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Section 3. Photochemical phenomena

Photosensitivity of germanium oxide and germanosilicate glass sol–gel films

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Abstract

Germanium oxide and germanosilicate glass films were fabricated using a sol–gel spin coating method. The formation and photobleaching of the optical absorption band of the films in the 5-eV region were measured as a function of annealing under a reducing atmosphere and ultraviolet (UV) illumination. A greater amplitude in the 5-eV absorption band was observed with increasing annealing time due to the formation of more germanium-related oxygen vacancies in the films. Also, the photobleaching of the absorption band increased with increasing illumination time. Although the amplitude of the absorption band in $50GeO_2$–$50SiO_2$ glass films is greater than that in germanium oxide glass films because of higher annealing temperature, germanium oxide glass films are more photosensitive due to the greater photobleachable neutral oxygen monovacancy (NOMV) concentration than non-photobleachable neutral oxygen divacancy (NODV) concentration in the films.

1. Introduction

Silica glass doped with GeO_2 has been investigated because of the ultraviolet (UV)-induced refractive index change that is responsible for the formation of distributed Bragg gratings [1]. This photosensitivity is due to the generation of Ge E′ centers by photobleached 5-eV absorption band of oxygen deficient centers. It has been known that there is an absorption band near 5 eV (~240 nm) in germanium oxide and that this absorption band is associated with germanium-related oxygen vacancies [2,3]. For these germanium-related defect centers, Cohen and Smith [2,4] in 1958 first showed that the absorption band near 5-eV band was attributed to a neutral oxygen vacancy caused by the reduction of Ge^{4+} to Ge^{2+}. Hosono et al. [5] reported that germanium-related oxygen vacancies were composed of neutral oxygen monovacancy (NOMV) at 5.06 eV and neutral oxygen divacancy (NODV) at 5.16 eV [6,7]. Only the absorption band at 5.06 eV of NOMV can be bleached by UV illumination and it forms a new absorption band with an energy >5.5 eV [6]. These UV absorptions contribute to a permanent increase in the refractive index of the glasses that can be used in the fabrication of Bragg gratings [6]. It was found that heat treatment of a germanosilicate glass preform in a H_2 atmosphere increased the intensities of an absorption band centered at 5 eV and that the intensities of the photobleachable component, which is the precursor of UV-induced Ge E′ centers and assigned to NOMV of the 5-eV band were

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increased more than those of the UV unbleachable component [8]. Thus, the greater concentration of the photobleachable NOMV which can be made by increasing germanium oxide content or heat treatment under reduced atmosphere [8] is desirable for the efficient production of grating devices. In this study, the germanium oxide and germanosilicate glass films were prepared by sol–gel method and heat-treated under reduced atmosphere. The optical absorption and photobleaching of the films by UV illumination were measured.

2. Experimental procedure

Germanium oxide (GeO_2) and germanosilicate ($50GeO_2$–$50SiO_2$) coating solutions were prepared using germanium ethoxide [$Ge(OC_2H_5)_4$, TEOG] of 99.99% purity and silicon ethoxide [$Si(OC_2H_5)_4$, TEOS] of 98% purity as starting precursors. Because of the moisture sensitivity of the germanium ethoxide, all reactions and manipulations were carried out under nitrogen atmosphere in a glove box. The procedure has been described elsewhere [9].

The prepared sol solutions were then deposited on fused silica glass substrates by the spin-coating method. The coated films were dried at 140°C for 20 min after each coating to allow for evaporation of the solvent from the films. To obtain a homogeneous glass film without cracking and a crystalline phase during the drying and densification process, the germanium oxide and germanosilicate films were heated at 600°C and 800°C for 10 min in air using a controlled heating rate, respectively. After the sintering process, germanium oxide and germanosilicate films were annealed under a flowing H_2/N_2 (1/9 volume ratio) atmosphere at 500°C for 2 h and at 600°C for 1 h, respectively. The amorphous phase of the thin film was confirmed by X-ray diffraction analysis (XRD, Rikagu D/MAX-RC). A 300 W Xe lamp (LX300UV, ILC Technology) with 248 nm bandpass filter (Coherent Auburn Group) was used to examine the change of the 5-eV absorption band with UV illumination.

3. Results

To produce more of the NOMV that is responsible for the photosensitivity of the germanium oxide films, the films were annealed under a reducing atmosphere after the densification process. It has been reported that more of the photobleachable component, NOMV, is generated than the non-photobleachable component, NODV, when films are heat-treated under the H_2/N_2 atmosphere [8]. Fig. 1 shows the XRD patterns of germanium oxide and germanosilicate films that had been annealed at 500°C for 2 h and 600°C for 1 h under the H_2/N_2 atmosphere and then after densification, respectively. It has clearly been shown that the perfect amorphous phase without a crystalline phase could be obtained with reduced heat-treatment. However, heat-treatment of germanium oxide and germanosilicate films in the H_2/N_2 atmosphere above 500°C and then again at 600°C induced the formation of a germanium oxide crystalline phase.

To examine the optical properties of the films, a fused silica glass that is transparent in the UV wavelength region was used as a substrate. Formation of the optical absorption bands in the 5-eV region were examined as a function of the annealing time at 500°C under a flowing H_2/N_2 (1/9 volume ratio) atmosphere. Fig. 2(a) shows the difference spectra of the germanium oxide films in the 5-eV region, which were obtained by

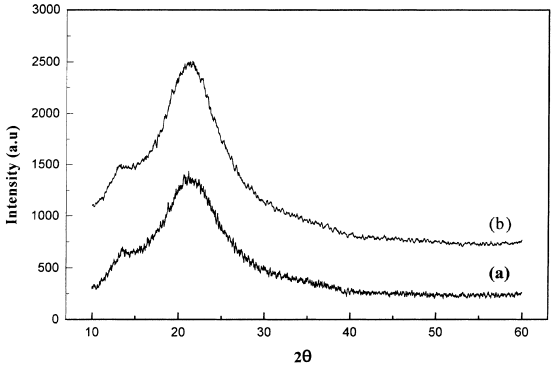

Fig. 1. XRD spectra of: (a) germanium oxide; (b) $50GeO_2$–$50SiO_2$ glass thin films annealed at 500°C for 2 h and at 600°C for 1 h under a flowing H_2/N_2 (1/9 volume ratio) atmosphere, respectively.

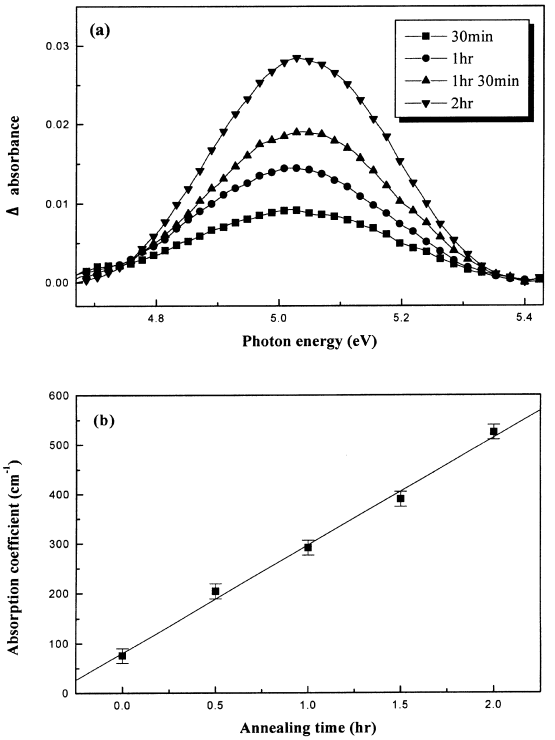

Fig. 2. (a) The difference spectra of the germanium oxide films at 5-eV band with the annealing time at 500°C under a flowing H_2/N_2 (1/9 volume ratio) atmosphere, which are obtained by subtracting the optical absorption spectra before annealing from that after annealing. (b) The absorption coefficient located at 5-eV in the absorption spectra of the germanium oxide films as a function of annealing time.

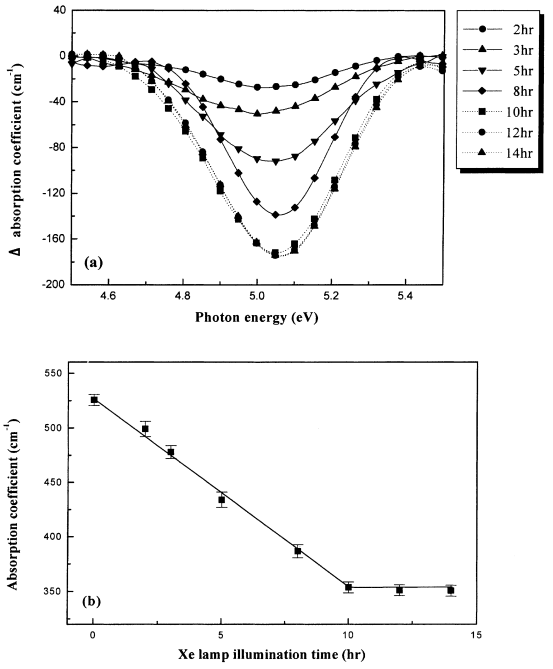

Fig. 3. (a) The difference spectra. (b) Absorption coefficient at 5 eV of the germanium oxide thin films with the irradiation time of the 248 nm beam emitted from a 300 W Xe lamp. The function, $Y = A + BT$, is fitted to the data for $T < 10$ h. The correlation coefficient is $R = -0.99794$, $A = 528.663$, and $B = -17.676$.

subtracting the optical absorption spectra before annealing from that after annealing. The growth of an absorption band at 5 eV by longer annealing was observed. The 5-eV absorption coefficient in the absorption spectra of the germanium oxide films as a function of annealing time is plotted in Fig. 2(b). A linear function is fitted to the absorption coefficients of the films as a function of the annealing time. The correlation coefficient of the fit is $R = 0.99724$. Thus, the concentration of germanium-related oxygen vacancy increases linearly with increasing annealing time.

Photobleaching of the optical absorption band in the 5-eV region was measured as a function of irradiation time of the 5-eV light. Fig. 3 shows the change of the absorption coefficients at 5 eV of the germanium oxide films with the UV illumination time. The absorption coefficient measured in germanium oxide films before UV illumination is about 525 cm^{-1}. A linear function was fitted to the absorption coefficients at 5 eV as a function of UV illumination time. The correlation coefficient in the period to ~10 h was $R = -0.99794$. For times >10 h, no bleaching was observed. The saturated absorption coefficient change ($-\Delta\alpha$) of the germanium oxide films is about 175 cm^{-1}.

To compare the photosensitivity of pure germanium oxide films with that of germanosilicate films, photobleaching of the optical absorption band at 5 eV for $50GeO_2$–$50SiO_2$ glass film sample was measured after UV illumination. Because the crystallization temperature of the SiO_2 is higher than that of GeO_2, the annealing of the $50GeO_2$–$50SiO_2$ films was conducted at a higher temperature than that of germanium oxide films. Fig. 4 shows the change of the absorption coefficients at 5 eV of the $50GeO_2$–$50SiO_2$ films with the UV

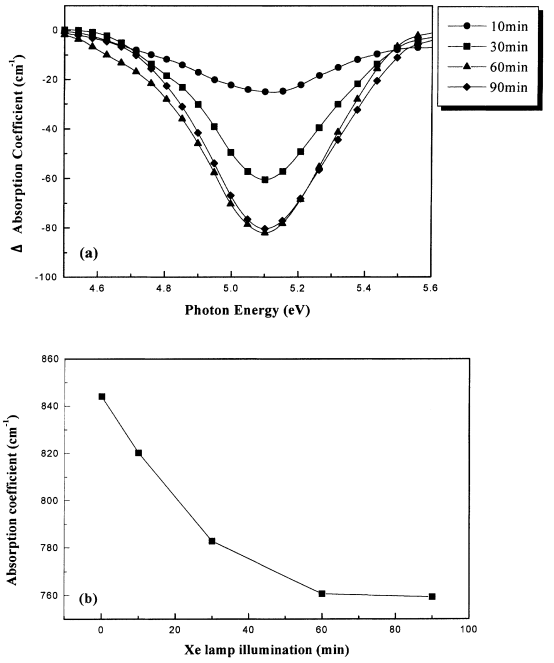

Fig. 4. (a) The difference spectra. (b) Absorption coefficient at 5 eV of the $50GeO_2$–$50SiO_2$ thin films with the irradiation time of the 248 nm beam emitted from a 300 W Xe lamp. The line is drawn as a guide for the eye.

illumination time. The absorption coefficient measured in $50GeO_2$–$50SiO_2$ films before UV illumination was about 845 cm^{-1}, which was larger than that in the germanium oxide films. As shown in the germanium oxide films, the absorption coefficients at 5 eV for the $50GeO_2$–$50SiO_2$ system also decrease linearly with the UV illumination time and then approach a constant magnitude. The saturated absorption coefficient change ($-\Delta\alpha$) of the $50GeO_2$–$50SiO_2$ films was about 85 cm^{-1}, which was smaller than that of the germanium oxide films.

4. Discussion

Only NOMV is bleached by UV illumination and it converts to Ge E′ center, whereas NODV is not bleached by UV illumination [6]. Assuming that the absorption band at 5 eV is only composed of NOMV and NODV, only the NODV remained after the UV illumination. Thus, we found from Figs. 3 and 4 that a decrease in the absorption coefficient was due to the NOMV and that the remainder of the absorption coefficient is due to the NODV. The ratios of the NOMV and NODV concentrations for germanium oxide and germanosilicate system were about 0.113 and 0.025 using the molar extinction coefficients 4×10^4 l/mol/cm [5] for ε_{NOMV} and 9×10^3 l/mol/cm [3] for ε_{NODV}, respectively.

Although the amplitudes of the 5-eV band in germanosilicate films were larger than that in the pure germanium oxide films because of the higher annealing temperature of the germanosilicate film samples, we found again in Figs. 3 and 4 that the NOMV that is responsible for the photosensitivity had a smaller amplitude in the germanosilicate system. Consequently, the larger refractive index change by UV illumination would be obtained with a larger germanium oxide content.

5. Conclusion

Although the intensities of the 5 eV in germanosilicate films were larger than that in pure germanium oxide films because of higher annealing temperature, pure germanium oxide glass films were more photosensitive.

Acknowledgements

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References

[1] K.O. Hill, Y. Fujii, D.C. Johnson, B.S. Kawasaki, Appl. Phys. Lett. 32 (1978) 647.
[2] A.J. Cohen, H.L. Smith, J. Phys. Chem. Solids 7 (1958) 301.
[3] M.J. Yuen, Appl. Opt. 21 (1982) 136.
[4] A.J. Cohen, Phys. Rev. 105 (1957) 1151.
[5] H. Hosono, Y. Abe, D.L. Kinser, R.A. Weeks, K. Muta, H. Kawazoe, Phys. Rev. B 46 (1992) 11445.

[6] H. Hosono, K. Kawamura, N. Ueda, H. Kawazoe, S. Fujitsu, N. Matsunami, J. Phys.: Condens. Matter 7 (1995) L343.
[7] T.E. Tsai, E.J. Friebele, M. Rajaram, S. Mukhapadhyay, Appl. Phys. Lett. 64 (1994) 1481.
[8] H. Hosono, H. Kawazoe, K. Muta, Appl. Phys. Lett. 63 (1993) 479.
[9] J.H. Jang, J. Koo, B.S. Bae, J. Am. Ceram. Soc., submitted.