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Paramagnetic centres induced in Ge-doped SiO_2 glass with UV irradiation

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Abstract. Changes in concentrations of the photo-induced paramagnetic centres, Ge E′ centre, Ge electron centre (GEC) and positively charged Ge lone-pair centre ($(GLPC)^+$) in four Ge-doped SiO_2 glasses with Ge contents of 1.0, 1.4, 6.9 and 9.2 mol% were investigated, using a KrCl excimer lamp (5.6 eV, 7.0 mW cm^{-2}) and a KrF excimer laser (5.0 eV, 4 MW cm^{-2}) as photon sources. When the glasses were irradiated with photons from the lamp, the Ge E′ centre and the GEC were induced in all the glasses. However, the $(GLPC)^+$ was observed only in the sample with Ge content of 1.4 mol% where the concentration of the induced Ge E′ centre was smaller than that of the induced GEC. The irradiation of photons from the laser induced the GEC and $(GLPC)^+$ in all the glasses. When the photon irradiation from the laser was continued onto the glasses, the Ge E′ centres were induced and the concentration of the $(GLPC)^+$ was found to decrease with an increase in the concentration of the Ge E′ centres. From these phenomena, it was concluded that the generation of the Ge E′ centres diminishes the concentration of the $(GLPC)^+$.

1. Introduction

Refractive-index changes accompanied by structural changes are induced in Ge-doped SiO_2 glass by the irradiation of ultraviolet (UV) photons. Because of the photo-sensitivity of Ge-doped SiO_2 glass, the glass is used as optical elements, such as an optical-filter which reflects a specific wavelength by Bragg gratings [1] fabricated in Ge-doped SiO_2 optical fibre by UV photons. It has been reported that the Ge oxygen-deficient centres (GODCs) existing in the oxygen-deficient type glass are considered to be responsible for the structural change which causes the refractive-index change [2–7]. Two kinds of GODC, the neutral oxygen monovacancy (NOMV) and the Ge lone-pair centre (GLPC), have been reported [2]. The structures of these defects are shown in figure 1. It has been reported that the NOMV and the GLPC have absorption bands at 5.06 and 5.16 eV, respectively [2]. As shown in figure 1, the NOMV becomes the Ge E′ centre by the irradiation of UV photons during which an electron is released [2].

Two electron spin resonance (ESR) signals, named Ge(1) and Ge(2) [8], are reported to appear in Ge-doped SiO_2 glass exposed to photons from a KrF excimer laser [9, 10]. The Ge(1) signal is known to be due to the Ge electron centre (GEC) [11–15]. In our previous paper, we reported that the Ge(2) signal is due to the positively charged GLPC ($(GLPC)^+$), which donated an electron to generate the GEC, by analysing the absorption change around 5.0 eV induced

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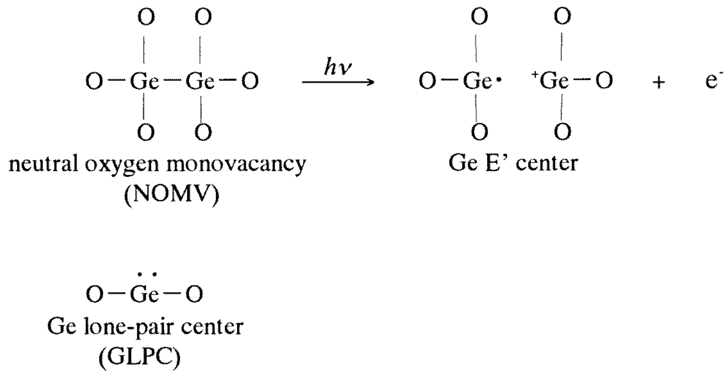

Figure 1. Structures of the defect centres in Ge-doped SiO_2 glass. The NOMV is known to become the Ge E′ centre by UV photon irradiation.

by photon irradiation from a KrF excimer laser and the thermally stimulated luminescence (TSL) which was observed at 3.1 eV in the sample pre-irradiated by the KrF excimer laser [9]. In the present research, further details of generation mechanisms of paramagnetic centres, GEC, $(GLPC)^+$ and Ge E′ centres, upon high-dose irradiation of UV photons are examined by observing the ESR signals induced in four different samples with different Ge contents.

2. 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 vapour-phase axial deposition method. The samples were cut and polished into plates of 0.3 mm thick. A KrF excimer laser (Lambda Physik, LPX 105i, 5.0 eV) and a KrCl excimer lamp (Ushio, UEM 20-222, 5.6 eV) were used as the irradiation photon sources. The pulse duration of the excimer laser is about 20 ns, and its energy density is 80 mJ cm^{-2} per pulse, which corresponds to 4 MW cm^{-2}, while the energy density of the excimer lamp is 7.0 mW cm^{-2}. Because of this difference in energy density, the KrF excimer laser induces a two-photon process in addition to a one-photon process, while only a one-photon process is induced by the KrCl excimer lamp. The ESR spectra were obtained by a JEOL RE-2XG spectrometer at the X band frequency. The concentration of paramagnetic centres was evaluated by double numerical integration of first-derivative spectra, and comparison with the signal from diphenylpicrylhydrazyl (DPPH, $g = 2.0036$) of a known weight. The accuracy of the standard is believed to be ±20%. All the experiments were done at room temperature.

3. Results

Figure 2(a) shows the ESR spectrum of sample A irradiated by the KrCl excimer lamp for 15 hours. In this spectrum, the ESR signal of Ge(1) which is due to the GEC and that of Ge E′ centres overlap each other as clearly indicated in figure 2(a′). The Ge(2) signal is not seen in this spectrum, which means that the $(GLPC)^+$ does not exist in the sample after the irradiation. Similarly, the GEC and Ge E′ centre were observed in samples C and D after similar irradiation, and the $(GLPC)^+$ was not. Figures 2(b) and 2(b′) are the ESR spectra observed in sample B after irradiation by the lamp for 15 hours. The Ge(2) signal due to the $(GLPC)^+$ is seen besides the signals due to the GEC and Ge E′ centre. Table 1 shows the concentrations of

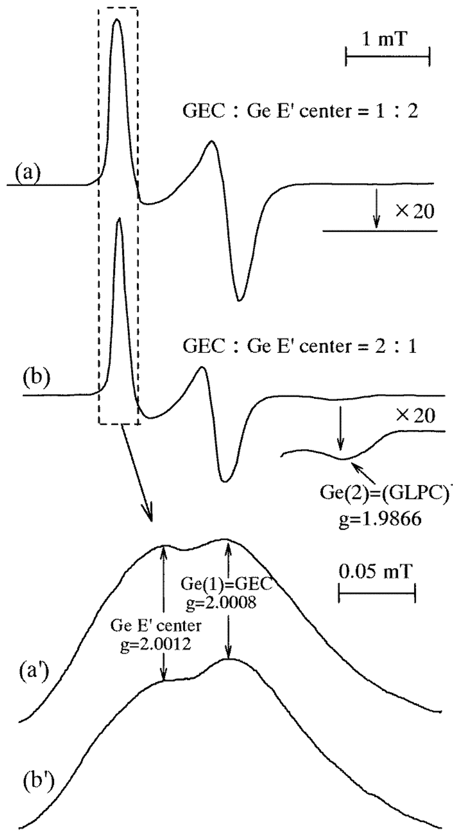

Figure 2. ESR spectra in sample A (a) and sample B (b) observed after the photon irradiation of KrCl excimer lamp for 15 hours. Spectra (a′) and (b′) represent the expansion of spectra (a) and (b) in the region surrounded by the dotted box, respectively.

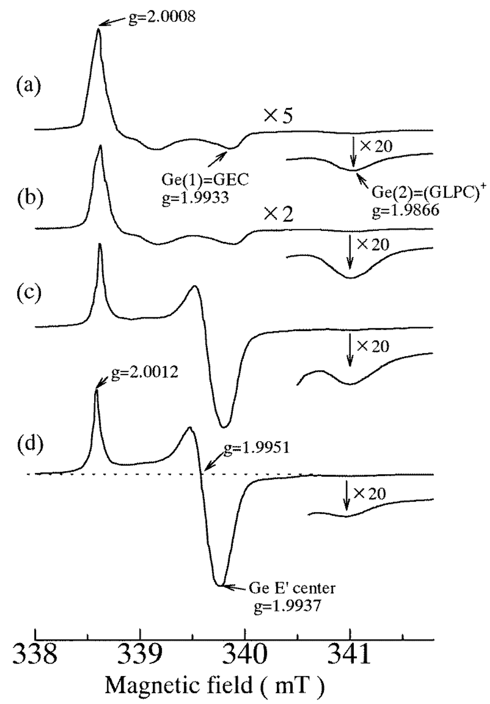

Figure 3. ESR spectra in sample C observed after the photon irradiation of KrF excimer laser. (a) 10 shots, (b) 1×10^2 shots, (c) 1.3×10^6 shots, (d) 2.3×10^6 shots.

Table 1. Concentrations of the paramagnetic centres, Ge E′ centre, GEC and $(GLPC)^+$ induced in the samples with photon irradiation from the KrCl excimer lamp. The ambiguity comes from errors in calibration of the total concentration and separation of the peaks.

Sample	Ge content (mol%)	Ge E′ centre (cm^{-3})	GEC (cm^{-3})	$(GLPC)^+$ (cm^{-3})
A	1.0	$(7 \pm 2) \times 10^{15}$	$(4 \pm 2) \times 10^{15}$	—
B	1.4	$(2 \pm 0.5) \times 10^{15}$	$(3 \pm 1) \times 10^{15}$	$(2 \pm 0.5) \times 10^{15}$
C	6.9	$(2.4 \pm 0.2) \times 10^{16}$	$(3.5 \pm 2) \times 10^{15}$	—
D	9.2	$(2.6 \pm 0.2) \times 10^{16}$	$(4 \pm 2) \times 10^{15}$	—

these paramagnetic centres induced in the samples. The concentration of the Ge E′ centre is higher than that of GEC in samples A, C and D, while it is smaller than that of GEC in sample B. The result shown in table 1 also implies that the efficiency of the generation of the Ge E′ centre might be higher in glasses with higher Ge contents.

The ESR spectrum of sample C was found to change as shown in figure 3 when irradiated with the KrF excimer laser. The GEC and $(GLPC)^+$ are observed in the sample which was

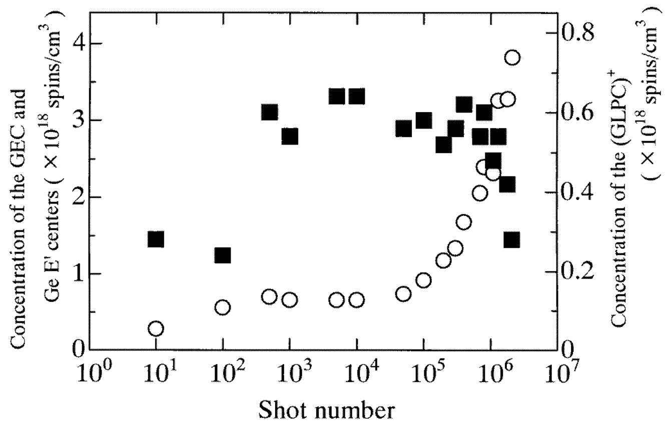

Figure 4. Change in the concentration of paramagnetic centres in sample C induced by the photon irradiation of a KrF excimer laser. The sum of the concentration of the GEC and Ge E′ centre (open circle) and the concentration of the $(GLPC)^+$ (solid square). The concentration of the $(GLPC)^+$ is estimated from the concavity at 341 mT.

irradiated with ten laser pulses. With the further irradiation, the Ge E′ centre was induced in addition to the GEC and $(GLPC)^+$. Figure 4 shows the change in the concentrations of the paramagnetic centres as a function of the number of laser shots. Since the accurate separation of the signals due to the GEC and Ge E′ centres was impossible, the sum of the two centres is shown by the open circle, while the solid square denotes the concentration of the $(GLPC)^+$. Here, the concentration of the $(GLPC)^+$ is estimated as follows. In [9], by investigating the decrease of the GLPC and the induction of the GEC by the photon irradiation from the same excimer laser that is used in the present research, we have confirmed that the concentration of the $(GLPC)^+$ is equal to that of the GEC when the glass is irradiated with a few tens of pulses by the present KrF excimer laser. Therefore, the concentration of the $(GLPC)^+$ is estimated to be a half of the total concentration of the induced paramagnetic centres, GEC and $(GLPC)^+$, in the sample irradiated with ten laser pulses. When further irradiation is applied to the glass, the concentration of the $(GLPC)^+$ can be estimated by the depth of the concavity of ESR spectrum around 341 mT ($g = 1.9866$), since no other signals overlap at this magnetic field and the concentration of the $(GLPC)^+$ is considered to be proportional to the depth. The concentration of the $(GLPC)^+$ showed saturation by the laser shots of about 5×10^2, and decreased with further irradiation. From our previous study, it is considered that the concentration of the GEC was saturated by the irradiation of 5×10^2 pulses and was virtually unchanged with further irradiation [7]. Therefore, the increment of the total paramagnetic centres with irradiation of more than about 10^5 shots is considered to be due to the increment of the Ge E′ centres.

4. Discussion

The $(GLPC)^+$ which are observed as the Ge(2) signal in the ESR spectrum were induced by the irradiation with the KrCl excimer lamp in sample B, while they were not in samples A, C and D. The result shown in table 1 indicates that the $(GLPC)^+$ is observed in the sample where the concentration of the induced Ge E′ centre is smaller than that of the induced GEC. From this result, it is expected that the generation of the Ge E′ centre diminishes the $(GLPC)^+$. As seen in figure 4, the concentration of the $(GLPC)^+$ begins to decrease when the concentration

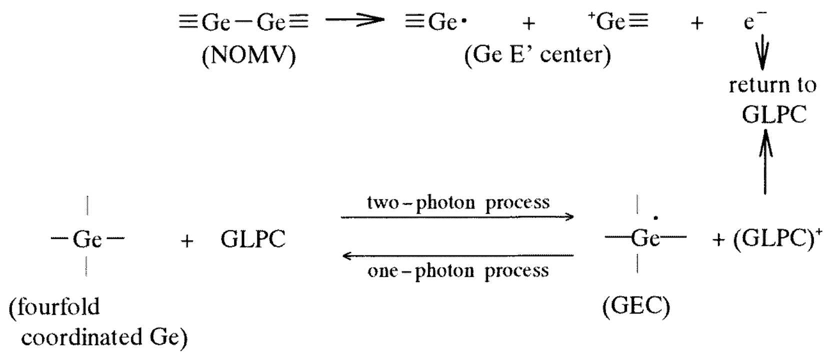

Figure 5. Proposed model for the structural changes induced by the photon irradiation of KrF excimer laser.

of the Ge E′ centres shows an increase after about 10^5 shots of the KrF excimer laser. This phenomenon validates the above-mentioned expectation. As shown in figure 1, electrons are known to be released upon the formation of the Ge E′ centres from the NOMVs [2]. The $(GLPC)^+$ traps the released electron and becomes the GLPC. Figure 5 shows the proposed series of structural changes. Since the Ge E′ centres are scarcely induced up to 5×10^2 shots of the KrF excimer laser [7, 10], the concentration of $(GLPC)^+$ or the Ge(2) signal intensity increases. If the number of $(GLPC)^+$ which become GLPCs by trapping the electrons released from the GECs [7] or the ones released from the NOMVs upon the formation of the Ge E′ centres is equal to that of the $(GLPC)^+$ which are induced from the GLPC's, the Ge(2) signal intensity should be unchanged. This is exactly what was observed during the irradiation of 5×10^2 to 10^6 shots of KrF excimer laser photons. With further irradiation, as the number of electrons released from the NOMVs increases, the decrease of $(GLPC)^+$ with trapping the electrons becomes larger than the increase of the $(GLPC)^+$, and thus the Ge(2) signal intensity decreases.

In [9] we assumed that the concentration of the GEC is equal to that of the $(GLPC)^+$, while in [3] and [12] the concentration of Ge(1) (=GEC) was reported to be larger than that of Ge(2) (=$(GLPC)^+$) when the glass was irradiated by UV photons or γ-rays. The model shown in figure 5 gives a clear solution to this discrepancy. The concentration of the GEC (=Ge(1)) and that of $(GLPC)^+$ (=Ge(2)) are considered to be equal, when the Ge E′ centre is not induced, which corresponds to the case reported in [9]. On the other hand, the concentration of the $(GLPC)^+$ becomes smaller than that of the GEC as reported in [3] and [12], when the Ge E′ centre is observed in addition to the GEC and $(GLPC)^+$. In [14], it has been reported that when Ce^{3+} is doped as an electron donor in Ge-doped SiO_2 glass, the GEC (=Ge(1)) is induced but the $(GLPC)^+$ (=Ge(2)) is not. In the present research, the NOMV plays the role of Ce^{3+} to be an electron donor and diminishes the $(GLPC)^+$ when high-dose UV photons are irradiated.

The above-mentioned conclusion is deduced based on the model that the Ge(2) signal is due to the $(GLPC)^+$ [9]. It might be unreasonable to assign the Ge(2) signal, whose g value is smaller than 2.0023, to a hole centre. However, it has been reported that the defect which shows the Ge(2) signal acts like a hole centre [14]. Furthermore, a trapped hole on Sn^{2+} shows the ESR signal with g values smaller than 2.0023, $g_{\parallel} = 1.972$ and $g_{\perp} = 2.000$, where Sn^{2+} indicates the Sn lone-pair centre in tin oxide [16]. Since Sn is a congener of Ge, this fact supports the assumption that the Ge(2) signal is due to the $(GLPC)^+$, even though the g value is smaller than 2.0023.

5. Conclusion

Through the analysis of ESR spectra induced by photon irradiation, the following conclusions were obtained. The Ge(1) signal is due to the GEC, while the Ge(2) signal is due to the $(GLPC)^+$ which donated an electron for the formation of the GEC. When both the Ge E′ centres and the GECs exist in the glass, the $(GLPC)^+$ trap electrons which were released from the NOMVs during the formation of the Ge E′ centres and become the GLPCs.

Acknowledgments

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