Defect formation in SiO_2:GeO_2 glasses studied by irradiation with excimer laser light

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The formation of germanium electron centers in $[SiO_2]_9[GeO_2]$ glasses by irradiation with excimer laser light was found to occur via two-photon absorption processes for ArF, KrF, and XeCl lasers. Although the wavelength of KrF laser light corresponds to the absorption band of preexisting oxygen-deficient defects associated with Ge ions, no significant difference in the formation efficiency was seen between ArF and KrF laser lights. The efficiency for XeCl laser light was smaller by four orders of magnitude than that for ArF or KrF light, but was still larger by an order of magnitude than the formation efficiency of Si E' centers in SiO_2 glasses with ArF laser light. It was shown that defect-formation efficiencies for the case where the two-photon energy is close to the optical band gap are much lower than for that when the two-photon energy is enough to exceed the band gap. [S0163-1829(96)51718-2]

Defect formation in SiO_2:GeO_2 glasses with ultraviolet (uv) radiation is now attracting much interest because it is considered to be closely related to photoinduced refractive index changes (PIRC's) leading to the formation of Bragg gratings.[1–4] It is agreed that PIRC's in SiO_2:Ge glasses by Ar^+ laser (488 nm)[2] or filtered Xe/Hg lamp (Ref. 5) irradiation originate from the photochemical conversion of Ge-related oxygen-deficient centers (ODC's) giving an optical absorption band centered at 5 eV into Ge E' centers having an intense absorption band peaking at 6.3 eV.[6] A different channel to induce the PIRC's was proposed by Albert *et al.*,[7] who demonstrated that photosensitivity obtained with ArF excimer light (193 nm) is at least as efficient as when the on-resonance light (240~248 nm) is used, and in some cases much more efficient. Recently, we reported[8] that defect species created by irradiation with excimer laser lights differ from that with an Hg lamp, i.e., the former is a germanium-electron-center (GEC) (Ref. 9) with fourfold coordination of oxygens and a self-trapped oxygen hole center (STH) (Ref. 10) and the latter a Ge E' center.[11] An entirely different mechanism was suggested for the defect formation by ArF laser irradiation, i.e., Ge E' centers are produced by direct excitation of the preexisting oxygen vacancies with 5 eV light from the lamp, while the formation of GEC's and STH's by the laser occurs by a band-to-band excitation via two-photon absorption processes. It was also found in the preceding paper[8] that GED's created by irradiation with ArF or KrF laser light are converted into Ge E' centers upon prolonged irradiation. This conversion may be regarded as structural relaxation of a GEC with a negative charge into a Ge E' with no nominal charge. It is considered that the driving force is electrostatic repulsion between a trapped electron and the neighboring oxygens and the structural change occurs in order to restore local electroneutrality around the Ge ions by detaching a nonbridging oxygen (with a negative charge) from its coordination sphere.

Therefore, the concentration of Ge E' centers in the long-irradiated glasses exceeds preexisting Ge-related ODC concentrations because GEC's, which are the precursors of Ge E' centers in this case, are created from the intrinsic structural units. In this paper we report a quantitative relation between GEC formation in SiO_2:Ge glasses and photon densities of various excimer lasers and a comparison of defect formation by excimer lasers between SiO_2-GeO_2 and SiO_2 glasses.

Samples used were glass plates with ~0.2-mm thickness, which were cut from a germania-silica glass rod prepared by the vapor phase axial deposition method and then optically polished. The nominal chemical composition is $[SiO_2]_9[GeO_2]$ in mol.

Vacuum ultraviolet (vuv) and uv absorption spectra were measured with a Seya-Namioka–type spectrometer using synchrotron radiation light as the light source and with a conventional dual beam spectrophotometer (light source; D_2 lamp).

The specimen used for vuv absorption measurements to evaluate the optical band gap was a thin film (~5 μm thick) deposited on a SiO_2 glass substrate by an rf sputtering method. The measurements of uv absorption were performed on a glass plate (~0.2 mm thick).

Irradiation with excimer laser light was carried out at ambient temperature using ArF (photon energy; 6.4 eV), KrF (5.0 eV), and XeCl (4.0 eV) lasers. The repetition and the duration of a laser pulse were 10 Hz and ~20 ns, respectively. Electron spin resonance (ESR) spectra were measured at 20 °C using a Brucker model ESP-300 and concentrations of the GEC's were evaluated by the comparison method employing a known weight of $CuSO_4 \cdot 5H_2O$ single crystal as a standard.

Figure 1 shows the relation between GEC concentrations created per laser pulse and the energy density of a pulse. Here, data were taken from the linear region in the log-log plots of GEC concentrations vs laser shot number, i.e., 50

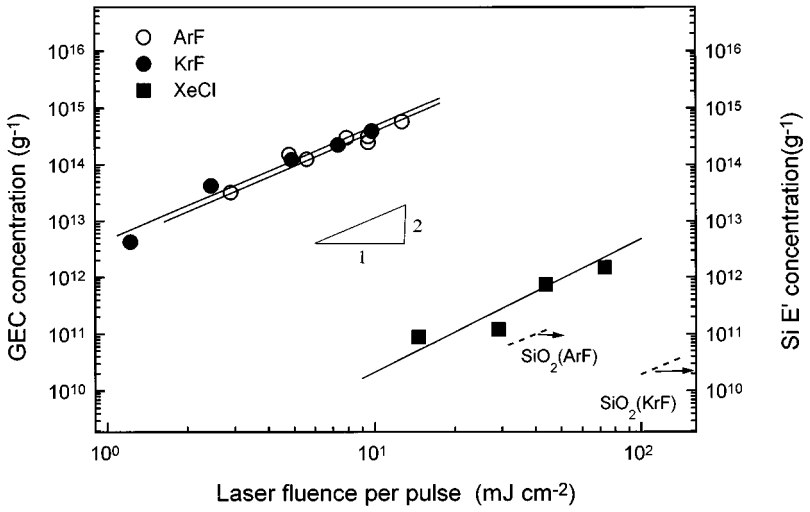

FIG. 1. Concentrations of GEC created per pulse of various excimer lasers as a function of laser fluence per pulse. The slope in the figure is 2. Also shown are data on Si E' center creation in SiO_2 glasses (taken from Ref. 13).

pulses for ArF or KrF laser and 5000 pulses for XeCl laser (ESR signal of GEC's were too weak after irradiation of 50 pulses). For comparison we show by dotted lines the relation for Si E' centers[12] induced with ArF or KrF laser light in oxygen-deficient-type synthetic SiO_2 glasses (the formation of Si E' centers with XeCl laser light was *not* detected even for $\sim$700 mJ/cm^2/pulse $\times 10^5$ shots). The data are taken from our previous paper.[13] The following two facts are evident from the figure. First, the GEC concentration produced per pulse (N) is proportional to the energy density of laser light of a pulse (I) in log-log plots and the slope for each wavelength of excimer laser, 1.8 ± 0.2 (standard deviation) for ArF and KrF lasers, 1.7 ± 0.4 for XeCl laser. This result demonstrates that the GEC formation is primarily controlled by the two-photon processes for each excimer laser light, i.e., as a first approximation N may be expressed as $N=kI^2$, where k denotes the apparent formation efficiency. Second, the k value for an ArF laser is almost the same as that for an KrF laser, and its value for a XeCl laser is smaller by 4 orders of magnitude than that for ArF or KrF laser but still larger by 1$\sim$2 orders of magnitude than that of Si E' formation in SiO_2 glasses by ArF or KrF laser irradiation.

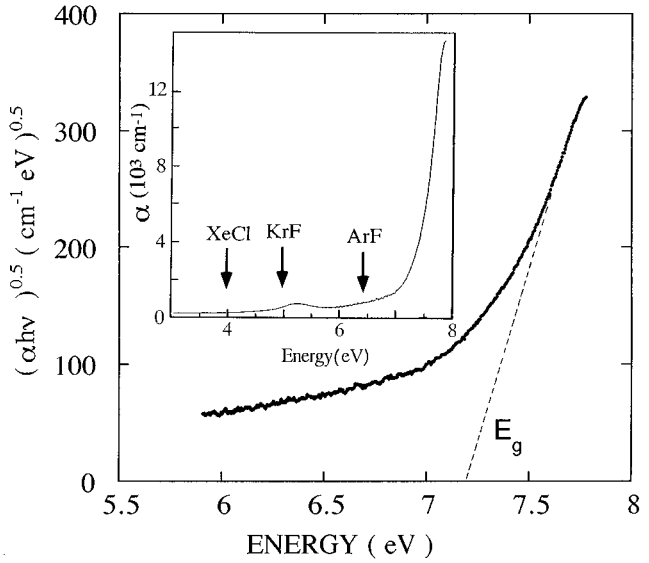

FIG. 2. Tauc plot of vacuum uv-uv absorption of $[SiO_2]_9[GeO_2]$ glass thin film ($\sim$5 μm thick). The optical band gap (E_g) is estimated to be 7.2 eV from the plot. Inset is the uv absorption spectrum of the glass plate ($\sim$0.2 mm thick). Arrows indicate one-photon energy of relevant excimer lasers.

Figure 2 shows the Tauc plot[14] [the energy dependence of optical absorption near the absorption edge of amorphous materials may be expressed as $\alpha\propto(h\nu-E_{\rm opt})^2/h\nu$, where α and $E_{\rm opt}$ denote absorption coefficient and optical band gap, respectively] of the optical absorption depicted in the inset. The optical band gap evaluated from the Tauc plot is $\sim$7.2 eV.

Table I summarizes the ratio, $2h\nu/E_{\rm gap}$, of two-photon energy of various excimer laser lights to the optical band gap of $[SiO_2]_9[GeO_2]$ and SiO_2 glasses. The $2h\nu/E_{\rm gap}$ value in the $[SiO_2]_9[GeO_2]$ glass larger than unity for all laser lights examined here, while in SiO_2 glasses the value (0.85) for XeCl laser is smaller than unity. It is evident from Fig. 1 that two-photon processes primarily control defect formation by excimer laser lights in both types of glass. Provided that defect formation occurs by a band-to-band excitation via two-photon absorption processes, the relation $2h\nu/E_{\rm gap}>1$ must be met as a prerequisite. The values of $2h\nu/E_{\rm gap}$ are consistent with the experimental results.

Next to be considered is a difference in the k value for the three different excimer laser lights. Two facts worth noting are seen in the experimental results. First is the fact that the efficiency of KrF laser light is almost the same as that of ArF light notwithstanding that the one-photon energy (5 eV) of the KrF laser light corresponds to the absorption band (on

TABLE I. Ratio of two-photon energy of various excimer laser lights to the optical band gap (E_g) of $[SiO_2]_9[GeO_2]$ and SiO_2 glasses.

Glasses	XeCl	KrF	ArF
$[SiO_2]_9[GeO_2]$ [a]	1.1	1.4	1.8
SiO_2 [b]	0.85	1.1	1.4

[a] E_g ($[SiO_2]_9[GeO_2]$)=7.2 eV (this work).
[b] E_g (SiO_2)=9 eV [Z. A. Weinberg, G. W. Rubloff, and E. Bassous, Phys. Rev. B **19**, 3107 (1979)].

resonance) of the ODC associated with Ge ions, while the energy of the ArF laser is off resonance. This observation underlines the fact that GEC's are not derived from the precursor defects but from intrinsic GeO_4 units. The formation of the Ge E' center from the ODC's coordinated by 2 Ge ions occurs by trapping a positive hole following a structural relaxation of the pyramidal GeO_3^+ into a planar form as shown in Eq. (1).[15]

$$\begin{array}{ccccc} O & & O & & O \quad O\ O \\ \backslash & & / & & \backslash \quad \backslash\ / \\ O\text{—}Ge\text{-(vacancy)-}Ge\text{—}O & + h^+ \rightarrow & O\text{—}Ge\cdot & + & Ge^+, \\ / & & \backslash & & / \quad \vert \\ O & & O & & O \quad O \end{array} \qquad (1)$$

where h^+ denotes a positive hole. On the other hand, such a distinct displacement of relevant atoms is not involved in the formation process of the GEC's from GeO_4 units. Thus, we consider that the formation of GEC's is energetically favorable over the Ge E' formation from the ODC's [Eq. (1)].

Second is the fact that the efficiency for XeCl laser light is extremely small (by four orders of magnitude) as compared to KrF and ArF laser lights. It is known that two-photon absorption coefficients do not vary drastically in the region $2h\nu/E_{gap}>1$.[16] Therefore, the observed difference in k results form the difference in the quantum efficiency of the GEC formation between XeCl and KrF (or ArF) laser lights. A similar difference is noted in the efficiency of the Si E' formation between ArF and KrF laser lights. The $2h\nu/E_{gap}$ value for a combination of XeCl laser and the GeO_2-SiO_2 glass or of KrF laser and SiO_2 glass is 1.1, indicating that a hole-electron pair is generated near the band edge by a band-to-band excitation via two-photon absorption processes. These experimental results suggest that the nature of hole-electron pairs generated by laser lights corresponding to $2h\nu/E_{gap}\sim1$, differs considerably from that by laser lights with $2h\nu/E_{gap}>1$. A plausible difference in the nature is that the lifetime of the hole-electron pair in the former is much shorter than that in the latter. A shorter lifetime would lead to the reduction of quantum efficiencies because a GEC is created by trapping an electron on a GeO_4 unit. Since it is believed that the mobility gap, which originates from a structural disorder, exists above the optical band gap in amorphous materials,[17] it would be of interest to examine the relation between the mobility gap and the defect formation efficiency by band-to-band excitation using a tunable laser.

Last, the difference in the formation efficiency between GEC and Si E' centers is discussed. The k value for the GEC formation in GeO_2-SiO_2 glasses is larger by $\sim$5 orders of magnitude than that for Si E' center in SiO_2 glasses when using ArF laser light, and the difference goes up to $\sim$7 orders of magnitude for KrF laser light. No Si-electron trapped centers, which are analogs of the GEC's, has been found so far (it is considered that vacant Si 3d orbitals are unavailable for electron trapping). There are two possible routes for Si E' formation, i.e., an intrinsic route and an extrinsic (precursor) route. The latter is an analog of Eq. (1) and involves a large atom (Si) displacement process as described above. Of course, the intrinsic route involves bond scission processes because Si E' centers with threefold coordinated oxygens are derived from SiO_4 units. Therefore, it is reasonable to assume that the formation efficiency of Si E' centers is much lower than that of the GEC's. No formation of Si E' centers has been observed experimentally in SiO_2-GeO_2 glasses irradiated with ArF or KrF laser light. A large difference in the k value between GEC and Si E' centers obtained here quantitatively substantiates this observation.

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