

Fabrication and Ultraviolet Absorption of Sol–Gel-Derived Germanium Oxide Glass Thin Films

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Germanium oxide glass thin films were prepared by the sol–gel method and annealed under reduced atmosphere to create more oxygen-deficient defects. The densification and crystallization were examined depending on sintering and annealing conditions. Thus, homogeneous germanium oxide thin films with a high content of oxygen vacancies were fabricated. Ultraviolet absorption and oxygen vacancies of the films were investigated as a function of annealing temperature and time. Optical absorption in the 5-eV region due to the formation of oxygen vacancies is enhanced with increasing annealing temperature and time. The formation energy of oxygen vacancies is calculated to be about 1.0 eV.

I. Introduction

It is known that there is an absorption band near 5 eV (~240 nm) for germanium oxide and that this absorption band is associated with an oxygen-deficient defect.^{1,2} The 5-eV absorption band of germania-related oxygen-deficient defects is responsible for the photosensitivity of germanium oxide doped silica glasses.^{3,4} This allows diffraction-type gratings to be written into optical fibers by light near 5 eV^{5,6} or at longer wavelengths by means of two-photon absorption.⁷ The 5-eV absorption band of germanium oxide glasses is attributed to neutral oxygen vacancies caused by the reduction of Ge⁴⁺ to Ge²⁺.^{1,8} The 5-eV absorption band is bleached and a new absorption band above 5.5 eV is formed on UV light exposure.^{5,9,10} Hosono *et al.*⁹ reported that the 5-eV absorption band is composed of two components: the absorption band centered at 5.06 eV formed by a neutral oxygen monovacancy (NOMV) and the absorption band centered at 5.16 eV formed by a neutral oxygen divacancy (NODV).^{10,11} Only the absorption band at 5.06 eV of NOMV is photobleachable due to the conversion of NOMV to a Ge E' center to form the intense absorption band above 5 eV by illumination with 5-eV light.¹⁰ These UV absorptions contribute to a permanent increase in the refractive index of the glasses that can be used in the fabrication of gratings.^{4,6,10,12–15}

There have been many studies on the 5-eV absorption band in germanium-doped silica or germanosilicate glasses and thin films prepared by melting,^{1,16} flame hydrolysis,¹⁷ vapor axial deposition (VAD),^{9,18} sputtering deposition,¹⁹ chemical vapor deposition (CVD),^{2,20} and the sol–gel method.^{21,22} Jackson *et al.*¹⁶ found that the fusion temperature during melting dependence of the optical

absorption is Arrhenius in nature with an activation energy for the formation of defects in GeO₂ glasses of 2.3 eV. It was shown by Hosono *et al.*⁹ that the ratio of the NOMV to the NODV increased as the germanium oxide content increased. It was also shown that photochemical conversion of the NOMV to the Ge E' center obeyed first-order kinetics. It was found that heat treatment of a germanosilicate glass preform in a H₂ atmosphere increased the intensity of an absorption band centered at 5 eV.¹⁸ It was also found that the photobleachable NOMV component was further enhanced by reduced heat treatment than the unbleachable NODV component. Thus, the higher concentration of the photobleachable NOMV which can be made by higher germanium oxide content or heat treatment under reduced atmosphere^{18,23} is desirable for efficient design of grating devices.

Recently, germanosilicate glasses films containing up to 45 mol% germanium oxide were fabricated by the sol–gel method for application of planar optical waveguides.^{21,22} Photosensitive gratings can be consistently written in sol–gel-derived germanosilicate thin film waveguides. It was found that sample photosensitivity and the 5-eV absorption band are directly related to the heat treatment time in a reduced (H₂) atmosphere. In addition, it was found that samples with stronger 5-eV absorption bands show much greater photosensitivity. Thus, the 5-eV absorption band of the NOMV can be strongly enhanced in pure germanium oxide film heat-treated under reduced atmosphere.

For the present study, optical-quality pure germanium oxide glass thin films were fabricated using the sol–gel spin-coating method. The densification and crystallization behaviors of the films were examined depending on sintering and annealing conditions. The films were annealed under reduced atmosphere to create more oxygen-deficient defects. Thus, the 5-eV absorption band of the films was investigated as a function of annealing temperature under reduced atmosphere.

II. Experimental Procedure

(I) Sample Preparation

Tetraethyl orthogermanate [Ge(OC₂H₅)₄, TEOG] of 99.99% purity was used as the starting raw material. Because of the moisture-sensitive characteristics of the germanium ethoxide, all reactions and manipulations were conducted under dry nitrogen atmosphere in a glove box. TEOG was first dissolved in ethanol and then stirred for 30 min at room temperature. Water diluted with ethanol for hydrolysis was added to the solution and stirred for 30 min at room temperature. The molar ratio of water to TEOG was 4:1. The prepared sol solution was then deposited on a Si(100) wafer or fused silica glass substrates by the spin-coating method at 1200 rpm for 30 s. The coated film was dried at 140°C for 20 min after every coating to allow for evaporation of the solvent from the film. To obtain a homogeneous glass film without cracking and a crystalline phase during the drying and densification process, the films were heated at 600° and 700°C for 10 min in air using controlled heating rate. The procedure for preparing the coating solution and film is shown in Fig. 1. After a sintering process,

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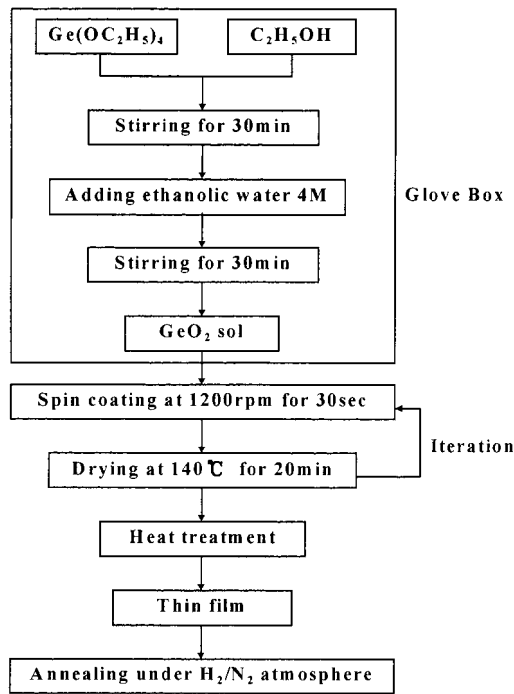


Fig. 1. Schematic procedure for preparation of germanium oxide sol solution and glass thin films.

germanium oxide glass films were then annealed under a flow of various H_2/N_2 atmospheres in the range 300° to $550^\circ C$ for 30 min to 30 h.

(2) Characterization

The amorphous phase of the thin film was confirmed by thin film X-ray diffraction analysis (TFXRD, Rigaku D/MAX-RC). The molecular structures and hydroxyl contents of the germanium oxide films depending on the heat treatments were investigated by Fourier-transform infrared (FT-IR, Bruker EQUINOX55) spectroscopy. All of the measurements were performed in the $4000\text{--}400\text{ cm}^{-1}$ range with a resolution of 4 cm^{-1} . The refractive index and the thickness of the films deposited on silicon wafers were measured with an ellipsometer (GAERTNER, L116C) at a wavelength of 632.8 nm. The surface morphology of the film was observed with an atomic force microscope (AFM, Park Scientific Instruments, Autoprobe 5M). Optical measurements of the films before and after the thermal annealing under reduced atmosphere were conducted at room temperature. The optical absorption spectra in the 5-eV region were examined using an ultraviolet/visible/near-infrared spectrophotometer (Shimadzu, UV-3101PC). The fraction of oxygen sites vacant in the film with annealing were examined with a wavelength dispersive spectrometer (WDS, Microspec., 3-PC).

III. Results and Discussion

(1) Preparation of Glass Thin Films

Since the porosity and the refractive index of the film can be related empirically,²⁴ the consolidation behavior of the films was monitored by measuring the change of the refractive index. We measured the refractive index and thickness of the films after heat treatment at various temperatures for 10 min in air. Figure 2 shows the densification behavior of the germanium oxide films. The decrease in refractive index in the initial stage is due to the loss of organic additives before the beginning of densification.²⁵ After then, the refractive index of the film increases slowly with increasing temperature and reaches 1.607 at $600^\circ C$. However, the thickness of the film decreases continuously with heat treatment temperatures in overall range. Generally, for TE mode, the range

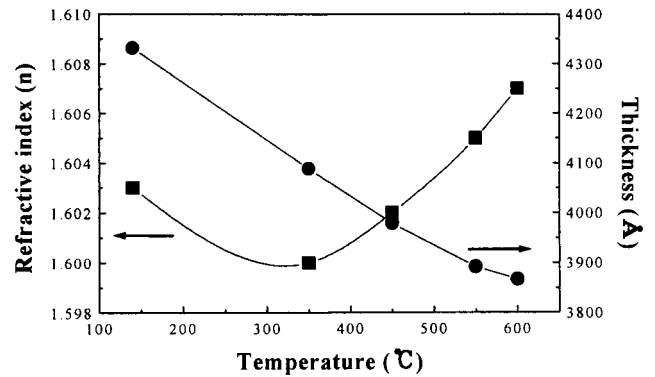


Fig. 2. Refractive index and thickness for germanium oxide films which were sintered in air at various temperatures for 10 min following a heating rate of $4^\circ C/min$.

of the film thickness to meet the single-mode propagation requirement can be found easily using Eq. (1).²⁶

$$\frac{\tan^{-1} \sqrt{\frac{n_s^2 - n_c^2}{n_f^2 - n_s^2}}}{k_0 \sqrt{n_f^2 - n_s^2}} < T \leq \frac{\tan^{-1} \sqrt{\frac{n_s^2 - n_c^2}{n_f^2 - n_s^2}} + \pi}{k_0 \sqrt{n_f^2 - n_s^2}} \quad (1)$$

where the propagation constant $k_0 = 2\pi/\lambda$; n_s , n_c , and n_f are the refractive indexes for the substrate, the cladding (air), and the film, respectively. For this study, at $\lambda = 632.8\text{ nm}$ with $n_s = 1.459$, $n_c = 1$, and $n_f = 1.607$, only the fundamental mode is supported over the range of $1500\text{ \AA} < T < 6200\text{ \AA}$. The films had a thickness of about 3900 \AA , which ensured that a single TE mode could propagate in the waveguide.

Generally, glass is a suitable waveguide material because glasses without scattering sources such as specific crystal surface roughness or grain boundary are highly transparent in visible and IR wavelength regions and the composition change can easily control the refractive index of these glasses. Thus, we must obtain glass thin films without the detection of crystalline phase. XRD spectra were used to identify the amorphization of the germanium oxide thin films. Figure 3 shows the XRD patterns of the films sintered at various temperatures in air. This indicates that the crystallization behavior was influenced by the sintering conditions. A hexagonal GeO_2 crystalline phase appeared when the films were heated at $600^\circ C$ for 30 min, and their crystallinity was enhanced with increased temperature. However, no crystalline phase was detected when the films were heated at $600^\circ C$ for 10 min. Therefore, sufficiently densified germanium oxide glass thin films

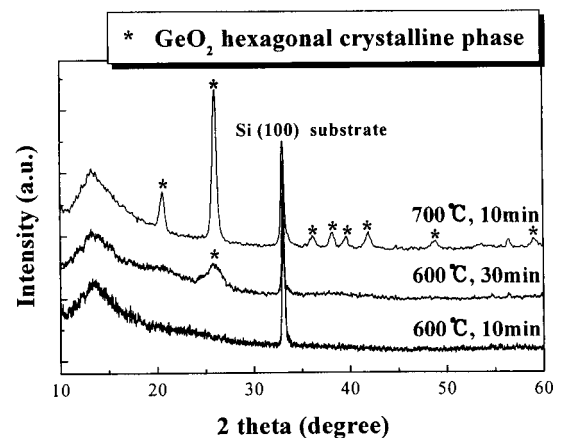


Fig. 3. XRD of germanium oxide thin films sintered at different sintering temperatures.

without any detection of crystalline phases were obtained with sintering at 600°C for 10 min.

FT-IR spectroscopy was used to examine the structural evolution of the films depending on the heat treatments. Figure 4(a) shows the FT-IR spectrum of the film which was dried at 140°C in air. Figure 4(b) shows the FT-IR spectrum of the film which was sintered at 600°C for 10 min in air. The absorption peaks at 750 cm^{-1} associated with the Ge-(OH) stretching mode and 3400 cm^{-1} associated with the O-H stretching mode were observed before the films were heat-treated. However, these peaks disappeared after sintering the films at 600°C for 10 min in air. In a waveguide device, pore or residual -OH molecules causing optical loss must be minimized. Thus, it is confirmed that dense germanium oxide glass thin films without significant amounts of residual organics and hydroxyls at the level of detection were obtained during the sintering process. The assignments of these peaks are listed in Table I.^{27–29} The strong absorption bands appearing at 880 cm^{-1} with a shoulder at 960 cm^{-1} are associated with the vibration mode ν_3 fundamental of the GeO_4 group. The absorption band appearing at 750 cm^{-1} is associated with the Ge-(OH) stretching mode. The band in the region 500 and 600 cm^{-1} may be related to mixed stretching–bending motions.³⁰ It is well known that the appearance of a sharp triplet at 530, 560, and 590 cm^{-1} with heat treatment indicates the formation of hexagonal GeO_2 crystalline phase, as shown in Fig. 4(d).²⁷ Therefore, since no triplet bands were detected in the FT-IR spectra, we could also detect no crystallization of the films.

The surface morphology of the film was observed with an AFM. RMS roughness of the film was as small as about 29 Å, which could minimize the propagation loss due to surface scattering. Thus, a dense, homogeneous, and smooth surface having germanium oxide glass thin films could be obtained by using a sol-gel spin coating method. Also, the measured refractive index of the films did not change for more than a month. Thus, it was found that the prepared films were chemically stable without an aging effect.

(2) Annealing under Reduced Atmosphere

To produce more oxygen-deficient defects responsible for the photosensitivity of the germanium oxide films, the films were

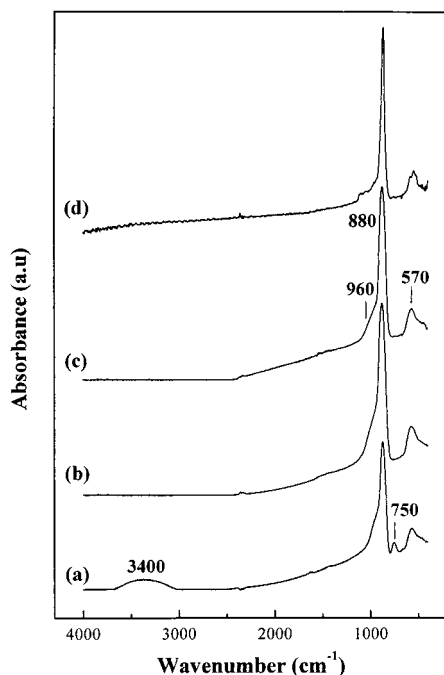


Fig. 4. FT-IR absorbance spectra of the germanium oxide thin film (a) dried at 140°C, (b) sintered at 600°C for 10 min in air, (c) annealed at 500°C for 2 h under a flowing H_2/N_2 (1:9 volume ratio) atmosphere, and (d) sintered at 600°C for 30 min in air

Table I. Infrared Band Frequencies and Vibrational Mode Assignment for Germanium Oxide Gels^{27–29}

Position (cm^{-1})	Assignment
500–600	ν_8 (Ge–O–Ge) deformation mode
750	Ge–(OH) stretching mode
880	ν_{as} (Ge–O–Ge) TO antisymmetric stretching mode
960	ν_{as} (Ge–O–Ge) LO antisymmetric stretching mode
3400	O–H stretching of hydrogen bonded molecular water

annealed under reduced atmosphere after the densification process. Generally, it is well known that the crystalline phase in the films is more easily generated when the films are heated under reduced atmosphere. Therefore, it is important that more oxygen vacancies are produced, while the films maintain an amorphous phase without the detection of crystalline phase. Figures 5 and 6 show the XRD patterns of the films annealed at 500°C for 2 h under different atmospheres and the films annealed at various temperatures under a flowing H_2/N_2 (1:9 volume ratio) atmosphere, respectively. It was found that the crystallization behavior was also influenced by the annealing conditions. For the films annealed at 500°C for 2 h, while the Ge metal phase was crystallized under pure H_2 or $\text{H}_2/\text{N}_2 = 1/5$ atmosphere, no crystallization at the level of detection occurred under $\text{H}_2/\text{N}_2 = 1/9$ atmosphere, as shown in Fig. 5. However, Ge metal or hexagonal GeO_2 crystalline phases appear in Fig. 6 where the films were annealed for 500°C for 5 h or 550°C for 2 h under $\text{H}_2/\text{N}_2 = 1/9$ atmosphere. Thus, it was found that heat treatment at 500°C for 2 h under a flowing H_2/N_2 (1:9 volume ratio) atmosphere is appropriate for annealing conditions to create the most oxygen vacancies compared with other available conditions in glass thin films.

Figure 4(c) shows the FT-IR spectrum of the film which was annealed at 500°C for 2 h under a flowing H_2/N_2 (1:9 volume ratio) atmosphere. It is known that Ge–OH is formed by diffusing hydrogen atoms into films during heat treatment under hydrogen atmosphere.²³ However, changes in the absorption spectra of the annealed films compared with the sintered films in Fig. 4(b) are below the level of detection. Thus, it is confirmed that the film is not hydrated during annealing under reduced atmosphere.

(3) Ultraviolet Absorption

Optical absorption of the germanium oxide films induced in the UV and visible region during annealing under a flowing H_2/N_2 (1:9 volume ratio) atmosphere was examined. Figure 7 shows changes in the UV absorption spectra of the germanium oxide glass thin films depending on the annealing time at 500°C under a flowing H_2/N_2 (1:9 volume ratio) atmosphere. The growth of a

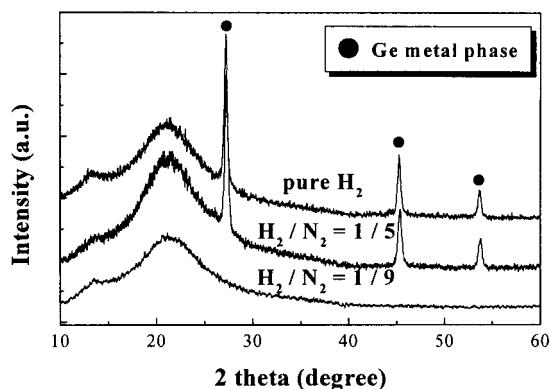


Fig. 5. XRD of densified germanium oxide thin films annealed at 500°C for 2 h under different atmospheres.

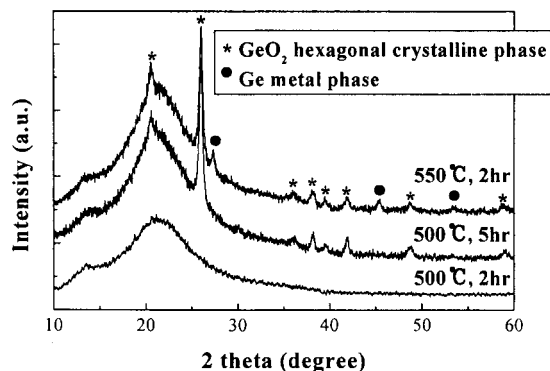


Fig. 6. XRD of densified germanium oxide thin films annealed at different annealing temperatures under a flowing H_2/N_2 (1/9 volume ratio) atmosphere.

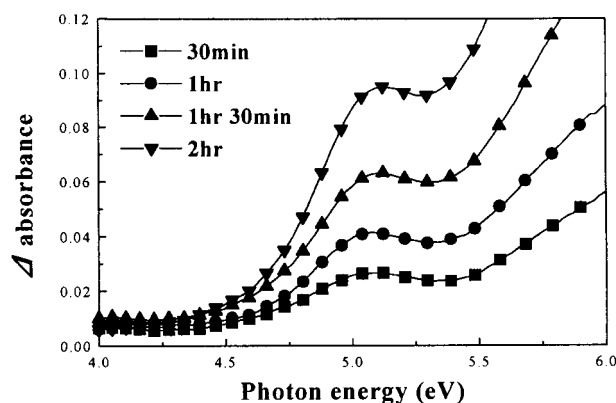
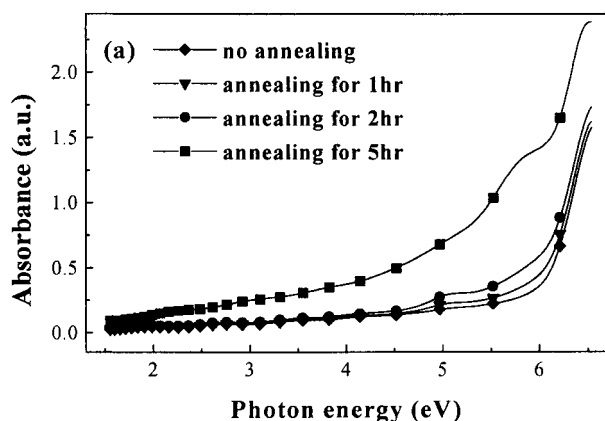


Fig. 7. (a) UV absorption spectra and (b) difference spectra for germanium oxide thin films that annealed at 500°C for various times under a flowing H_2/N_2 (1:9 volume ratio) atmosphere.

distinct absorption band centered at 5 eV is observed. However, it is observed that UV absorption of the films annealed for 5 h increases suddenly. This is due to crystallization of the film. It is consistent with the XRD results as shown in Fig. 6. To distinguish the 5-eV absorption band, the absorption spectrum of the film without annealing is subtracted from those after annealing. The difference spectra are plotted in Fig. 7. It is definitely shown that the 5-eV absorption band grows with increasing annealing time. A curve-fitting technique is used to obtain the component absorption peak area. The change in the integrated band intensity of the 5-eV absorption depending on annealing time at various annealing

temperatures is represented in Fig. 8. For all the annealing temperatures, the integrated band intensity representing the formation of oxygen vacancies increases almost linearly with increased annealing time.

To determine the relationship between the integrated band intensity of the 5-eV absorption and the formation of oxygen vacancies, the oxygen content was analyzed using WDS. The fraction of oxygen vacancies in addition to the integrated band intensity of the 5-eV absorption depending on annealing temperature for the films are plotted in Fig. 9. Arrhenius plots of the integrated band intensity of the 5-eV absorption and the fraction of oxygen vacancies are linear and nearly parallel. This indicates that the 5-eV absorption band is a result of the formation of oxygen vacancies. Assuming that a thermally activated process governs the formation of the oxygen vacancies, the concentration n of oxygen vacancies as a function of temperature can be given as

$$n \propto N_0 \exp(-Q/kT) \quad (2)$$

where N_0 is the number of oxygen sites per unit volume, Q is the energy to form a vacancy, and k is Boltzmann's constant. Since nonstoichiometry, x , in GeO_{2-x} , is given by

$$x = 2 \left(\frac{n}{N_0} \right) \quad (3)$$

the fraction of oxygen sites vacant V_O in GeO_{2-x} can be written as

$$V_O = \frac{x}{2} = \frac{n}{N_0} \quad (4)$$

As shown in Fig. 9, because the integrated band intensity of the 5-eV absorption band, I_{5-eV} , is proportional to the fraction of oxygen sites vacant, the integrated band intensity of the 5-eV absorption band is given by a relation using Eqs. (2) and (4)

$$I_{5-eV} \propto V_O \propto \exp(-Q/kT) \quad (5)$$

It is possible to determine the activation energy Q for the thermally activated process by taking the logarithm of both sides of Eq. (5)

$$\ln I_{5-eV} \propto \ln V_O = \ln(A) - Q/kT \quad (6)$$

where A is constant for a particular process. Thus, the slope of the curve represents the formation energy for oxygen vacancies. When least-squares fitted to this function, the activation energy Q for the formation of oxygen vacancies in the sol-gel films is 1.0 ± 0.15 eV. This is appreciably smaller than the formation energy of the oxygen vacancies for bulk GeO_2 glasses, which is known to be 2.3 ± 0.1 eV.¹⁶ Thus, it is found that oxygen vacancies are more

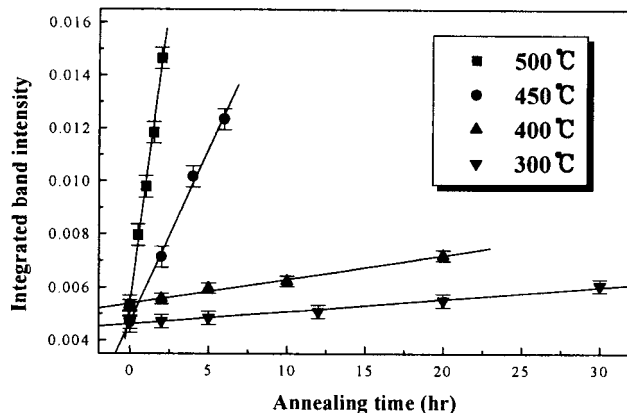


Fig. 8. Integrated band intensity of the 5-eV absorption band for germanium oxide thin films annealed at (a) 500°, (b) 450°, (c) 400°, and (d) 300°C depending on annealing time under a flowing H_2/N_2 (1:9 volume ratio) atmosphere. Error bars arise from uncertainty in the curve-fitting analysis of the data.

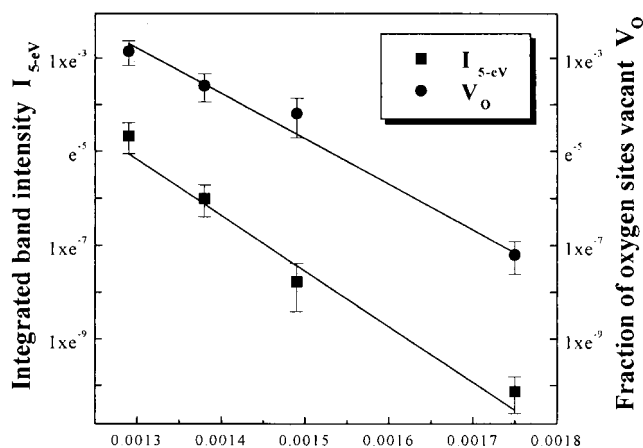


Fig. 9. Integrated band intensity of the 5-eV absorption band and the fraction of oxygen vacancies as a function of annealing temperature for germanium oxide thin films annealed for 2 h under a flowing H_2/N_2 (1:9 volume ratio) atmosphere. Error bars arise from uncertainty in the curve-fitting technique of the data and the measurement error of the WDS.

easily formed in sol-gel films than in bulk glasses. This implies that higher photosensitivity of germanium oxide can be obtained in sol-gel thin films than in bulk glasses.

IV. Conclusions

Germanium oxide glass thin films were prepared by the sol-gel spin coating method. The sol-gel films were sintered to be densified and annealed under reduced atmosphere to create more oxygen vacancies. The crystallization of the films was affected by the annealing atmosphere and temperature as well as the sintering temperature. The prepared glass films showed dense, homogeneous, and smooth surfaces having a germanium oxide phase without hydroxyl content. The intensity of the 5-eV absorption band of the films increases exponentially with annealing temperature and linearly with annealing time. The integrated band intensity of the 5-eV absorption band is proportional to the fraction of oxygen vacancies, since the 5-eV absorption band is produced by the formation of oxygen vacancies. Thus, the calculated formation energy of oxygen vacancies for the germanium oxide glass thin films is about 1.0 ± 0.15 eV, which is less than that for the bulk glass. Therefore, controlled annealing under reduced atmosphere creates more oxygen vacancies in sol-gel-derived germanium oxide glass thin films, which can produce higher photosensitivity.

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