

Photochemical reaction of divalent-germanium center in germanosilicate glasses under intense near-ultraviolet laser excitation: Origin of 5.7 eV band and site selective excitation of divalent-germanium center

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The photochemical reaction of Ge^{2+} in $10\text{GeO}_2\text{-}90\text{SiO}_2$ optical fiber preform and the origin of the 5.7 eV optical absorption band induced by intense ultraviolet laser excitation have been investigated using a near-ultraviolet XeF excimer laser (3.7 eV) as the main excitation source. Based on the previous and present experimental results, it is concluded that the 5.7 eV optical absorption band does not originate from the Ge(2) electron trapped center. In place of this model, we have proposed an alternative structural model for the origin of the 5.7 eV band taking into account the experimental fact that the corresponding center is diamagnetic. In addition, it is found that the site selective excitation of the Ge^{2+} center can be achieved by using laser sources with different photon energies.

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I. INTRODUCTION

Highly functional photorefractive glasses based on silicon dioxide are promising materials for optical devices in the field of dense and rapid information processing systems. Glasses have long been playing a crucial role in optical telecommunication systems as optical fibers, which correspond to the conducting wire in electronic systems. All optical processing of information signals is, however, strongly required to fulfill the potential demand for information technology. Optically nonlinear single crystals and rare-earth-doped glasses can be utilized as active devices such as phase modulators and optical amplifiers, respectively.¹ If we succeed in developing active functional fibers and waveguides based on silicate glasses, a convenient manufacturing process with high cost effectiveness can be developed. So far, photoactivated processes in silicate glasses, especially in germanosilicate glasses, have been utilized for this purpose. For example, a large optical second order nonlinearity induced by the ultraviolet (UV)-light assisted poling² and the formation of fiber Bragg gratings^{3,4} are based on the photoactivated process, mainly due to the photoionization of structural defects in Ge-doped silica glasses.⁵⁻⁷ Although many sophisticated studies have been done for the development of photonic devices, the related defect photochemistry of Ge-doped silica glasses still remains an open question.

The authors have been dealing with the photosensitivity of the Ge^{2+} center in $\text{Ge}:\text{SiO}_2$ glasses prepared by the sol-gel method and vapor phase axial deposition (VAD)

method.⁸⁻¹¹ It has been considered that the Ge^{2+} center is one of the dominant species responding to dense UV photons.^{8,9,12} This is also the case for H_2 -loaded $\text{Ge}:\text{SiO}_2$ glasses.¹³

It is reported that the optical absorption band due to the Ge^{2+} center is observed at 5.16 eV.^{14,15} In addition to this center, many intrinsic and extrinsic defect levels are observed around 5 eV.¹⁶ This feature makes it complicated to investigate the photoactivated processes of the Ge^{2+} center. A weak absorption due to the Ge^{2+} center is also observed at 3.7 eV, corresponding to the singlet-triplet transition.^{17,18} It was reported that a long-periodic fiber grating can be fabricated by exciting the 3.7 eV absorption band in a germanosilicate fiber core¹⁹ and a H_2 -loaded one as well.²⁰ It is then expected that only the Ge^{2+} center can be excited using a 3.5 eV ($\lambda = 351$ nm) photon from a XeF excimer laser.

In the present study, we examined photoactivated processes of the Ge^{2+} center in the core region of optical fiber preforms using a XeF excimer laser as an excitation laser source. KrF ($\lambda = 248$ nm, $E = 5.0$ eV), XeCl ($\lambda = 308$ nm, $E = 4.0$ eV), and ArF ($\lambda = 193$ nm, $E = 6.4$ eV) excimer lasers were also used as excitation sources for comparison. We also report that the energy of the induced optical absorption can be controlled by selecting the excitation laser photon energies. Thus site selective excitation of the Ge^{2+} center is possible.

II. EXPERIMENTAL PROCEDURE

Optical fiber preform (Shin-Etsu Chemical, Japan) of $10\text{GeO}_2\text{-}90\text{SiO}_2$ prepared by a vapor axial deposition method was used as a testing sample. The preform rod was

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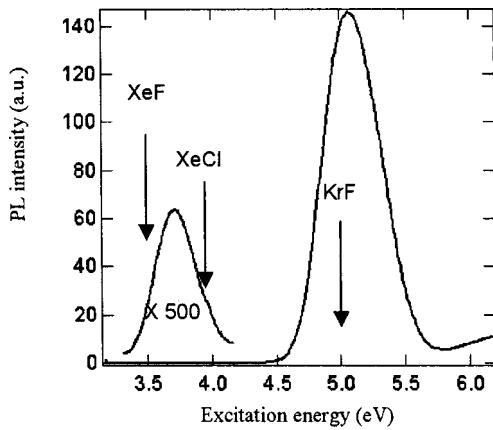


FIG. 1. Photoluminescence excitation (PLE) spectrum of 10GeO₂-90SiO₂ optical fiber preform measured by monitoring 3.2 eV photoluminescence. Arrows show photon energies of different excimer lasers used in the present study.

cut into thin round slices of about 500 μm in thickness and polished into an optical finish. The center of the core region was used for the investigation. XeF (λ = 351 nm, E = 3.5 eV), XeCl (λ = 307 nm, E = 4.0 eV), KrF (λ = 248 nm, E = 5.0 eV), and ArF (λ = 193 nm, E = 6.4 eV) excimer lasers (Lambda Physik COMPex100, Germany) were used as excitation sources. The irradiation powers and repetition rates were set to ~100 mJ/cm² per pulse and 10 Hz for all excimer lasers. Photoluminescence, optical absorption, and electron spin resonance (ESR) were measured before and after the irradiation. Photoluminescence and photoluminescence excitation spectra were measured with a Hitachi 850 spectrophotometer. Optical absorption spectra were collected by a Hitachi U-3500 spectrophotometer. X-band ESR signals were measured by a Bruker EMX-100 spectrometer. The magnetic field was calibrated by an NMR gauss meter.

III. RESULTS AND DISCUSSION

A. The origin of 5.7 eV band

Figure 1 shows the photoluminescence excitation (PLE) spectrum of a 10GeO₂-90SiO₂ optical fiber preform measured by monitoring 3.1 eV photoluminescence (PL). Note that the photon energy of the XeF excimer laser is about 0.2 eV smaller than that of the absorption maximum. The PL spectra of 10GeO₂-90SiO₂ optical fiber preform before and after the XeF excimer laser irradiation (3 kJ/cm²), which were taken under the excitation of 5-eV light from the monochromated Xe lamp, are shown in Fig. 2. By irradiating with the XeF excimer laser, the PL intensity originating from the Ge²⁺ center is decreased, indicating that the center possesses photoactivity under the near-UV laser light. Figure 3 shows the optical absorption and difference absorption spectra of the same sample. The profile of the difference absorption spectrum before and after the XeF excimer laser irradiation seems to be essentially the same as that after the KrF excimer laser irradiation, which is used for the fabrication of fiber bragg grating (FBG).⁸ It is obvious that the difference absorption spectra of the XeF excimer laser irradiation shifts

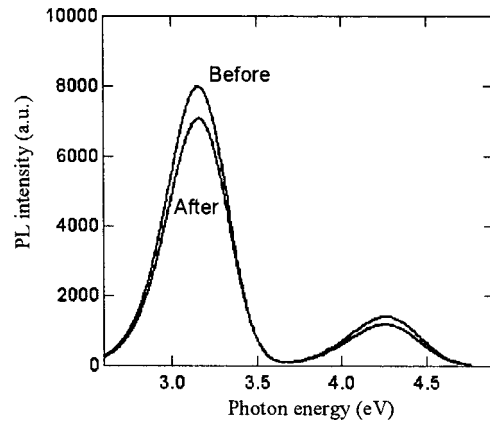


FIG. 2. Photoluminescence spectra of 10GeO₂-90SiO₂ optical fiber preform before and after the XeF excimer laser irradiation at 3 kJ/cm² of total dose.

by ~0.1 eV to smaller energies compared to the case of KrF laser irradiation. We will discuss more on this topic in Sec. III B. The difference absorption spectra can be tentatively decomposed into four components; Ge(1), Ge ODC, Ge(2), and Ge E' center as shown in the inset of Fig. 3(b).²¹ Structural models of corresponding Ge-related defects and results

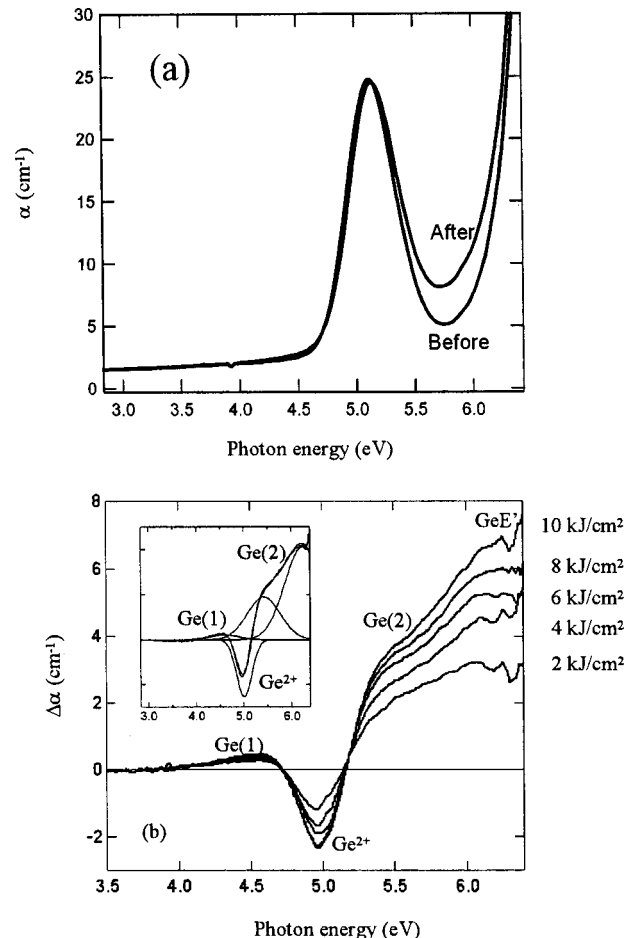


FIG. 3. (a) Optical absorption of 10GeO₂-90SiO₂ optical fiber preform before and after the XeF excimer laser irradiation at 3 kJ/cm² of total dose and (b) difference absorption spectra before and after XeF excimer laser irradiation (inset shows an example of band deconvolution).

TABLE I. Proposed structural models of Ge-related defects.

| Defect (commonly used name) | | Suggested structure ^c | Transition energy (eV) |
|--|--|--|----------------------------------|
| Ge E' ^a | | $\equiv\text{Ge}\cdot$ | 6.3 |
| Ge ODC ^b (oxygen deficient center) | | Neutral oxygen mono vacancy (NONV) divalent center, Ge^{2+} | 5.06 |
| GEC ^a | | $\equiv\text{Ge}\cdot-\text{O}-\text{Ge}$ | 3.7, 5.16 (PL 3.1 and 4.2 eV) |
| | | $\equiv\text{Ge}\cdot-\text{O}-\text{Si}$ | 4.7 |
| | | | 5.7 |

^aReference 20.^bReference 14.^c \equiv : three Ge–O bonding, \cdot : an electron.

of the band deconvolution are summarized in Tables I and II. The Ge ODC represents the Ge^{2+} center in the present study because the XeF excimer laser is considered to excite only this center. Ge(1) and (2) are supposed to be electron trapped centers consisting of a fourfold coordinated Ge (GEC).²² Although the absorption energy of each center was about 0.1 eV smaller than those of the KrF excimer laser irradiation as shown later, the intensity ratio of the induced optical absorption bands to the reduced one is almost the same. This clearly shows that the Ge^{2+} center is a photosensitive structure and is responsible for the photoinduced densification or photorefractivity of optical fiber cores.

Figure 4 shows the ESR spectra before and after XeF laser irradiations. The as-received $10\text{GeO}_2\text{-}90\text{SiO}_2$ optical fiber preform contains an intrinsic Ge E' center as shown in Fig. 4(d). Irradiation by the XeF excimer laser resulted in the formation of various paramagnetic centers [Figs. 4(a) and 4(b)]. The g values of the obtained signal also suggest the formation of Ge(1), Ge(2), and Ge E' centers in the glass.^{14,22} Although the total spin density continued to increase to 11 kJ/cm^2 of cumulative fluence, the intensity of the signal corresponding to the Ge(2) center tended to be saturated below 2 kJ/cm^2 . Curve (c) in Fig. 4, which indicates the difference in the ESR signal between (a) 10 kJ/cm^2 and (b) 2 kJ/cm^2 of cumulative fluence, seems to be almost the same as curve (d) of the unirradiated sample, indicating that no additional generation of the Ge(2) center took place but the Ge E' center was mainly produced from the Ge^{2+} center at higher fluences. It was reported that only the Ge E' center is generated when the Ge-doped fiber core was irradiated with a KrF laser at higher fluences such as those in the present study.²³

It has been believed that the induced optical absorption band at 5.5 eV (which corresponds to the so-called 5.7 eV band shown in Table I) as shown in Fig. 3(b) is assigned to the Ge(2) electron trapped center. However, we found that the annealing of the irradiated glasses (400°C , 30 min) bleached the 5.7 eV band and increased the 5.1 eV band as shown in Fig. 5. This means that the so-called 5.7 eV band originates from the Ge^{2+} center. In contrast to the ESR results, the induced absorption around 5.5 eV successively increased in intensity with an increasing laser dose. These results clearly indicate that the origin of the 5.5 eV band (the 5.7 eV band in Table I) observed after the XeF laser irradiation is different from that of the ESR signal assigned to the Ge(2) center. It has also been reported that based on the optically detected magnetic resonance (ODMR) study, the 5.7 eV band assigned to the Ge(2) center is diamagnetic.²⁴ The authors of Ref. 24 conclude, on the basis of ODMR measurements, that the absorption band at 5.7 eV does not arise from a paramagnetic center and that the origin is not the Ge(2) center as had been thought earlier. Recently, the authors have proposed a metastable structure derived from the Ge^{2+} center, in which the bridging oxygen nearby correlates with the Ge^{2+} center to form a compressed structure as shown in Fig. 6.¹⁰ The transition energy of the compressed Ge^{2+} center was calculated to be 5.8 eV,²⁵ which is in good agreement with the observed absorption. The formation of the Ge E' center by correlating the Ge^{2+} center and the oxygen nearby was also reported for H_2 -loaded germanosilicate glass.¹³ Therefore the compressed Ge^{2+} center is assumed to be one of the most likely candidates for the 5.7 eV band produced in the irradiated germanosilicate glasses.

TABLE II. Results of band deconvolution of induced optical components.^a

| Laser | Ge(1) | | Ge ODC (Ge^{2+}) | | Ge(2) | | Ge E' | |
|-------|-------|-------------------|-----------------------------|-------------------|-------|-------------------|---------|-------------------|
| | E^b | FWHM ^c | E^b | FWHM ^c | E^b | FWHM ^c | E^b | FWHM ^c |
| XeF | 4.60 | 1.25 | 5.00 | 0.62 | 5.42 | 1.39 | 6.25 | 1.56 |
| XeCl | 4.84 | 1.73 | 5.28 | 0.74 | 5.84 | 1.39 | 6.49 | 1.47 |
| KrF | 4.76 | 2.50 | 5.10 | 0.70 | 5.56 | 1.72 | 6.35 | 1.61 |
| ArF | 4.76 | 2.26 | 5.09 | 0.70 | 5.73 | 1.92 | 6.27 | 1.16 |

^aUnit: eV.^b E : peak position.^cFWHM: full width at half maximum.

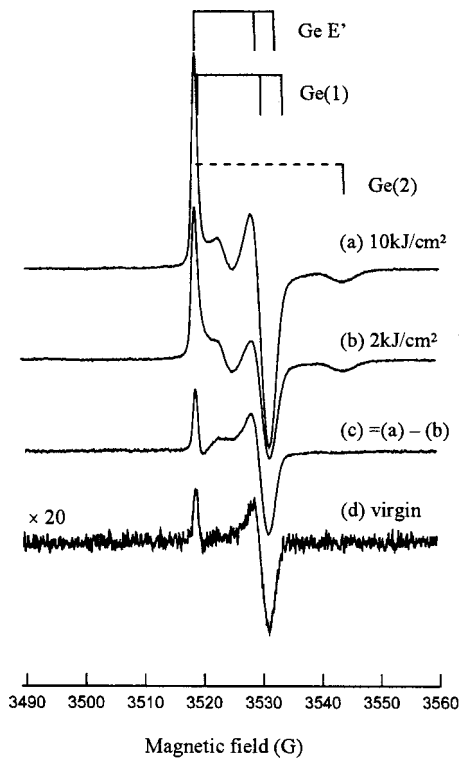


FIG. 4. ESR spectra before and after XeF excimer laser irradiation. (a) 10 kJ/cm², (b) 2 kJ/cm² of cumulative fluence, (c) difference signal, and (a), (b), and (d) before irradiation.

B. The site selective excitation of the Ge²⁺ center

It was observed in Fig. 3(b) that the difference absorption spectra before and after XeF excimer laser irradiation shifted by about 0.1 eV to the lower energy side compared with KrF laser irradiation. As shown in Fig. 1, the photon energy of the XeF excimer laser is about 0.2 eV smaller than the absorption peak top due to the singlet-triplet transition (3.7 eV). This result leads us to the idea that site selective excitation is possible by using lasers with different photon energies. Figure 7 shows the normalized difference absorption spectra before and after the irradiation of XeF, XeCl, KrF, and ArF excimer lasers. Here, the vertical axis is nor-

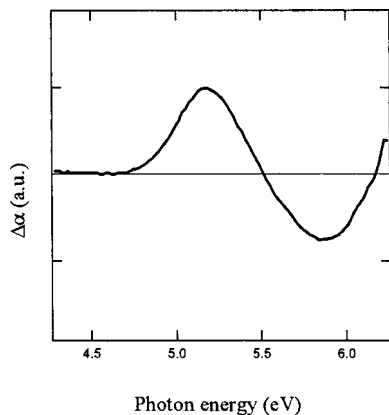


FIG. 5. Difference absorption spectrum before and after thermal annealing of irradiated sample (11 kJ/cm² of cumulative fluence). Annealing conditions: 400 °C, 30 min, ambient atmosphere.

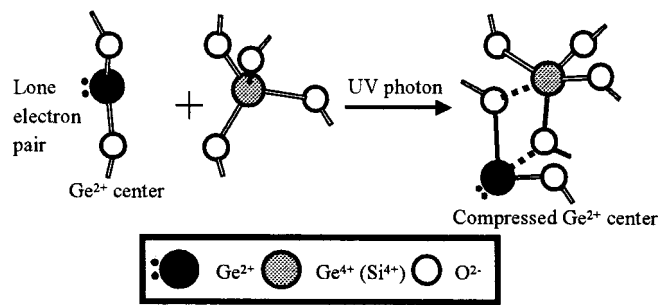


FIG. 6. Suggested structural model accounting for the origin of the 5.7 eV band.

malized to the intensity of the bleaching components around 5 eV except for ArF laser irradiation. The intensity of the difference absorption spectrum of ArF laser irradiation is normalized arbitrarily for the presentation. The magnification of each spectrum is shown in the figure relative to the case of KrF laser irradiation. Because of the larger transition probability of a singlet-singlet transition observed at 5 eV, the magnitude of the induced absorption is much larger for the case of KrF and ArF excimer laser irradiation than for the other near-UV excimer lasers. As is shown in Fig. 7, except for the case of ArF excimer laser irradiation, one can find that the respective spectra exhibit almost the same spectral profile, but they are different from each other in the bottom position. Differences in photon energy between the peak top of the singlet-triplet transition energy (3.7 eV) and the XeF and XeCl excimer lasers are -0.18 and 0.29 eV, respectively. In addition, the photon energy of the KrF excimer laser is 0.07 eV smaller than the singlet-singlet transition energy of the Ge²⁺ center (5.07 eV in the PLE spectrum, Fig. 2). The order of the energy shift of each difference spectrum seems to be related to the energy shift from the peak top as summarized in Fig. 7, but the degree of deviation in the difference absorption spectra is smaller than that of the excitation lasers. This is explained by considering that the ab-

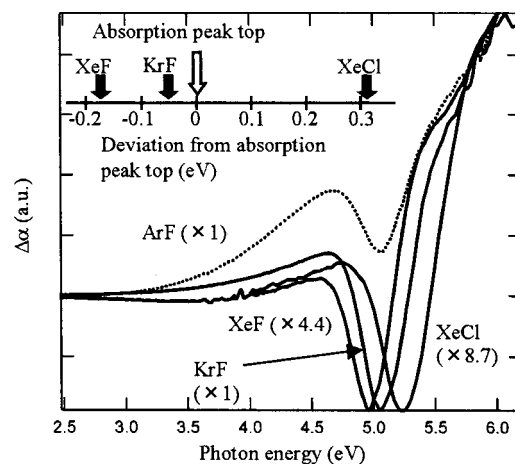


FIG. 7. Normalized difference absorption spectra of XeF, XeCl, KrF, and ArF laser irradiation. Δα of each spectrum is normalized to the intensity of the bleaching component around 5 eV except for the case of ArF excimer laser irradiation. Δα of ArF excimer laser irradiation is magnified arbitrarily for clarity. Inset shows the deviation of excitation laser photon energy from the absorption peak maximum.

sorption coefficient is not homogeneous within the laser line width because of the peak tail excitation. From these results, it can be concluded that the site selective excitation of the Ge^{2+} center is possible by choosing a suitable exciting photon energy irrespective of the singlet-singlet and singlet-triplet transitions, suggesting the precise control of induced phenomena such as photorefractivity and optical nonlinearity.

As shown in Fig. 7, ArF excimer laser excitation exhibited different spectral features compared with other excimer lasers. Considering that several kinds of defects and fundamental interband transitions can correlate with the 6.4 eV photons, many unexpected processes different from the case for other excimer lasers should take place simultaneously.²⁶

IV. CONCLUSION

Photoactivated processes of the Ge^{2+} center were investigated using a XeF laser as an excitation source. It is found that the induced optical absorption observed at 5.7 eV does not originate from the electron-trapping center. The Ge^{2+} center with a compressed structure was proposed as the substitute model for the origin of a 5.7 eV induced absorption band. It is also found that site selective excitation is possible for the Ge^{2+} center.

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