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Nature and origin of the 5-eV band in SiO_2:GeO_2 glasses

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The sources of an absorption band at ~5 eV observed in SiO_2:GeO_2 and GeO_2 glasses have not been unambiguously identified. Results reported here are consistent with the source of two types of neutral oxygen vacancies. Samples of $95SiO_2$:$5GeO_2$ and $90SiO_2$:$10GeO_2$ were prepared by a chemical vapor deposition soot-remelting method. Optical-absorption and electron paramagnetic resonance spectra were measured. An absorption band centered at 5 eV in as-prepared SiO_2:GeO_2 glasses is composed of two components. One has a peak at 5.06 eV and a FWHM (full width at half maximum) of 0.38 eV. Illumination with uv light bleached this band, and generated Ge E' centers. A linear relation was found between the decrement in the intensity of the 5.06-eV component and the concentrations of uv-induced Ge E' centers. This relation is a basis for attributing the defect responsible for this component to the precursors of uv-induced Ge E' centers. We propose that the 5.06-eV band is due to neutral oxygen monovacancies (NOV's) coordinated by two Ge ions. The oscillator strength of this band was evaluated to be approximately 0.4 ± 0.1 assuming that the NOV's are converted into Ge E' centers by absorption of uv quanta. The activation energy for this conversion process was of the order of 10^{-2} eV. The second component of the absorption spectra has a peak at 5.16 eV and a FWHM of 0.48 eV. This band is not bleached but emits luminescence bands at 3.2 eV (intense) and 4.3 eV (weak) when irradiated with 5-eV light. Based on other research, we assign this band to Ge^{2+} ions coordinated by two oxygens and having two lone pair electrons (neutral oxygen divacancies). The concentrations of Ge^{2+} ions were much larger than those of the NOV's and the ratio of the NOV's to Ge^{2+} ions increases with increasing GeO_2 content. A similarity was found in the characteristics of these two types of oxygen-deficient defects to those in SiO_2 glasses.

I. INTRODUCTION

The presence of an intense absorption band near 5 eV in as-prepared GeO_2 glasses was independently reported by Garino-Carina[1] and Cohen and Smith[2] in 1958. Since then, properties and behaviors of this band have been examined. Cohen and Smith found that uv illumination reduces the intensity of this band and concluded that a reduced germanium specie, probably Ge^{2+}, was the source of this band. Vergano and Uhlmann[3] examined the effect of oxygen deficiency, based on the intensity of the 5-eV band, on crystallization kinetics of GeO_2 glasses. Jackson *et al.*[4] reported that the oxygen-deficient defects were not single oxygen vacancies and suggested the possibility of dioxygen or trioxygen vacancy based on analysis of effects of oxygen partial pressure during melting on the intensities of the 5-eV band. Schultz[5] found that this band also occurs in binary germania silica and germania-doped silica glasses. In 1982 Yuen[6] reported that the origin of the 5-eV band in germanium silicate glasses is divalent germanium ions, based upon the close similarity of uv absorption between these glasses and GeO gas molecules. Ge^{2+} concentrations are evaluated (the molar extinction coefficient 9×10^3 cm^{-1}/g mole of Ge^{2+}/L) (Ref. 5) to be of the order of 10^{-2} wt %.

Germania-silica or SiO_2:GeO_2 glasses show photosensitive grating effects (PGE) and second-harmonic generation (SHG). Hill *et al.*[7] reported the buildup (PGE) of Bragg reflection in germania-silica glass fibers illuminated with Ar^+ laser light (488 nm). Osterberg and Margulis[8] found high-efficiency (>5%) second-harmonic generation from Ge-doped silica-core single-mode fibers with exposure to intense light (1.06 μm) from yttrium aluminum garnet (YAG):Nd laser light. Tsai *et al.*[9] found a close correlation between the conversion efficiency of the SHG and the laser-induced Ge E' center concentrations. Simmons *et al.*[10] demonstrated a similar wavelength-dependent response for the generation of Ge E' centers and the formation of PGE in germania-doped silica glass fibers. Their results support a model for the grating formation by two-photon absorption into the uv-bleachable absorption band of an oxygen-deficient germania site which creates hole traps or Ge *E*′ centers.

There is general agreement that the origin of 5-eV band is an oxygen-deficient defect related with germanium ions but no quantitative information on the 5-eV band including uv response and models for the defects identification has been reported to our knowledge. Here we report the absorption characteristics of the 5-eV band, photochemical responses to 5-eV light, concentrations of defects responsible for the 5-eV band in SiO_2:GeO_2 glasses, and we propose models. Optical characteristics and structural models of the 5-eV band in GeO_2 or SiO_2:GeO_2 glasses are compared with those in SiO_2 glasses.

II. EXPERIMENT

Sample rods (3 cm diam × 10 cm) of $5GeO_2$·$95SiO_2$ (mol %) and $10GeO_2$·$90SiO_2$ glasses were prepared by a chemical vapor deposition (CVD) soot-remelting method using $SiCl_4$ and $GeCl_4$ as starting materials. Each rod was cut into plates ~0.5 mm thick and polished to an optical finish. Illumination of ultraviolet radiation was carried out at 300 or 77 K with a 500-W Hg/Xe lamp through filters to remove visible and near-infrared lights. Samples were illuminated with wavelengths in the range 220–360 nm. The light intensity measured with a thermopile was approximately 450 mW/cm.[2] A cryostat for optical use was used for illumination at low temperature. Optical-absorption and photoluminescence spectra of samples were measured at room temperature with conventional microcomputer-interfaced spectrophotometers. Electron paramagnetic resonance (EPR) spectra were measured at 300 and 77 K at *X*-band frequency with a computer interfaced JEOL model FE1XG. Resonance fields were calibrated with a standard [diphenylpicrylhydrazyl (DPPH), $g = 2.0036$]. Absolute spin concentrations were obtained by double numerical integration on first-derivative spectra and comparison to a $CuSO_4$·$5H_2O$ reference crystal of known weight (the accuracy of the standard is believed to be ±20%). The optimum microwave power to obtain the spectra of Ge *E*′ centers was 20 μW. The relative error of Ge *E*′ concentrations was within ±10%.

III. RESULTS

Figure 1 shows changes in the optical-absorption spectra of $10GeO_2$·$90SiO_2$ glass with duration of uv illumination at 300 K. An intense absorption band (full width at half maximum, FWHM = 0.48 eV) centered at 5.16 eV was observed in as-prepared samples as previously reported.[11] Intensity of this band decreased while intensity of absorptions >5.5 eV increased with increasing uv-illumination time. Also shown in the figure are absorptions bleached by the uv light which were obtained by subtracting the absorption spectrum of the sample before illumination from that after illumination. It is evident that a band centered at 5.06 eV is bleached and absorptions above 5.5 eV including a shoulder centered at around 5.7 eV are induced, and an isosbestic point appears at 5.4 eV. The peak position (5.06 eV) and the full width at half maximum amplitude (FWHM) (0.38 eV) of the bleached band differ significantly from the (5.16 eV, FWHM = 0.48 eV) of the band before illumination, indicating that the 5-eV band in the as-prepared glass is comprised of two components. Similar results were obtained after bleaching a sample of the $5GeO_2$·$95SiO_2$ glass.

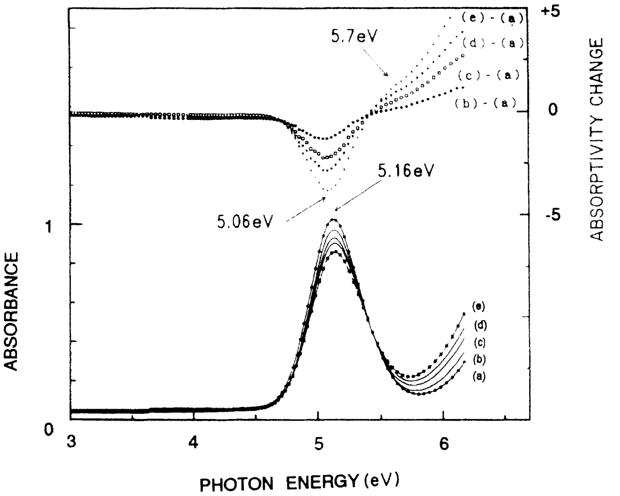

FIG. 1. Changes in optical-absorption spectra of $10GeO_2$:$90SiO_2$ glass (0.45 mm thick) on illumination with ultraviolet radiation (a) Before illumination, (b) 1.5 h, (c) 24 h, (d) 175 h, and (e) 223 h. Top is an effectively changed absorption spectrum with duration of uv illumination. An arrow indicates a shoulder centered around 5.7 eV.

Figure 2 shows intensity changes of the uv-bleached band at 5.06 eV as a function of uv illumination. Intensities for both samples decrease and approach constant values which are considerably smaller than intensities of the band before illumination. The bleaching rate at 77 K is much smaller than that at 300 K.

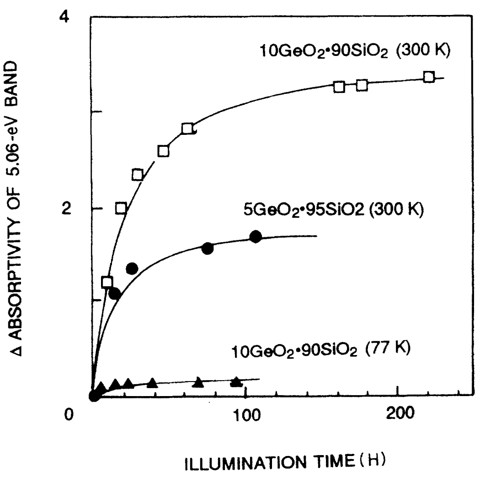

FIG. 2. Intensity of uv-bleached optical band centered at 5.06 eV as a function of illumination time. The GeO_2 content in samples and illumination temperature is described in the figure.

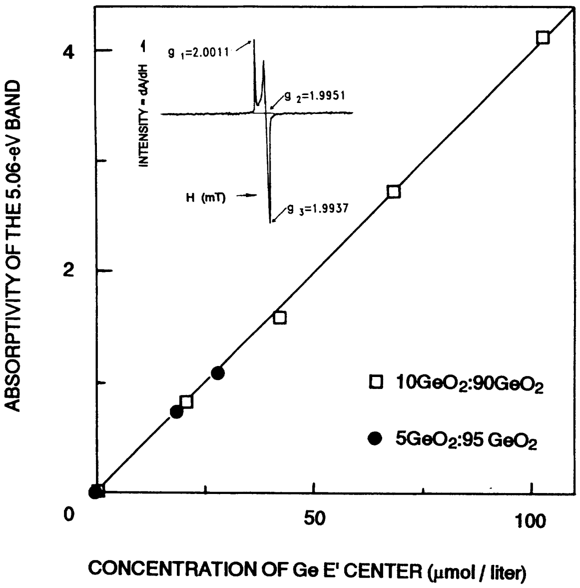

FIG. 3. Correlation between the concentrations of uv-induced Ge *E'* center and the absorptivity of uv-bleached 5.06-eV band. A plate sample for each specimen with different composition was used for optical and EPR experiments. The inset is the EPR signal of the uv-induced Ge *E'* center.

Figure 3 shows photoluminescence emission bands detected near 4.3 (weak) and 3.2 eV (intense). Excitation spectra for both emission bands were in the same range, having a peak at 5 eV and a FWHM of ~0.5 eV. No differences were observed between samples before uv illumination and after illumination for 240 h within experimental uncertainty (±10% in intensities).

Figure 4 shows the observed shape of the uv-bleached band centered at 5.06 eV (hereafter the 5.06-eV band) with least-squares-fitted Gaussian and Lorenzian functions. It is evident that the observed shape is Gaussian.

An EPR signal shown in Fig. 5 (inset) was observed for as-prepared samples. Three *g* values of the signal agree with those of the Ge *E'* center[11] in GeO_2 glasses. Concentrations in as-prepared $5GeO_2 \cdot 95SiO_2$ and $10GeO_2 \cdot 90SiO_2$ glasses were 1.8×10^{14} cm^{-3} and 1.1×10^{14} cm^{-3}, respectively. Although the intensity of the Ge *E'* center increased by uv illumination, no other signals such as Ge-electrons centers,[12] oxygen-related centers, or Si *E'* centers were observed. Figure 5 shows a plot of the uv-induced 5.06-eV band intensity versus the concentration of uv-induced Ge *E'* centers. Data for the bleached band at 5.06 eV of $5GeO_2 \cdot 95SiO_2$ and $10GeO_2 \cdot 90SiO_2$ glasses illuminated with uv radiation for various times was fitted by a root-mean-square method to a function $I(5.06\ \text{eV}) = AN(E')$ in which $I(5.06)$ is the amplitude of the 5.06-eV band, A is a constant, and $N(E')$ is the concentration of uv-induced Ge *E'* centers.

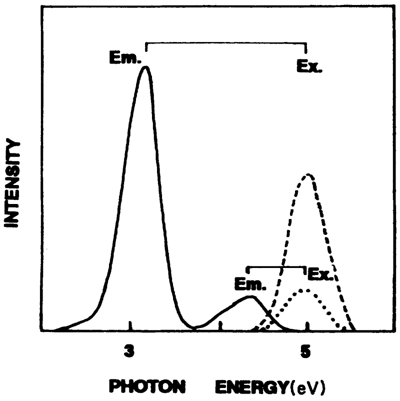

FIG. 4. Photoluminescence spectra. Excitation and emission spectra are expressed as Ex and Em, respectively.

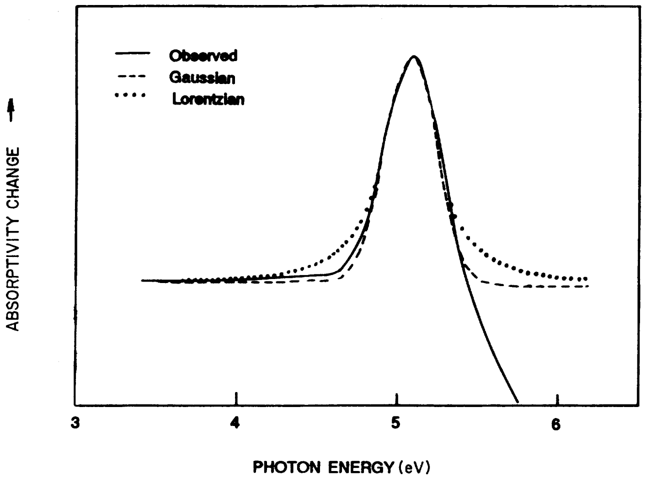

FIG. 5. Shape of uv-bleached absorption band centered at 5.06 eV.

IV. DISCUSSION

A. Structural models for uv-bleachable and nonbleachable 5-eV bands

It is evident from the results that two components with differing properties constitute the 5-eV band in as-prepared glasses. One may be bleached by uv-light illumination and has a peak position (E_0) at 5.06±0.05 eV and the FWHM of 0.38±0.05 eV. The other band is not uv bleachable and has $E_0 = 5.16 \pm 0.05$ eV and a FWHM of 0.48±0.05 eV (hereafter the 5.16-eV band).

Structural models of the defects responsible for the 5.16-eV band are considered. Since no changes were observed in the photoluminescence spectra of the samples before and after uv illumination, we conclude that the defect responsible for the 5.16-eV band is the source of the luminescence. Divalent germanium ions give an absorption band at 5 eV.[6] They are coordinated by two oxygens through two of the three sp^2 hybridized orbitals and have their remaining two electrons as a lone pair which occupies the uppermost level. Therefore, when 5-eV light illuminates a Ge^{2+}, the lone pair electrons, which do not participate in chemical bonding, are excited, and they are deactivated by luminescene [ions having lone pair electrons with high-S character are known to be luminescent centers, e.g., Tl^+ with (Xe) $(6s)^2$ and Sb^{3+} with (Kr) $(5s)^2$].[13]

The origin of the uv-bleachable (5.06-eV) band may be explained as follows. Linear relations between band intensity and uv-induced Ge E' center concentrations provide a basis for attributing the 5.06-eV band to the precursor site of the Ge E' center. It is known that in most cases Si E' centers are generated by trapping a positive hole at the site of an oxygen vacancy in $\mathrm{SiO_2}$ glass.[14] In $\mathrm{SiO_2}$ glass having a structure analogous to that of $\mathrm{GeO_2}$ glass two types of oxygen vacancies, Si-Si bonds with a bond distance close to a $\mathrm{Si_2H_6}$ molecule and neutral oxygen monovacancies with a Si-Si distance similar to regular Si-O-Si, were proposed in 1982[15] as a model based on theoretical calculations and were supported by experiments.[16,17] It has been reported that neutral oxygen monovacancies and Si-Si bonds give an absorption band at 5 and 7.5 eV, respectively, and the former is converted into E' centers by illumination with 5-eV light.[16] From a close similarity of the defect responsible for the 5.06-eV band in the present glasses to neutral oxygen monovacancies in $\mathrm{SiO_2}$ glass, we assign the 5.06 band to be due to a neutral oxygen monovacancy coordinated by two germanium ions.

B. uv-bleaching kinetics

Figure 6 illustrates a model for the formation of the Ge E' center from a neutral oxygen vacancy (NOV). The rate of conversion of NOV to Ge E' centers can be written

$$\frac{dN}{dt}=k_1\phi(N_0-N)\ , \tag{1}$$

where N_0 and N denote the NOV concentrations before illumination and concentrations of bleached NOV (=uv-induced Ge E' concentrations) after illumination for time t, respectively. ϕ is the incident photon flux and k is a constant. Here ϕ is constant because the intensity of uv light used to illuminate the specimen was constant. Then Eq. (1) becomes Eq. (2),

$$\frac{dN}{dt}=k(N_0-N)\ , \tag{2}$$

where k is a rate constant depending on the incident photon flux and sample temperature. The quantity measured was the absorptivity of the uv-bleached 5.06-eV band, $\alpha(t)$. N and $\alpha(t)$ are connected by Eq. (3),

$$\alpha(t)=\varepsilon_{5.06}N\ , \tag{3}$$

where $\varepsilon_{5.06}$ denotes the molar extinction coefficient of the 5.06-eV band. Therefore, N_0 is given by Eq. (4),

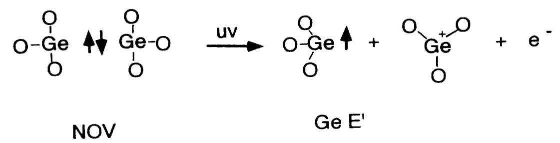

FIG. 6. Formation model for Ge E' center from neutral oxygen vacancy.

$$N_0=\alpha(\infty)/\varepsilon_{5.06}\ . \tag{4}$$

Here $\alpha(\infty)$ means the value of α for which there is no change with increasing bleaching time. Putting Eqs. (3) and (4) into Eq. (2), we obtain

$$\frac{d[\alpha(t)]}{dt}=k[\alpha(\infty)-\alpha(t)]\ . \tag{5}$$

Integration yields

$$\ln[\alpha(\infty)-\alpha(t)]=-kt+\mathrm{const}\ .$$

When $t=0$, $\alpha(t)=0$, $\mathrm{const}=\ln[\alpha(\infty)]$. Therefore, the integrated rate law is

$$\ln\left[1-\frac{\alpha(t)}{\alpha(\infty)}\right]=-kt\ . \tag{6}$$

Figure 7 shows a semilogarithmic plot of $[1-\alpha(t)/\alpha(\infty)]$ versus illumination time t for $10\mathrm{GeO_2}\cdot90\mathrm{SiO_2}$ glass. The value of $\alpha(\infty)$ was so determined by the least-squares fit of data to Eq. (6). Data on the specimen illuminated at 77 K were plotted by adapting the value determined for the data at 300 K. Both sets of data at 77 or 300 K fit with first-order kinetic functions, indicating that the scheme in Fig. 6 is consistent with the experimental results. The activation energy (E) of the conversion process form the NOV to the E' center is 3×10^{-2} eV on the assumption that the temperature of k is expressed by $k=k_0\exp(-E/RT)$.

C. Concentrations of neutral oxygen vacancy and Ge^{2+} ion

The NOV concentrations (N_{NOV}) in as-prepared specimens can be evaluated by Eq. (7),

$$N_{\mathrm{NOV}}=\frac{\alpha(\infty)}{\varepsilon_{\mathrm{NOV}}}\ . \tag{7}$$

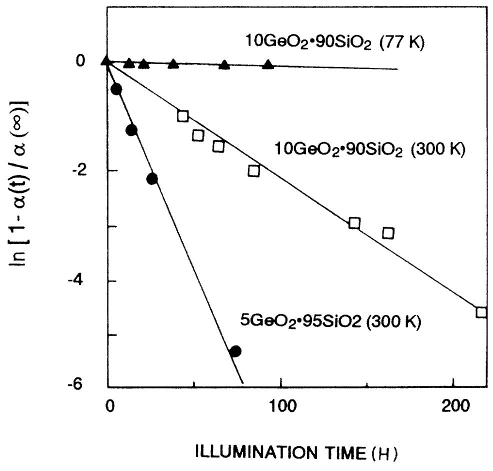

FIG. 7. First-order kinetic plots for the intensity of the uv-bleached optical band centered at 5.06 eV. The saturated values ($3.4\ \mathrm{cm^{-1}}$ for $10\mathrm{GeO_2}{:}90\mathrm{SiO_2}$ glass or $1.6\ \mathrm{cm^{-1}}$ for $5\mathrm{GeO_2}{:}95\mathrm{SiO_2}$ glass) were determined using a computer program for the nonlinear least-squares method.

TABLE I. Concentrations of Ge^{2+} ions and neutral oxygen vacancies(NOV) in SiO_2:GeO_2 glasses.

	[NOV] (cm^{-3})	[Ge^{2+}] (cm^{-3})	[NOV]/[Ge^{2+}]	Off-stoichiometry of oxygen in GeO_2, x in GeO_{2-x}
$5GeO_2$ $95SiO_2$	2.2×10^{16}	1.8×10^{18}	0.012	1.6×10^{-3}
$10GeO_2$ $90SiO_2$	6.0×10^{16}	1.3×10^{18}	0.046	6.0×10^{-4}
GeO_2	2.2×10^{18}	1.3×10^{19}	0.18	6.4×10^{-4}

ε_{NOV} denotes the molar extinction coefficient of the NOV. The values of $\alpha(\infty)$ were determined by applying least-squares procedures to data of $\alpha(t)$ as described above. The slope of the curve to which the data were fitted in Fig. 5 corresponds to the molar extinction coefficient ε_{NOV}. We use 4×10^4 (L/mol/cm) and 9×10^3 (L/mol/cm) as ε_{NOV} and $\varepsilon_{Ge(II)}$, respectively. The latter value was reported by Schultz.[5] Table I summarizes the concentrations of Ge^{2+} and NOV's, and the ratio of the NOV's to Ge^{2+} ions in samples. Concentrations of these two defects in pure GeO_2 glass were calculated by applying the same procedures to data in Fig. 2 of Ref. 2. With increasing GeO_2 content the ratio of the NOV's to Ge^{2+} increases, but Ge^{2+} ions are the major defects over the entire composition range. Jackson *et al.*[4] reported that the defect responsible for the 5-eV band is more complex than a single neutral oxygen vacancy. Since Ge^{2+} ions may be regarded as oxygen divacancies, this conclusion is consistent with the present results provided that oxygen-deficient type defects are limited to NOV's and Ge^{2+} ions. Nonstoichiometry GeO_{2-x} may be calculated as follows: The nominal formula of Ge^{2+} and NOV are described by GeO and $GeO_{1.5}$, respectively. When each content of GeO_2, $GeO_{1.5}$, or GeO is X, Y, or Z, x in GeO_{2-x} is expressed by

$$x=\frac{0.5Y+Z}{X+Y+Z} . \tag{8}$$

We can readily calculate x using chemical composition, density, and experimental Y and Z data. Results summarized in Table I show that the values of x are of the order of $10^{-3}-10^{-4}$.

D. Comparison of 5-eV band in GeO_2 and SiO_2 Glass

It is known that a weak absorption band near 5 eV is seen in some type-IV glasses. In 1989 Tohmon *et al.*[18] reported the band to be composed of one component with peak at 5.15 eV and a FWHM of 0.48 eV and a second at 5.02 eV with a FWHM of 0.35 eV. The appearance of these two bands is limited to oxygen-deficient type-SiO_2 glasses. Tohmon *et al.* suggested the latter to be due to a Si^{2+}, following Kohketsu *et al.*[19] [Castle *et al.* discussed the possible existence of an oxygen divacancy in crystalline quartz, Phys. Rev. **130**, 577 (1963)]. The latter band agrees with the absorption which was assigned to neutral oxygen vacancies by Imai *et al.*[20] Responses to uv radiation of these two bands were also reported. The 5.02 band and 5.15-eV band give emission bands near 4.3 eV (Ref. 20) and two emission bands[19] near 4.2 and 2 eV, respectively. Imai *et al.* reported that the 5.02-eV band is bleached by uv, and a band centered at 5.7 eV appears accompanying the EPR signal of E' center.[21] Table II summarizes characteristics of two absorption bands near 5 eV in SiO_2:GeO_2 (GeO_2) glasses and SiO_2 glasses. It is evident that peak positions, peak widths, and luminescence properties are similar in SiO_2:GeO_2 and SiO_2 glasses. It is of interest to note close similarities between optical bands of Si E' and Ge E' centers. A shoulder appears near 5.7 eV and intensity increases with the decrease of the 5.06-eV band (top of Fig. 1). Bandwidth and oscillator strength were estimated approximately to be the same order (0.5–0.7 eV, 0.1–0.2) as those of the Si E' center (0.60, 0.14) (Ref. 22) (exact evaluation of oscillator strength of this band is difficult because of the overlap of the uv-induced deep-vacuum uv tail). This result is com-

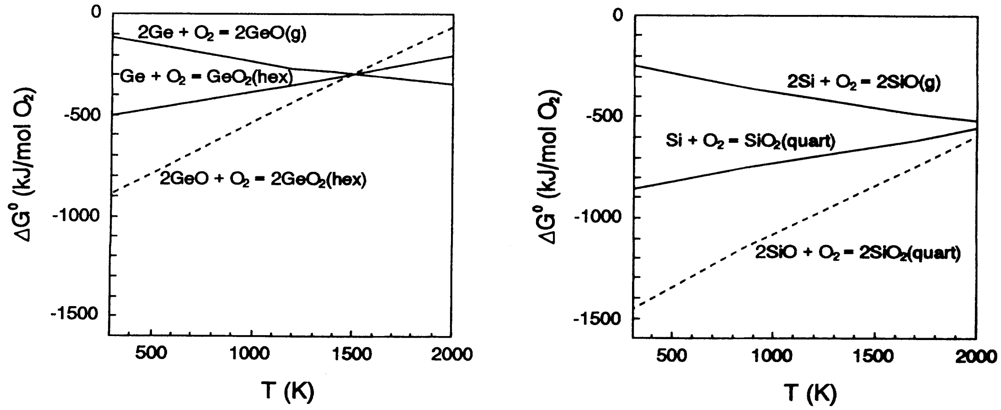

FIG. 8. Standard free energy of formation of oxides of Ge and Si as a function of temperature.

TABLE II. Characteristics of two optical bands near 5 eV in SiO_2:GeO_2 and SiO_2 glasses.

Peak position (eV)	FWHM (eV)	Oscillator[a] strength	Structural model	Luminescence
		SiO_2:GeO_2 glasses		
5.16	0.48	0.12	Ge^{2+}	3.2 eV (intense) +4.3 eV (medium)
5.06	0.38	0.40(±0.1)	neutral oxygen monovacancy	4.3 eV (weak)?
		SiO_2 glasses[b]		
5.15	0.48	⋯[c]	Si^{2+}	2.7 eV (intense) +4.3 eV (medium)
5.02	0.35	⋯	neutral oxygen monovacancy	4.3 eV (weak)

[a] Oscillator strength f was calculated by the following Smakula's formula [A. Smakula, Z. Phys. **59**, 603 (1930)]: $Nf = 0.87\times10^{17}\, n\alpha_e w/(n^2+2)^2$, where n is the refractive index of the glass, α_e (cm^{-1}) the absorption coefficient at the peak of the absorption band, and w (eV) the FWHM, assumed to be Gaussian in shape.

[b] Data of the peak positions and widths was cited from Ref. 18, and luminescence data were adapted from Refs. 19 and 20.

[c] No data have been reported.

patible with the conclusion obtained from analysis of g shifts of Si E' and Ge E' centers.[11]

A striking difference between SiO_2 and GeO_2 glasses is the concentrations of these defects, i.e., off-stoichiometry of oxygen. In GeO_2 and SiO_2:GeO_2 glasses the concentrations of the sum of these two defects are of the order of 10^{-3}–10^{-4} of the total Ge ions. Concentrations are of the order of 10^{-9} of the total Si ions at most in SiO_2 glasses. The concentrations are lower than the detection limit in all SiO_2 glasses except those prepared by methods involving the dechlorination process to remove Si-OH groups. We assume that this difference is due to the difference in thermodynamic stability between SiO_2 and GeO_2. Figure 8 shows the standard free energy of formation of oxides of Ge and Si as a function of temperature. GeO_2 is much less stable than SiO_2 and thus reduction of GeO_2 to GeO is much easier than that of SiO_2 to SiO. Reduction from the tetravalent to divalent state is more favorable for both with increasing temperature. Since no serious differences in the free energy are considered between crystal and glass of SiO_2 and GeO_2, these data may explain that nonstoichiometry in GeO_2 glass is much greater than that in SiO_2 glass.

V. CONCLUSION

(1) Concentrations of the Ge E' center increase with bleaching of the 5.06-eV band, and changes in their concentrations parallel changes in the 5.06-eV band. On the assumption that the defect responsible for the 5.06-eV band is converted into the Ge E' center, the oscillator strength of the 5.06-eV band is 0.4 ±0.1.

(2) The 5.06- and 5.16-eV bands are attributed to a neutral oxygen vacancy (NOV) coordinated with two Ge ions and a Ge^{2+} coordinated with two oxygens, respectively.

(3) The ratio of the NOV to the Ge^{2+} ion was approximately 1% in $5GeO_2 \cdot 95SiO_2$ glass, 5% in $10GeO_2 \cdot 90SiO_2$ glass, and 18% on GeO_2 glass.

(4) Photochemical conversion of the NOV to the Ge E' center obeyed first-order kinetics, and the activation energy was approximately 3×10^{-2} eV. The ratio of the rate at 77 K to that at 300 K was approximately 1/50, which is comparable to that of the buildup of second-harmonic generation in SiO_2:GeO_2 glass fibers.[23]

(5) A close similarity was found in the absorption and emission characteristics of the divalent state and neutral oxygen vacancy between GeO_2 and SiO_2 glasses.

ACKNOWLEDGMENTS

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