Photochemical reactions in GeO_2-SiO_2 glasses induced by ultraviolet irradiation: Comparison between Hg lamp and excimer laser

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GeO_2-SiO_2 glasses prepared by vapor-phase axial deposition were exposed to ultraviolet (uv) radiation from a Hg discharge lamp (4.9 eV) and excimer lasers (KrF laser: 5.0 eV, XeCl laser: 4.0 eV). Two photochemical reaction channels were ascertained: (1) The exposure of the glasses to the Hg lamp radiation ($\sim$16 mW/cm^2) induced Ge E' centers accompanied by bleaching of the absorption band due to oxygen-deficient defects near 5 eV (5-eV band) and the emergence of an intense band near 6.4 eV. (2) The irradiation with KrF and XeCl lasers (power densities of 10 and 90 mJ/cm^2/pulse, respectively, pulse duration of 20 ns) generated two types of paramagnetic defects, electron trapped centers associated with fourfold coordinated Ge ions (GEC) and a self-trapped hole center (STH: bridging oxygen trapping a hole). The former and the latter were considered to be caused via one-photon and two-photon absorption processes, respectively. These alternative reactions proceeded independently depending on the power densities of uv photons. The formation of GEC's was saturated easily by irradiation with KrF laser pulses, and then the conversion of GEC to Ge E' centers was caused by prolonged irradiation.

I. INTRODUCTION

Irrespective of the fact that the ultraviolet (uv)-induced permanent refractive index change in germanosilicate glasses is closely associated with the presence of an absorption band near 5 eV (5-eV band),[1] the complex electron transfer phenomena triggered by irradiation with in-band uv light remains obscure. The 5-eV band in GeO_2-SiO_2 glasses is induced by two possible components, the neutral oxygen monovacancy (Ge-Ge or Si-Ge) or the neutral oxygen divacancy (Ge^{2+}).[2] The conversion of the former defect to Ge E', GeO_3^+ (or SiO_3^+), and the formation of an electron was confirmed by irradiation with a filtered Hg/Xe lamp.[2] The photon-induced electron was confirmed by the measurement of the photocurrent during uv irradiation.[3] The latter defect emits intense luminescence at 3.2 and 4.3 eV, but is stable against *low-power* 5-eV photons.[2] The exposure of glasses to a dense flux of uv photons such as excimer laser pulses causes exceedingly distinct spectral changes. The large positive absorptivity change was induced quickly above 3 eV by irradiation with KrF laser pulses.[4] It is, therefore, assumed that alternative photochemical reaction channels can be present in GeO_2-SiO_2 glasses depending on the power densities of uv light.

In order to clarify these intricate phenomena, we investigated the photochemical reactions in GeO_2-SiO_2 glasses induced by three different uv light sources, i.e., a Hg lamp, and KrF and XeCl excimer lasers. The formation process of color centers was investigated by the measurements of electron-spin resonance (ESR) and optical-absorption spectra.

II. EXPERIMENT

A 10 mol %GeO_2–90 mol %SiO_2 glass preform was sliced and polished into plates with 0.1–0.3-mm thickness. Irradiations with a Hg lamp ($\sim$16 mW/cm^2 at 4.9 eV), KrF laser (10 mJ/cm^2/pulse at 5.0 eV), and XeCl laser (90 mJ/cm^2/pulse at 4.0 eV) were carried out at room temperature. The pulse duration of the excimer lasers was 20 ns. Absorption and emission spectra of the uv-irradiated specimens were measured at 300 K by using Hitachi Model 330 and F-4500 spectrometers, respectively. The optical band-gap energy (E_g) of the glasses was estimated using GeO_2-SiO_2 thin glass films (3.8 μm thick) deposited on a SiO_2 substrate by the rf magnetron sputtering method.[5] The chemical composition of the thin films was analyzed by x-ray-photoelectron spectroscopy (excitation source: Mg $K\alpha$). The absorption spectra between 6.5 and 8 eV were measured with a Seya-Namioka-type spectrometer. X-band ESR spectra were measured at 300 K with a Brucker Model 300 E applying a 100-kHz field modulation. Resonance fields were calibrated with diphenylpicrylhydrazyl (DPPH, $g=2.0036$). The spin concentration of the uv-induced radials was evaluated by double numerical integration of first-derivative spectra, and comparison with the signal from a $CuSO_4 \cdot 5H_2O$ reference crystal of a known weight.

III. RESULTS

A. Absorption spectra

Figure 1 shows the optical-absorption spectra of $10GeO_2$-$90SiO_2$ glass disks. A distinct absorption band

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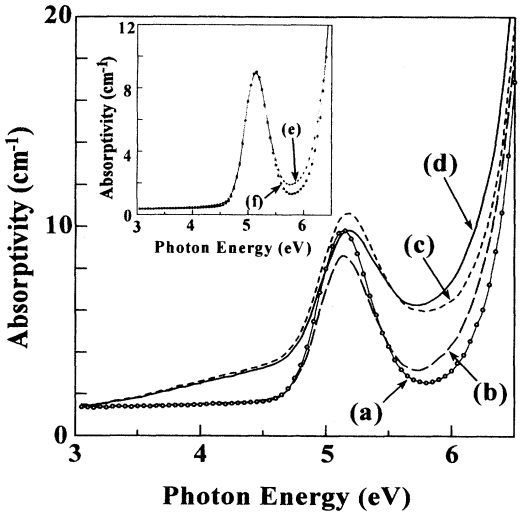

FIG. 1. Absorption spectra of $10GeO_2$-$90SiO_2$ glasses: (curve *a*) as polished, (curve *b*) illuminated with a Hg lamp for 230 h, (curve *c*) irradiated with 10^2 KrF laser shots, and (curve *d*) irradiated with a Hg lamp (230 h) and KrF laser (10^2 shots). The inset is the absorption spectrum of $10GeO_2$-$90SiO_2$ glasses (e) before and (f) after irradiation with 5×10^4 XeCl laser shots.

due to the oxygen-deficient defects was observed at 5.1 eV in the spectrum of an as-prepared specimen (curve *a*). The bleach of the 5-eV band and the increase in absorptivity above 5.7 eV were caused simultaneously by illumination with a Hg lamp. The spectral change was apparently saturated by illumination longer than 100 h. The intensity of the 5-eV band decreased by 1.3 cm^{-1} (see curve *b*). As shown by curve *c*, the exposure of the specimen to the KrF laser pulses induced remarkably different spectral changes. The pronounced increase in absorptivity above 3 eV was caused quickly by the irradiation. A notable spectral change was observed by subsequent irradiation with the Hg lamp (> 100 h) followed by irradiation with the KrF laser (10^2 shots). The absorption spectrum is represented by curve *d* in Fig. 1. It is noteworthy that the difference in absorptivity above 5.5 eV between curves *c* and *d* was almost the same as that between curves *a* and *b*. These results imply that at least two kinds of color centers were formed via independent photochemical reaction channels depending on the power density of the 5-eV photons.

The spectral changes in GeO_2-SiO_2 glasses can be caused by uv photons lower than 5 eV. The inset of Fig. 1 shows the spectral change before (curve *e*) and after (curve *f*) irradiation with 5×10^4 shots of XeCl laser pulses. It is apparent that a positive absorptivity change above 3 eV was caused. Therefore, the oxygen-deficient defects associated with the 5-eV band are not necessarily related to spectral changes above 3 eV.

B. ESR spectra

The formation of Ge *E'* centers was confirmed after exposure of the specimen to the Hg lamp radiation. The spectrum is represented by curve *a* in Fig. 2. The concentration of Ge *E'* centers was estimated at 4×10^{15} spins/cm^3; it increased linearly with the decrease in absorptivity of 5-eV band. Intense signals were observed near the resonance signal of the Ge *E'* center after irradiation with a KrF laser. The spectrum obtained is shown by curve *b*. The specimens irradiated with XeCl laser pulses exhibited similar ESR signals to curve *b*. The signals in the region of $g<2$ can be assigned to electron trapped centers associated with fourfold-coordinated Ge ions (GEC's),[6-8] which were abbreviated as Ge(1) and Ge(2) depending on the number of nearest-neighbor Ge ions.[7] The resonance signal at $g=2.01$ is attributed to hole trapped centers because of its positive *g*-shift ($g-2.0023>0$). There are three candidates: nonbridging oxygen hole centers (NBOHC),[9] peroxy radicals (PR)[9] and self-trapped hole centers (STH's).[10] Since the *g* value in question is very close to that of the third one ($g=2.008$–2.009), we assign the resonance at $g=2.01$ to the STH's.

Curve *c* in Fig. 2 represents the spectrum of the specimen irradiated with 3×10^4 KrF laser pulses. While the integrated intensity (total spin concentration) was not changed by irradiation with KrF laser pulses exceeding 10^3 shots, the shape of the resonance signal in the region of $g<2$ differs completely from curve *b*, suggesting some structural change of GEC's was caused by the continuous irradiation. Curve *d* shows the difference spectrum between curves *b* and *c*. A typical line shape of the Ge *E'* center appears after subtraction. The *g* values were identical to those of the Ge *E'* center induced by illumination with Hg lamp.[2] It was, therefore, considered that a part of GEC was converted photochemically to a Ge *E'* center during continuous irradiation with a KrF laser.

The total concentration of paramagnetic centers

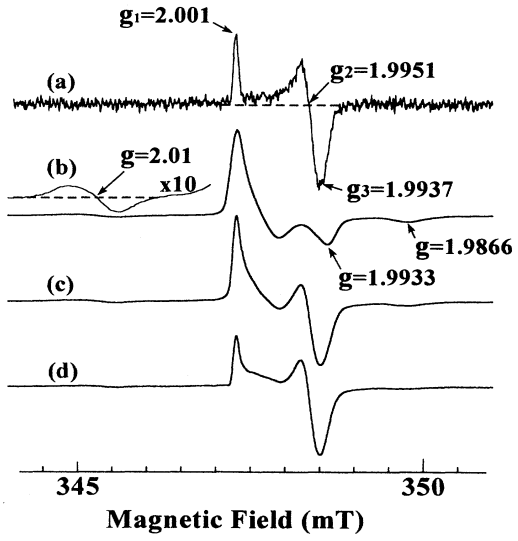

FIG. 2. ESR spectra of $10GeO_2$-$90SiO_2$ glasses irradiated with a Hg lamp and a KrF laser: (curve *a*) illuminated with a Hg lamp (230 h), (curve *b*) irradiated with 10^2 KrF laser shots, (curve *c*) irradiated with 3×10^4 KrF laser shots, and (curve *d*) difference spectrum between curves *b* and *c*.

formed by irradiation with the KrF laser was 2.6×10^{17} spins/cm^3, which was higher by two orders of magnitude than that of Ge E' center after illumination with the Hg lamp. The majority of the paramagnetic centers were formed quickly at the initial stage of irradiation ($<10^3$ shots). The same tendency was recognized in the absorption spectrum changes.

C. Emission spectra

Figure 3 shows the emission spectra of the glasses upon photoexcitation with 5.2-eV light. Two emission bands were recognized at 3.2 and 4.3 eV for the as polished sample (curve *a*). The intensity of these emission bands did not change following illumination with the Hg lamp. An obvious decrease in the intensities of these two bands was caused by irradiation with 10^2 KrF laser pulses (curve *b*). The inset shows the relation between the cumulative dose of laser pulses and the integrated emission intensity of the two bands, normalized to the initial intensity for an unirradiated specimen. The intensity was drastically decreased to ~60% of its magnitude after irradiation with less than 10^3 shots.

IV. DISCUSSION

A. Correlation between optical-absorption bands and ESR signals

Figure 4 shows the difference spectra of the specimens before and after irradiation with the Hg lamp and the KrF laser. It becomes clear that the bleached and induced bands due to irradiation with the Hg lamp are centered at 5.1 and 6.4 eV, respectively. The concentration of Ge E' centers estimated by the integrated intensity of the ESR signals increased linearly with the change in absorptivity of the 5-eV band.[2] Although the position of the absorption band of the Ge E' center has not been assigned definitely, it should be one of the dominant color centers causing the absorption above 5.5 eV. Subsequent irradiation with the Hg lamp followed by irradiation with the KrF laser resulted in an interesting spectral shape. Curve *c* in Fig. 4 shows the difference spectrum before and after irradiation with the Hg lamp (230 h) and the KrF laser (10^2 shots). The difference spectrum for the specimen before and after irradiation with the KrF laser (10^2 shots) is shown by curve *b*. As shown by curve *d*, curve *c* can be successfully produced by a simple addition of curves *a* and *b*, which indicates that independent formation channels of color centers exists in the glass matrix depending on the power densities of the uv photons. Friebele and Griscom[8] reported that the absorption bands of Ge(1) and Ge(2) induced in a GeO_2-SiO_2 optical fiber by irradiation with γ rays are located at 4.4 and 5.8 eV, respectively. As shown in the inset of Fig. 4, the absorption bands due to these GEC's can be recognized in the initial stage of irradiation with KrF laser pulses ($<10^2$ shots). The measured spectrum could be separated into two main Gaussian bands centered at 4.4 and 5.8 eV. The weak band at 4.8 eV, which has not been assigned yet, was required to improve the fit. This peak separation strongly suggests the simultaneous formation of Ge(1) and Ge(2) by irradiation with a KrF laser.

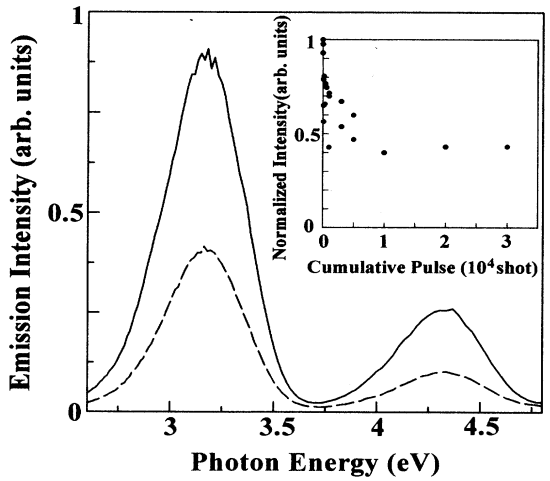

FIG. 3. Emission spectra of $10GeO_2$-$90SiO_2$ glasses (curve *a*) before and (curve *b*) after irradiation with 10^3 KrF laser shots. The inset is the relationship between the number of laser pulses and the integrated emission intensity.

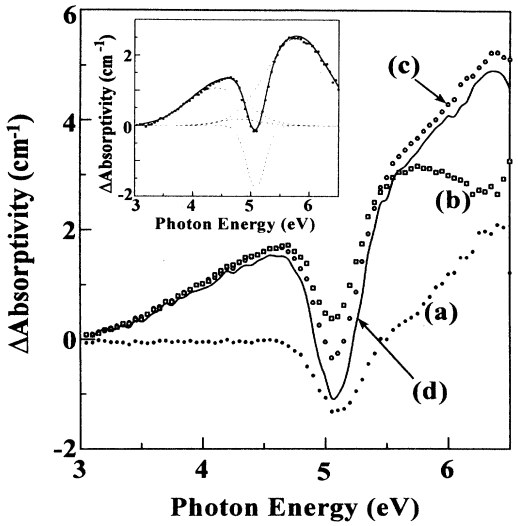

FIG. 4. Difference absorption spectra of $10GeO_2$-$90SiO_2$ glasses before and after irradiation with (curve *a*) Hg lamp (230 h), (curve *b*) KrF laser (10^2 shots), and (curve *c*) Hg lamp (230 h) + KrF laser (10^2 shots). Curve *d* is the sum of curves *a* and *b*. The inset is the difference absorption spectra of $10GeO_2$-$90SiO_2$ glasses before and after irradiation with 60 KrF laser shots. The dashed lines are the separate Gaussian components.

B. Two reaction channels via one-photon and two-photon absorption processes

The formation of the Ge E' center should proceed through a one-photon absorption process, since it can be generated using the low-power density of a Hg lamp radiation.[2] The photon flux densities of excimer lasers used

in this study are calculated as >500 kW/cm^2 (the pulse duration is 20 ns), which is higher by seven orders of magnitude than that of the Hg lamp. We must, therefore, consider the two-photon absorption process for the formation of GEC's and STH's. Albert *et al.*[11] reported that a large positive absorptivity change was caused by irradiation with ArF laser pulses (6.4 eV, 40 mJ/cm^2), and mentioned that the importance of in-band bleaching of the 5-eV band is questionable. Furthermore, we confirmed that GEC's were formed by irradiation with a XeCl laser. It is, therefore, suggested that GEC's can be generated through a two-photon absorption process. A reliable value of E_g of GeO_2-SiO_2 glass is required in order to justify our suggestion. We previously measured the absorption edge of $5GeO_2$-$95SiO_2$ glassy thin films prepared by the sputtering method, and the E_g was estimated as 7.1 eV via the Tauc plot.[12] The E_g of $10GeO_2$-$90SiO_2$ glasses used for this study should be located below 7.1 eV [$E_g(SiO_2)=9.3$ eV (Ref. 13) and $E_g(GeO_2)=5.63$ eV (Ref. 14)], which is sufficiently smaller than twice the photon energies from KrF and XeCl lasers. Thus we may reasonably conclude that the GEC's and STH's were generated via two-photon absorption process.

C. Conversion of GEC to Ge E' center

Figure 5 shows the difference absorption spectra of $10GeO_2$-$90SiO_2$ glasses before and after irradiation with a KrF laser. The spectral changes below 5 eV was almost saturated following an irradiation of 10^3 shots, while the absorptivity around 6.4 eV was increased gradually until the number of pulses reached 3×10^4. These spectral changes can be well explained by the results of ESR measurement, namely the conversion of GEC's to Ge E' centers by continuous irradiation with the KrF laser. The color center giving an intense absorption near 6.4 eV is closely related to the Ge E' centers. The structural conversion of GEC's to Ge E' centers has also been observed in germanosilicate glass irradiated with γ rays.[15] A similar structural relaxation of a photon-induced electron-trapped center localized on tetrahedrally coordinated ions has been reported for As (Ref. 16) and P.[17]

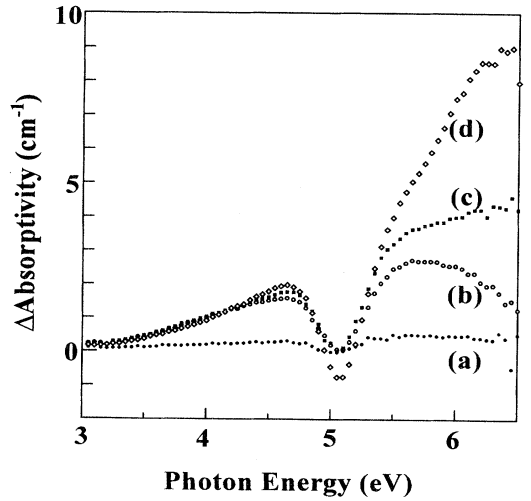

FIG. 5. Difference absorption spectra of $10GeO_2$-$90SiO_2$ glasses before and after irradiation with a KrF laser: (curve *a*) 10 shots, (curve *b*) 60 shots, (curve *c*) 10^3 shots, and (curve *d*) 3×10^4 shots.

D. Model of photochemical reactions

Figure 6 represents the schematic energy diagram showing relevant defect levels and the photochemical reactions in GeO_2-SiO_2 glasses induced by uv irradiation. In the case of irradiation with a Hg lamp, the following reaction proceeds through a one-photon absorption process.[2]

$$\text{Ge-Ge (or Ge-Si)} \xrightarrow{h\nu} \text{Ge E'} + \text{GeO}_3^+(\text{or SiO}_3^+) + e^- . \quad (1)$$

This reaction will be rapidly saturated because of the low concentration of neutral oxygen monovacancies ($\sim10^{16}$ cm^{-3}).[2] GEC's and STH's were formed simultaneously by irradiation with an excimer laser (see Fig. 2). Therefore, we propose the next reaction path:

$$\text{—Ge— (four-fold coordinated)} + \text{O (bridging oxygen)} \xrightarrow{2h\nu} \text{GEC} + \text{STH}. \quad (2)$$

Since its energy level is located at the uppermost level of the valence band, the lone pair electrons on bridging oxygens are excited to the conduction band via two-photon absorption processes. The conversion of GEC's to Ge E' centers can be described by the following reaction.

$$\text{GEC} \rightarrow \text{Ge}E' + \text{O (nonbridging oxygen)} . \quad (3)$$

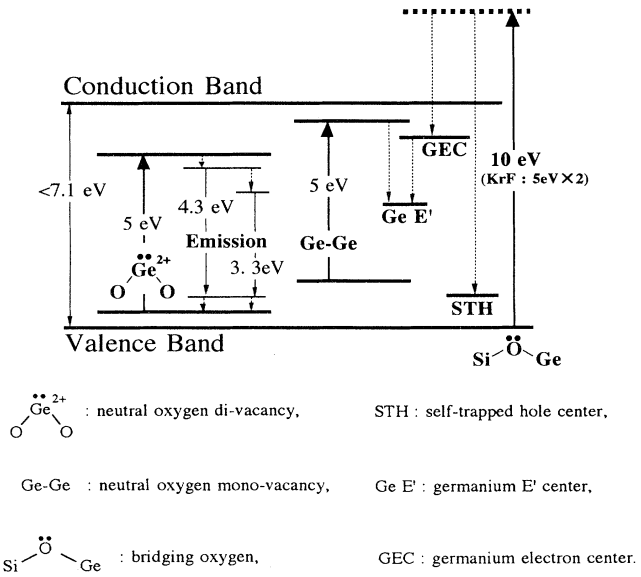

FIG. 6. Schematic energy diagram showing relevant defect levels and photochemical reactions in GeO_2-SiO_2 glasses caused by irradiation with uv light.

There is an intimate correlation between the formation of GEC's and the decrease in emission intensity. Poirier *et al.*[18] reported the decrease in luminescence intensity in GeO_2-SiO_2 optical fibers irradiated with the fourth harmonic light of a cw Nd-YGA (yttrium aluminum garnet) laser. As shown in Fig. 6, the emissions are due to the neutral oxygen divacancy (Ge^{2+}) with a lone pair electron occupying the uppermost level.[2] There is a possibility that the electrons in this nonbonding level can be excited to the conduction band via a two-photon absorption process. However, no ESR signal without Ge E', GEC's and STH's was observed by the ESR measurement. Although there is little experimental evidence, we suppose that one of the origins is the structural distortion of the ligand field around Ge^{2+}. Russell *et al.*[19] reported that densification of the glass occurred by uv irradiation, which should affect the structural distortion around Ge^{2+}. Further study is now in progress.

In conclusion, we investigated the spectral changes in GeO_2-SiO_2 glasses caused by uv photons emitted from a Hg discharge lamp (4.9 eV), KrF laser (5.0 eV), and XeCl laser (4.0 eV). Two kinds of photochemical reactions were observed depending on the power densities of the uv radiation.

1. One-photon absorption process

The photochemical reaction caused by illumination with a Hg lamp ($\sim$16 mW/cm^2), that is, the conversion of the neutral oxygen monovacancy to Ge E', GeO_3^+ (or SiO_3^+), and an electron, proceeded via a one-photon absorption process.

2. Two-photon absorption process

GEC's and STH's were formed by irradiation with a KrF laser. Because of the high-power density of the laser pulses (>500 kW/cm^2) and the optical band-gap energy of the glass (<7.1 eV), the two-photon absorption process was the dominant formation path for GEC's and STH's. The experimental evidence for the formation of these centers by irradiation with a XeCl laser supports our suggestion.

Subsequent illumination with a Hg lamp followed by irradiation with a KrF laser apparently demonstrated that the photochemical reactions through one- and two-photon absorption processes proceeded independently in the glass matrix depending on the power densities of the uv photons. The concentration of GEC's was rapidly saturated by irradiation with a KrF laser ($<10^3$ shots), and then the conversion of GEC to Ge E' was confirmed from the results of ESR and absorption spectra.

ACKNOWLEDGMENTS

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