

Photobleaching of sol-gel-derived germanium oxide glass thin films

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Photobleaching of the optical absorption band in the 5-eV region of sol-gel-derived germanium oxide glass thin films was examined with the irradiation of the 5-eV light. The photobleaching represented by the saturated absorption coefficient change ($-\Delta\alpha$) and the ratio of the neutral oxygen monovacancies to neutral oxygen divacancies concentrations for the germanium oxide were 175 cm^{-1} and 0.113, respectively. These values are larger than those of the pure germanium oxide bulk glass as well as germanosilicate thin films. The changes in bonding configuration around Ge atom by ultraviolet illumination were analyzed using x-ray photoelectron spectroscopy.

A permanent increase in the refractive index of GeO_2 doped silica waveguides by ultraviolet (UV) illumination can be used in the fabrication of Bragg gratings. In 1978, K.O. Hill *et al.*¹ first observed the photosensitivity in germanium doped silica glass. It has been shown that this photosensitivity is closely associated with germanium-related oxygen defect centers.²

In 1958, Cohen and Smith³ first showed that the presence of a strong absorption band near 5 eV was attributed to neutral oxygen vacancies caused by the reduction of Ge^{4+} to Ge^{2+} . Hosono *et al.*⁴ proposed that the 5-eV absorption bands were composed of two types of neutral oxygen vacancies. One has a peak at 5.06 eV and is due to neutral oxygen monovacancies (NOMV) coordinated by two Ge ions. Another component of the absorption spectra has a peak at 5.16 eV, which is assigned to neutral oxygen divacancies (NODV) coordinated by two oxygens and having two lone pair electrons. Only the absorption band at 5.06 eV of NOMV absorption band can be bleached and converted into Ge E' centers by UV illumination.⁵ In the color center model,⁶ the refractive index change is thought to arise from bleaching of NOMV and the growth of other absorption bands above 5.5 eV. The increase in intensity of the latter is much larger than the decrease in that of the former. As a consequence, the net absorption change enhances positive refractive index changes through the Kramers-Kronig conjugate mechanism.⁷ The higher photosensitivity is made by the higher concentration of the photobleachable NOMV which is dependent on the composition and the fabrication processing. It has been known that the higher germanium oxide content⁴ or heat treatment under reduced atmosphere⁸ enhances the photosensitivity. Thus, it is expected that oxygen deficient germanium

oxide glass produces the higher photosensitivity. It was found that melted germanium oxide bulk glass³ showed extremely high photobleaching as shown Table I. It was also reported that a film is more photobleached than the bulk for same composition.⁹ However, the photobleaching of pure germanium oxide glass film has not been yet studied.

Recently, we fabricated homogeneous and dense germanium oxide glass thin films using a sol-gel method.¹⁰ The germanium-related oxygen defect centers were obtained by annealing the films under reduced atmosphere. In this letter, we report an investigation of the photobleaching of the pure germanium oxide glass thin films fabricated by sol-gel method. Also, we will report on qualitative interpretations in the change of germanium-related deficient center by UV illumination using x-ray photoelectron spectroscopy (XPS).

Germanium oxide glass thin films were fabricated using a sol-gel spin coating method. The prepared sol solutions were then deposited on *p*-type (100) Si wafer and fused silica glass substrates. In order to produce oxygen deficient defects, the films were annealed under a flowing H_2/N_2 atmosphere at 500 °C for 2 h after the densification process. The densified film had a thickness of about 400 nm and exhibited excellent thermal and chemical stability. The detail procedure was described in previous report.¹⁰ UV irradiation of the films was carried out at room temperature using a 300-W Xe lamp (ILC Technology, LX300UV, Sunnyvale, CA), with 248 nm bandpass filter (Coherent Auburn group, Auburn, CA). Optical measurements of the films as a function of the UV illumination were conducted at room temperature. The optical absorption spectra in the 5-eV region were examined using an ultraviolet/visible/near-infrared

(UV/VIS/NIR) spectrophotometer (Shimadzu, UV-3101PC, Kyoto, Japan). The chemical environment of the germanium atom was examined by XPS (ESCALAB 200R, West Sussex, U.K.). The x-ray source was Al K_{α} at the energy of 1486.6 eV.

Figure 1 shows the change of the absorption coefficients at 5-eV of the germanium oxide films as a function of the UV illumination time. The absorption coefficients at 5-eV decrease linearly with the UV illumination time showing photobleaching at the initial stage and then approach a saturated level. The absorption coefficients evaluated in the films before and after the UV illumination are 525 and 350 cm^{-1} , respectively. It is well known

TABLE I. Comparison of the saturated absorption coefficient change ($-\Delta\alpha$) and the ratio of the NOMV to NODV concentrations for the films and bulk glasses.

Composition	$-\Delta\alpha$ (cm^{-1})	[NOMV]/ [NODV]	Preparation method	Reference
5GeO ₂ -95SiO ₂ (bulk)	1.4	0.013	VAD	(8)
5GeO ₂ -95SiO ₂ (bulk)	11	0.038	VAD (H ₂ reduced)	(8)
10GeO ₂ -90SiO ₂ (bulk)	3.4	0.046	VAD	(4)
GeO ₂ (bulk)	145		Melting	(3)
5GeO ₂ -95SiO ₂ (film)	50		Sputter	(9)
55GeO ₂ -45SiO ₂ (film)	400		Sputter	(9)
GeO ₂ (film)	175	0.113	Sol-gel	This study

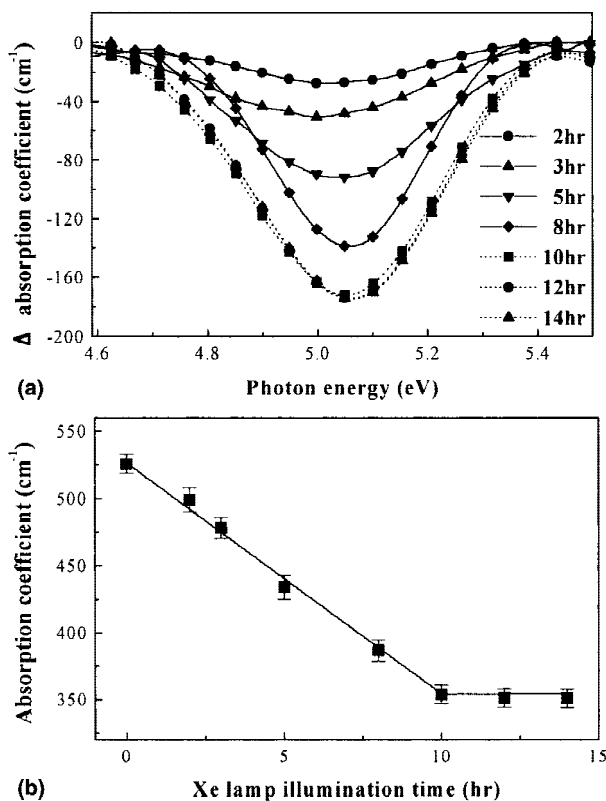


FIG. 1. (a) Change in optical absorption spectra and (b) absorption coefficient at 5 eV for germanium oxide films after H_2/N_2 heat treatment (500 °C for 2 h) by the UV illumination time of the 248 nm beam emitted from a 300 W Xe lamp.

that only NOMV is bleached by UV illumination and it converts to Ge E' center, whereas NODV is not bleached by UV illumination.⁵ Assuming that the absorption band at 5 eV is only composed of NOMV and NODV, only the NODV remains after the UV illumination. Thus, it could be deduced that the decrease in the absorption is due to the NOMV and that the remaining absorption is due to the NODV. The ratio of the NOMV to NODV concentrations for germanium oxide thin film is calculated to be about 0.113 using the molar extinction coefficients 4×10^4 l/mol/cm for ϵ_{NOMV} and 9×10^3 l/mol/cm for ϵ_{NODV} .^{4,11} The photobleaching represented by the saturated absorption coefficient change ($-\Delta\alpha$) and the ratio of the NOMV to NODV concentrations for the sol-gel-derived germanium oxide film were compared with those of other results in Table I. It is shown that the concentration of the photobleachable NOMV increases with germanium oxide content and by heat treatment at reduced atmosphere. Also the concentration of the NOMV for the film samples is higher than that for the bulk samples. Thus, the photobleaching of the sol-gel-derived germanium oxide glass thin film is higher than germanium oxide bulk glass as well as other compositions, because the pure germanium oxide glass thin film creates more NOMV by heat treatment under reduced atmosphere. However, the sol-gel thin film has lower photobleaching than the sputtered one since the heat treatment under reduced atmosphere is limited due to its easy crystallization under reduced atmosphere.¹⁰

Figure 2 shows the Ge 3d XPS spectrum from germanium oxide films before and after annealing under reduced atmosphere, and UV illumination. The binding energy of Ge 3d electrons shifts to lower energy after annealing the film under reduced atmosphere and moves back to higher energy after UV illumination. It has been shown that the binding energy of Ge 3d electrons in-

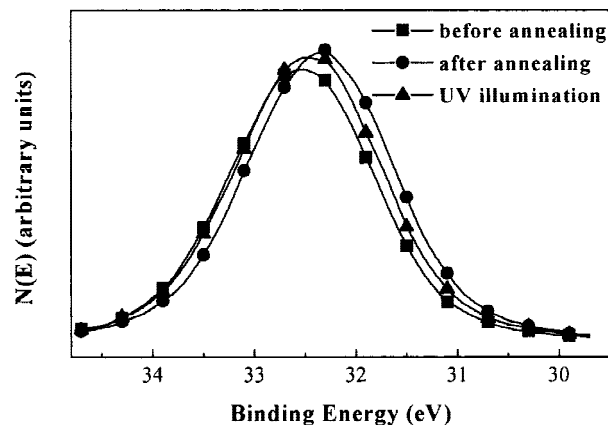


FIG. 2. XPS spectrum of Ge 3d photoelectrons of the germanium oxide films before and after H_2/N_2 heat treatment and after UV illumination where $N(E)$ is the number of the detected photoelectrons as a function of their binding energy.

