Laser-power dependence of absorption changes in Ge-doped SiO_2 glass induced by a KrF excimer laser

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The generation mechanism of the absorption changes, which cause a photorefractive change through the Kramers-Kronig relation in Ge-doped SiO_2 glass, has not been clarified yet. In the present paper, we examined the laser-power dependence of the absorption changes around 5 eV, induced by a KrF excimer laser. The induced absorption around 5 eV is composed of three different components, centering at 4.50, 5.08, and 5.80 eV. The increasing behavior of each absorption component depends strongly on the energy density. The three absorption components reach different saturation levels, depending on the energy density. Furthermore, the absorption induced by a high-power KrF excimer laser is bleached by a laser, the energy density of which is about one-twentieth of the inducing laser. Combining the results of mathematical analysis, it was found that a two-photon process and a one-photon process are, respectively, involved with the induction and the bleach of each absorption. It was also found that the precursor defect, which causes the absorption change, is of an oxygen-deficient type.

Since the fact that Ge-doped SiO_2 glasses have large absorption bands in the ultraviolet to vacuum ultraviolet (UV–VUV) range was reported, many studies have been done to elucidate the structures responsible for these bands. Especially, the research has been focused on the strong absorption at 5 eV.[1–6] Through this research, it has become clear that the 5-eV absorption appears only in oxygen-deficient glasses.[3] It has been reported that two structures, twofold coordinated germanium[4] (or germanium lone pair center, GLPC, $-\dot{\underset{\cdot\cdot}{G}}\text{e}-$), and neutral oxygen vacancy[7] (NOV, $\equiv\text{Ge}-T\equiv$), are responsible for this absorption. Here, the symbols "$\cdot\ \cdot$" and "$\equiv$" denote lone-pair electrons and bonds with three separate oxygens, respectively, and T is either Ge or Si.

It has been well known that absorption changes are induced in Ge-doped SiO_2 glass, when irradiated by UV photons.[7,8] Recently, the manufacture of optical filters[9–11] with Bragg gratings in communication fibers was reported. A photorefractive change through the Kramers-Kronig relation induced by some absorption change is utilized for these gratings.[10] Since this was reported, there have been many papers on the absorption changes responsible for the photorefractive change. As the most probable model, the NOV is believed to release one electron and become the E' center ($\equiv T^+ + \cdot\ T\equiv$, T: Ge or Si) by absorbing 5-eV photons; here "$\cdot$" denotes an unpaired electron.[7] The generation of the germanium electron trapped centers (GEC's) is also responsible for the absorption change.[11–14]

A discrepancy has been reported for the energy density necessary to make a Bragg grating.[15–17] The difference in efficiency of the generation and bleach of E' centers with the energy density of irradiated photons seems to be responsible for this discrepancy.[8] It was also reported that the induced absorption shows the saturation at different intensities, depending on the incident energy density.[18] It was further reported that the absorption induced by intense photons is partially bleached when the sample is irradiated by weaker photons.[18] These reports indicate the existence of a certain relation between the absorption change and the energy density, but the details are unknown.

In the present paper, the absorption around 5 eV is very carefully examined, by changing the incident energy density significantly. Based on the observed energy-density dependence of the absorption change, a mathematical analysis is made. The role of a two-photon process and a one-photon process is also discussed.

The samples used are germanium-doped silica glasses of $99SiO_2{:}1GeO_2$ prepared by the vapor-phase axial deposition method. The soot rods were sintered to dense glass rods under reducing atmosphere (H_2:He=1:10). The samples were cut and polished into plates of 0.3 mm thick. Two KrF excimer lasers (248 nm, 5.0 eV) were used as the irradiation photon sources. The one with a higher energy density of 20 to 80 mJ/cm^2 per pulse (Lambda Physik, LPX105i) is referred to as laser H, while the other (MPB Technologies, PSX-100) has an energy density of about 0.5 mJ/cm^2 per pulse and is called laser L. Since the pulse duration of laser H is about 20 ns and that of laser L is about 5 ns, the average energy density becomes about 1–4 MW/cm^2 for laser H and 100 kW/cm^2 for laser L. The energy density was monitored by a thermopile-type measurement system (Scientech, AD30). The absorption spectra from the visible to UV region were measured by a Shimadzu UV160 spectrophotometer.

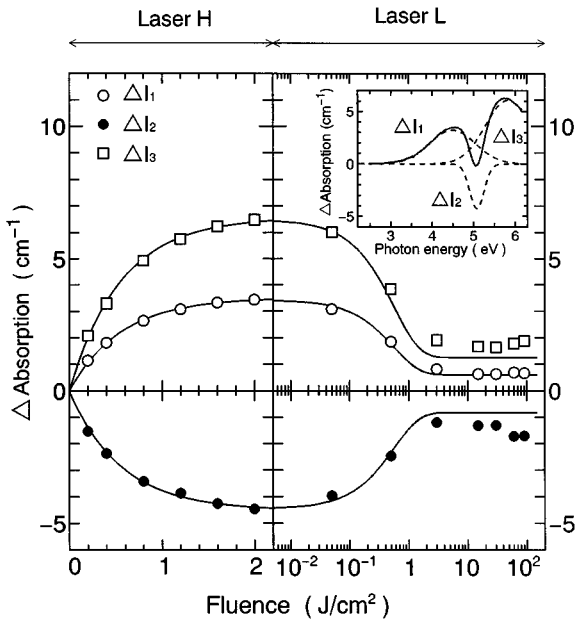

FIG. 1. Change in intensity as a function of fluence for the three absorption components induced by photon irradiation of lasers H and L. The inset is the induced absorption spectrum by the irradiation of laser H of 2 J/cm^2. $\overset{\text{Laser } H}{\leftrightarrow}$ denotes the period of the irradiation of laser H, and $\overset{\text{Laser } L}{\leftrightarrow}$ denotes the period of the irradiation of laser L following the irradiation of laser H. The energy density of laser H used in this experiment is 40 mJ/cm^2 per pulse.

Electron-spin-resonance (ESR) signals were obtained by a JEOL RE-2XG spectrometer at the X band frequency. All the experiments were done at room temperature.

Figure 1 shows the change in absorption with fluence observed by the irradiation of intense 5-eV photons. As shown in the inset, the induced absorption is divided into three spectral components with Gaussian line shape, two (ΔI_1 around 4.50 eV and ΔI_3 around 5.80 eV) are positive and the remaining one (ΔI_2 around 5.08 eV) is negative. The peak positions of the three components and their values of the full width at half maximum (FWHM) are shown in Table I. This spectrum is clearly different from the absorption spectrum induced by the irradiation of a Hg/Xe lamp, in which absorption peaks appear at 5 and 6.3 eV.[7] Although the absorption at 6.3 eV also emerges slowly but clearly, in the present study, after the three absorption changes become saturated at the fluence of about 2 J/cm^2, this is not the scope of the present paper. Figure 2 shows the dependence of the saturated value of the absorption change on the energy density of laser H for the three components. The saturation level is found to depend on the energy density.

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

	Peak position (eV)	FWHM (eV)
ΔI_1	4.50±0.03	1.31±0.03
ΔI_2 (<0)	5.08±0.01	0.39±0.01
ΔI_3	5.80±0.03	1.27±0.03

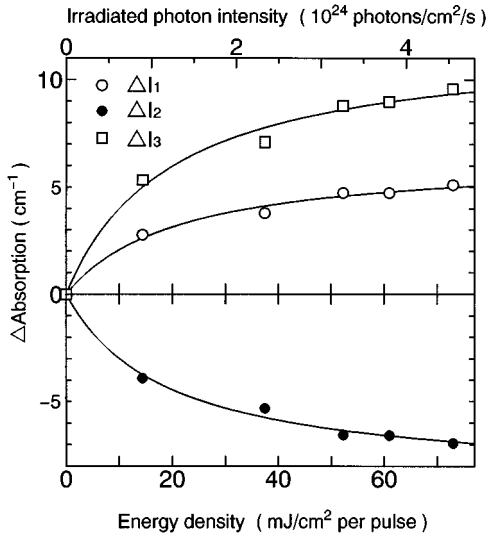

FIG. 2. Change in the saturated absorption intensity induced by laser H as a function of the energy density for the three absorption components. The solid curves are drawn by the lease-squares fitting to Eq. (7).

As shown in the right half of Fig. 1, the changes in the three absorption components induced by laser H are diminished by the ensuing photon irradiation by laser L. The three components approach to their respective stable levels when the total fluence by laser L reaches about 4 J/cm^2. These data indicate that the reaction, which causes the absorption changes, is an equilibrium reaction between the inducing and the bleaching processes.

The inset in Fig. 3 shows the ESR spectrum induced by the irradiation of 2 J/cm^2 by laser H. The spectrum is very close to what is believed to be due to the GEC's,[19] although the assignment is still debatable.[14] Figure 3 shows a good proportionality between the intensity of each induced absorption component and the density of the induced paramagnetic

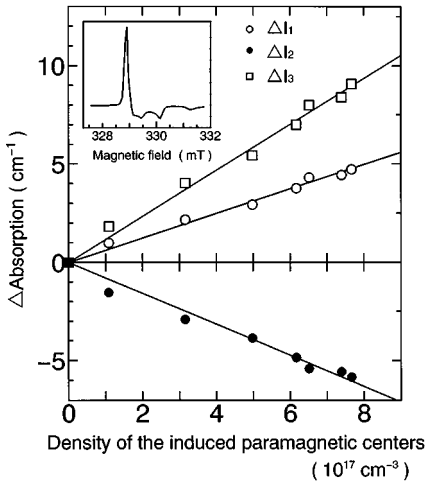

FIG. 3. Dependence of the intensity for three absorption components induced by the irradiation of up to 2 J/cm^2 by laser H, on the density of induced paramagnetic defect centers. The inset shows the ESR spectrum of the induced paramagnetic centers.

defect centers. That is to say, the absorption around 4.50 eV (ΔI_1) and the one around 5.80 eV (ΔI_3) are induced concomitantly with the decrease of the absorption around 5.08 eV (ΔI_2), keeping the ratios $\Delta I_1/\Delta I_2$ and $\Delta I_3/\Delta I_2$ constant. This strongly suggests that the defect responsible for ΔI_2 is converted to the defect(s) responsible for ΔI_1 and ΔI_3 Namely, ΔI_2 is caused by the precursor defect and ΔI_1 and ΔI_3 are caused by the induced defect(s).

As already mentioned, the results of Figs. 1 and 2 suggest that the behavior of the absorption change is determined by the equilibrium between the inducing and the bleaching processes, as expressed by the following:

$$\text{precursor } (N_p) \underset{c_2}{\overset{c_1}{\rightleftarrows}} \text{defect } (N_d), \tag{1}$$

where $c_1(s^{-1})$ and $c_2(s^{-1})$ are rate constants. Then, we start with a first-order kinetic equation involving both the forward and the backward reactions as follows:

$$\frac{dN_p}{dt} = -c_1 N_p + c_2 N_d, \tag{2a}$$

$$N_p + N_d = N_0, \tag{2b}$$

$$N_p(t=0) = N_0, \quad N_d(t=0) = 0. \tag{2c}$$

Here, we define N_p and N_d as the numbers of precursor defects and induced defects, respectively. N_0 is the initial number of N_p. The solution of these equations is given by

$$N_d = N_0 - N_p = \frac{c_1}{c_1 + c_2} N_0 \{1 - \exp[-(c_1 + c_2)t]\}. \tag{3}$$

The numbers of the defects, N_p and N_d, will be saturated as follows:

$$N_d(t \to \infty) = N_0 - N_p(t \to \infty) = \frac{c_1}{c_1 + c_2} N_0. \tag{4}$$

If we assume, for example, that both the inducing and the bleaching processes are governed by respective one-photon processes, i.e., if the rate constants c_1 and c_2 are both proportional to the incident energy density, the value of $n_d(t \to \infty)$ should be constant. Contrary to this, however, the saturation values vary with the incident energy density, as shown in Fig. 2. Nishii *et al.*[12,20] reported that the formation of the GEC's, which are responsible for UV absorption bands, is caused by a two-photon process. Furthermore, we have confirmed that the absorption change shown in the inset of Fig. 1 does not occur when a Hg/Xe lamp is used as a light source. Therefore, we assume the following relations between the rate constants and the incident energy density:

$$c_1 = \alpha P^2 \quad \text{(two-photon process)}, \tag{5a}$$

$$c_2 = \beta P \quad \text{(one-photon process)}, \tag{5b}$$

where P ($\text{cm}^{-2}\,\text{s}^{-1}$) denotes the number of incident photons per unit area per second, which corresponds to the incident energy density, and α (cm^4 s) and β (cm^2) are constants. Therefore, we obtain the following relations for N_p and N_d form Eq. (3):

TABLE II. Constants α and β for lasers H and L.

	α (cm^4 s)	β (cm^2)
Inducing period by laser H	0.39×10^{-42}	0.49×10^{-18}
Diminishing period by laser L	1.0×10^{-42}	1.3×10^{-18}

$$N_d = N_0 - N_p = \frac{\alpha}{\alpha + \beta/P} N_0 \{1 - \exp[-(\alpha P^2 + \beta P)t]\}. \tag{6}$$

From Eq. (4), the dependencies of $N_p(t \to \infty)$ and $N_d(t \to \infty)$ on the incident energy density are as follows:

$$N_d(t \to \infty) = N_0 - N_p(t \to \infty) = \frac{\alpha}{\alpha + \beta/P} N_0. \tag{7}$$

While ΔI_1 and ΔI_3 are proportional to the number(s) of the corresponding induced defects (N_d), ΔI_2 is proportional to the number of the precursor defects, which have changed to the induced defects ($N_p - N_0$). Therefore, all the three absorption components can be calculated from Eq. (6). The solid curves, in the left half of Fig. 1, are drawn by assuming Eq. (6). Closely tracing the theoretical curves, the values ΔI_1, ΔI_2, and ΔI_3 approach to their respective saturation values. If, at this moment, the photon source is changed to laser L from laser H, the numbers of both defects again begin to approach to their respective saturation values. The absorption change in this period can be calculated similarly from Eq. (2a), by assuming that the saturation values of N_d and N_p of the previous period (namely, by laser H) are their initial values of this period. Solid curves in the right half of Fig. 1 are drawn in this way. Furthermore, the solid curves in Fig. 2 representing the change in the saturated absorption intensity induced by laser H are drawn by assuming Eq. (7). The fact that the experimental data in Figs. 1 and 2 are fitted very well by these solid curves suggests the validity of our assumed model.

The constants α and β, or the efficiency of the two-photon process and that of the one-photon process, should be independent of the energy density of irradiated photons. Table II shows the values of α and β used through the calculations for the inducing period by laser H and for the diminishing period by L. The difference of α between the inducing period and the diminishing period is about a factor of 2.6. So is the difference of β. If the difference in shape of the photon pulses from the two lasers and inevitable shot-to-shot differences are taken into account, such a difference can be considered to be small enough to indicate that both α and β are independent of the energy density. This strengthens the validity of our assumed model.

From these results, it has been confirmed that the defect responsible for the absorption around 5.08 eV is converted by a two-photon process to the defect(s) responsible for the absorption around 4.50 and 5.80 eV and that its backward

reaction occurs by a one-photon process. From Fig. 3, it is obvious that the 5.08 eV absorption band is the precursor of the GEC, and that either of the induced absorption bands at 4.50 and 5.80 eV or both are assigned to the GEC. One important fact that should be remembered is that the absorption at 5.08 eV is observed only in the oxygen-deficient-type Ge-doped SiO_2 glass. Therefore, the absorption at 5.08 eV should be assigned to a germanium oxygen-deficient center (GODC), no matter whether it is GLPC,[4] NOV,[7] or any other form,[21] or a combination thereof. The assignment of the absorption bands at 4.50 and 5.80 eV has been discussed in several papers. While the 4.50 eV (4.4 eV in Ref. 13) and the 5.80 eV bands are assigned to two types of GEC's, Ge(1) and Ge(2), respectively, in Ref. 13, the two bands are assigned to the GEC and the positively charged GODC, respectively, in Ref. 14. Combining these assignments with the results of the present study, the mechanism of the absorption change is expressed as follows:

$$\begin{array}{lcl} GeO_2 + GODC & \overset{\text{two photon}}{\underset{\text{one photon}}{\rightleftarrows}} & (GeO_2)^{e-} + (GODC)^{+}. \\ \quad 5.08\ \text{eV} & & 4.50,\ 5.80\ \text{eV (Ref. 13)} \\ & & 4.50\ \text{eV} \quad 5.80\ \text{eV (Ref. 14)}. \end{array}$$

Here $(GeO_2)^{e-}$ can be referred to as GEC. More analyses such as on the structural assignment of GODC will continue in a future paper.

In the right half of Fig. 1, it is observed that the experimental data of ΔI_2 decreases and ΔI_3 increases again with the irradiation of laser L, when the irradiation of laser L exceeds 4 J/cm^2. This phenomenon is understood if the generation of the E' center is taken into account. It has been reported that the irradiation of UV photons breaks the NOV into E' center and that this phenomenon is accompanied by the absorption decrease around 5 eV and the absorption increase around 6.3 eV.[7,22] As already mentioned, we have confirmed that this phenomenon becomes obvious with the prolonged irradiation of photons, thus putting ΔI_2 and ΔI_3 below and above the calculated curves, respectively.

Since the photorefractive index change in Ge-doped SiO_2 glasses is induced effectively by the irradiation of intense photons at 5 eV,[8,12,22] and the absorption change should be closely related with photorefractive index change through the Kramers-Kronig relation,[11,12,22] the present findings are very important. Furthermore, that the induced absorption changes are diminished by one-photon absorption of 5-eV photons is a negative factor for the utilization of the photorefractive effect.

To conclude, as for the absorption change, which consists of the induction of absorption bands at 4.50 and 5.80 eV and the bleaching of 5.08-eV absorption induced in Ge-doped SiO_2 glass by irradiation of 5-eV photons, a two-photon process at oxygen-deficient centers is responsible. The backward process is caused by a one-photon process.

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