{5.1}$), measured after each sequence of thermal annealing. The open and closed circles are for samples *N* and *H*, respectively, and the numbers next to them denote the annealing temperature. For sample *N*, $\Delta\alpha_{5.1}$ is linearly proportional to $-\Delta N_{\mathrm{GEC}}$, while such a proportionality is not observed for sample *H*.

IV. DISCUSSION

A. Photo-induced structural changes

The absorption changes shown in Fig. 2(a), which occurred in sample *N* by the photon irradiation, can be explained by Eq. (2). Ionization of the GLPC into $(\mathrm{GLPC})^+$

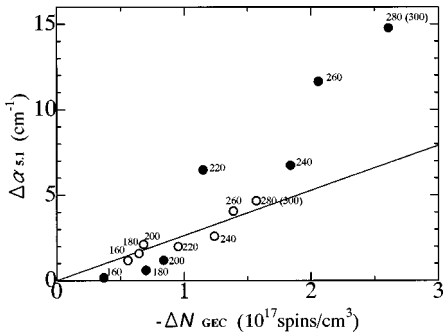

FIG. 6. Correlation between the decrease in the concentration of the GEC ($-\Delta N_{\mathrm{GEC}}$) and the increase in the intensity of the 5.1-eV absorption ($\Delta\alpha_{5.1}$) measured after each sequence of the thermal annealing. The open and the closed circles are for samples *N* and *H*, respectively, and the numbers next to them denote the annealing temperature.

decreases the 5.1-eV band and the generation of GEC induces the 4.5- and 5.8-eV bands.[19,26,27] This view is consistent with the result shown in Fig. 3(a). Since the Ge E' center is not observed in sample N after the photon irradiation, the photochemical reaction indicated by Eq. (1) does not occur in sample N under the irradiation condition. The decrease of GLPC ($-\Delta N_{\mathrm{GLPC}}$), i.e., the induction of $(\mathrm{GLPC})^+$, by $2.4\times10^{17}\,\mathrm{cm}^{-3}$ brings about the decrease in 5.1-eV absorption ($-\Delta\alpha_{5.1}$) by $7.2\,\mathrm{cm}^{-1}$ shown in Fig. 2(a). From these values, the oscillator strength of the GLPC for the 5.1-eV absorption f_{GLPC} is calculated using the following Smakula's formula:[30]

$$Nf=0.87\times10^{17}n\alpha\omega/(n^2+2)^2, \tag{3}$$

where N is the defect concentration (cm^{-3}), n the refractive index of glass, α (cm^{-1}) the absorption intensity at the peak of the absorption band, and ω (eV) the FWHM. By substituting $-\Delta N_{\mathrm{GLPC}}$ of $2.4\times10^{17}\,\mathrm{cm}^{-3}$, $-\Delta\alpha_{5.1}$ of $7.2\,\mathrm{cm}^{-1}$, n of 1.46, and ω of 0.4 eV, f_{GLPC} is calculated to be 0.09, which is the same value as the one reported in Ref. 19. From the result, the relation between ΔN_{GLPC} and $\Delta\alpha_{5.1}$ is expressed as follows:

$$\Delta\alpha_{5.1}=3.0\times10^{-17}\times\Delta N_{\mathrm{GLPC}}. \tag{4}$$

The concentration of GEC induced in sample H by photon irradiation is $2.6\times10^{17}\,\mathrm{cm}^{-3}$. This indicates that this concentration of GLPC disappears in sample H, which brings about the decrease in 5.1-eV absorption. From Eq. (4), this decrease is calculated to be $7.8\,\mathrm{cm}^{-1}$.

The signal due to GR is also seen in Fig. 3(b) with a concentration of $2.6\times10^{17}\,\mathrm{cm}^{-3}$. The precursor of the photo-induced GR is the GLPC:[23]

$$\mathrm{GLPC}+\mathrm{H}\rightarrow\mathrm{GR}. \tag{5}$$

Therefore, the decrease in the 5.1-eV band associated with the generation of GR is calculated to be $7.8\,\mathrm{cm}^{-1}$ by substituting ΔN_{GLPC} of $-2.6\times10^{17}\,\mathrm{cm}^{-3}$ into Eq. (4). Therefore, the total decrease in the 5.1-eV band due to the loss of GLPC becomes $15.6\,\mathrm{cm}^{-1}$.

As shown in Figs. 2(b) and 3(b), the Ge E' center is induced in sample H. The NOV and the GLPC are the precursors of the Ge E' center in a H_2-loaded Ge-doped SiO_2 glass.[22] However, in the present case, only 30 pulses of the laser photons, which correspond to $2.1\,\mathrm{J/cm}^2$, were irradiated to the samples. It is known that the GLPC does not change into the Ge E' center with such a low dose.[22] Therefore, the observed Ge E' center was totally generated from the NOV. The induced concentration of Ge E' center is $0.6\times10^{17}\,\mathrm{cm}^{-3}$, which should be equal to the decreased concentration of NOV. Since the NOV shows the absorption at 5.1 eV with ω of 0.4 eV and f of 0.4, by using Eq. (3) the decrease in the 5.1-eV absorption is calculated to be $7.8\,\mathrm{cm}^{-1}$. As a result, the decrease in the 5.1-eV absorption accompanied with the three paramagnetic centers, GR, GEC, and Ge E' center is calculated to be $23.4\,\mathrm{cm}^{-1}$. This is quite similar to the observed value.

From the above-mentioned discussion, it is concluded that the electron donor to generate the GEC in sample H is also the GLPC. However, the Ge(2) signal, which is assigned to the $(\mathrm{GLPC})^+$, is not observed by the ESR measurement for sample H even after the laser photon irradiation. The $(\mathrm{GLPC})^+$ is considered to be terminated with a hydrogen atom in sample H, since only the existence of H_2 molecules is the difference between samples H and N. The $(\mathrm{GLPC})^+$ terminated with a hydrogen atom, written as $(\mathrm{GLPC})^+$-H hereafter, is a diamagnetic center, and is not detectable in the ESR measurement.

B. Thermal effects on the photo-induced structural changes

As shown in Fig. 6, $\Delta\alpha_{5.1}$ is linearly proportional to $-\Delta N_{\mathrm{GEC}}$ when the sample N is thermally annealed. Here, we assume that the reverse reaction of Eq. (2) occurs with the thermal annealing. This means $-\Delta N_{\mathrm{GEC}}$ is equal to the recovered concentration of the GLPC. Therefore, $-\Delta N_{\mathrm{GEC}}$ should be equal to ΔN_{GLPC}. From this relationship between $\Delta\alpha_{5.1}$ and ΔN_{GLPC} or the slope of the linear line in Fig. 6, f'_{GLPC} is calculated to be 0.081, which is 9% less than f_{GLPC}. This difference is negligible if we take account of the error of ESR measurements. This strongly confirms the above-mentioned assumption that the reverse reaction of Eq. (2) occurred during the thermal annealing of sample N that had been irradiated by laser photons.

As shown in Fig. 4, the concentration of GR increases in sample H with thermal annealing at 160 °C following the photon irradiation. Since the GR is not induced by the thermal annealing in sample H without the preirradiation of the laser photons, the precursor of thermally induced GR is a defect induced by the photon irradiation. The precursor is the $(\mathrm{GLPC})^+$-H induced in sample H by the irradiation. As mentioned above, electrons are released from GEC's by the thermal annealing, and $(\mathrm{GLPC})^+$'s trap the electrons in sample N. However, the $(\mathrm{GLPC})^+$ is terminated with a hydrogen atom and becomes the $(\mathrm{GLPC})^+$-H in sample H. Therefore, if an electron is trapped by the $(\mathrm{GLPC})^+$-H, the GR is induced. This reaction is expressed as

$$\mathrm{GEC}+(\mathrm{GLPC})^+\text{-H}\rightarrow\mathrm{GeO_4}+\mathrm{GR}. \tag{6}$$

This reaction explains the increase in the GR concentration caused in sample H by the thermal annealing at 160 °C shown in Fig. 4. When the annealing temperature is beyond 160 °C, the GR is bleached.

In sample N, $\Delta\alpha_{5.1}$ is linearly proportional to $-\Delta N_{\mathrm{GEC}}$, as mentioned above. Such proportionality is not observed for sample H. As shown in Fig. 6, the ratio of $\Delta\alpha_{5.1}$ to $-\Delta N_{\mathrm{GEC}}$ is lower in sample H than in sample N during the thermal annealing from 160 to 200 °C, while it becomes higher at higher annealing temperatures. As shown in Fig. 4, the GEC is bleached monotonically by the thermal annealing. The electron thermally released from the GEC is trapped at the $(\mathrm{GLPC})^+$-H and the $(\mathrm{GLPC})^+$-H becomes the GR as shown in Eq. (6). However, the GR is scarcely bleached by the thermal annealing from 160 to 200 °C. As a result, the intensity of the absorption band at 5.1 eV due to the GLPC scarcely increases at this temperature region. With the thermal annealing at higher temperatures, the GR is bleached and becomes the GLPC, which in turn increases the absorption intensity at 5.1 eV.

As mentioned in the previous section, the total decrease in the 5.1-eV band due to the loss of GLPC accompanied with the induction of GR and $(\mathrm{GLPC})^+$-H is $15.6\,\mathrm{cm}^{-1}$. There-

fore, the 5.1-eV band of 15.6 cm^{-1} should be induced with complete thermal bleaching of the GR and $(GLPC)^{+}$-H. This is quite similar to $\Delta\alpha_{5.1}$ of sample *H* that was annealed thermally at 300 °C (see Fig. 6). The 5.1-eV absorption band due to the NOV does not increase with the thermal annealing, since the concentration of the Ge E' center scarcely changes with the thermal annealing.

C. Assignment of the 5.8-eV absorption

As shown in Fig. 2, absorption bands are induced at 4.5 and 5.8 eV by the photon irradiation in sample *N*. In addition to these two bands, the 6.4-eV absorption is also induced in sample *H*. The bands at 4.5 and 6.4 eV are already known to be, respectively, due to the GEC (Refs. 19, 26 and 27) with the Ge(1) ESR signal and the Ge E' center.[25] However, the assignment of the 5.8-eV band is still a matter of discussion.

There have been papers[26,27] that assigned the 4.5- and 5.8-eV bands to two different defects that have the Ge(1) and Ge(2) ESR signals, respectively. On the other hand, the authors have indicated the possibility of both the 4.5- and 5.8-eV bands being due to the Ge(1) defect from the fact that the intensity of the 5.8-eV band is always linearly proportional to that of the 4.5-eV band with the identical proportionality coefficient regardless of the Ge content of the samples.[19] The present study gives a clear answer to this puzzle. By comparing Figs. 2 and 3, one can easily find that the photon-irradiated sample *H* shows the 5.8-eV band without showing the Ge(2) signals. This fact clearly contradicts the assumption that the 5.8-eV band and the Ge(2) signal are due to the same defect. By comparing the results shown in Fig. 2 (or Table I) and those in Fig. 3, it is found that the intensity of the 5.8-eV band is similar between samples *N* and *H* and that the Ge(1) signal intensity is also similar between the two samples. This similarity between the 5.8-eV band and the Ge(1) signal supports the model that the 5.8-eV band as well as the 4.5-eV band is due to the defect with the Ge(1) ESR signal, namely, GEC.

One might notice a difference of the FWHM value of the 5.8-eV band between the samples *N* and *H* shown in Table I. As for the absorption spectrum of sample *H* shown in Fig. 2(b), the calculated FWHM for the 5.8-eV band is not accurate due to the presence of the peak at 6.4 eV and the one located higher than 6.5 eV.[31] Because of the limitation of the measurement system, it was impossible to distinguish the three absorption bands clearly in the present calculation. Therefore, re-estimation of the FWHM was done based on the thermally decreased 5.8-eV absorption shown in Fig. 5, and the result came out to 1.2 ± 0.1 eV, the same FWHM as in the case of sample *N*. Since the thermal annealing does not change the concentration of the Ge E' center, the existence of the 6.4-eV band is negligible in the spectrum shown in Fig. 5. Therefore, the FWHM of 1.2 eV is more reliable for the 5.8-eV band. Although the Si E' center is known to have absorption at 5.8-eV,[32,33] there is no possibility of the present 5.8-eV band being due to the Si E' center since the ESR signal of the Si E' center never appeared. Therefore, the present 5.8-eV band is due to the same origin in both samples *N* and *H*, and the origin is the GEC with the Ge(1) ESR signal.

V. CONCLUSIONS

Structural changes induced in H_2-loaded Ge-doped SiO_2 glass have been investigated through absorption and ESR measurements using a KrF excimer laser as a photon source. Thermal annealing was also applied to the glass following the laser photon irradiation, and the behavior of absorption bands and that of paramagnetic centers were investigated. From the obtained results, the following conclusions are derived. (1) The paramagnetic centers, GEC, GR, and Ge E' center, are induced by the irradiation. (2) The GLPC, which donated an electron to generate the GEC, is terminated with a hydrogen atom and becomes the $(GLPC)^{+}$-H, an ESR-insensitive diamagnetic center. (3) The $(GLPC)^{+}$-H traps an electron thermally released from the GEC and becomes the GR at temperatures around 160 °C. (4) The GR becomes the GLPC with the thermal annealing. (5) The 5.8-eV absorption band induced by the KrF excimer laser photon irradiation is assigned to the GEC, which shows the Ge(1) signal in ESR measurements.

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