Periodic sub-wavelength structures with large phase retardation fabricated by glass nanoimprint

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One-dimensional periodic sub-wavelength structures (SWSs) with a period of 300 nm were fabricated on a bismuth germano-borate glass plate by a direct glass nanoimprint method using SiC molds. The borate glass had a refractive index of 1.82 at 587.6 nm wavelength, an internal transmittance higher than 80% at a thickness of 3 mm in the visible wavelength region, and a deformation temperature of 468°C. SWSs with height of a few hundred nanometers were simultaneously fabricated on both surfaces of the glass plate by the glass nanoimprint at 488°C for 120 s with 8 MPa in pressure. The SWSs showed form birefringence. A phase retardation of 0.23λ was observed between transverse electric (TE)- and transverse magnetic (TM)-polarized beams at 400 nm wavelength.

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1. Introduction

Periodic sub-wavelength structures (SWSs) have been attracting much attention as key elements for the realization of several optical functions such as antireflection,^{1),2)} polarization-independent diffraction,³⁾ polarization splitting,⁴⁾ isolation,⁵⁾ and phase control.^{6)–8)} The conventional fabrication process of these SWSs is electron-beam (EB) lithography followed by dry etching. Recently, the nanoimprint process has been investigated as a promising technology for reduction of the fabrication cost and time of SWSs. Several research groups have reported the fabrication of SWSs on resin plates or films using ultraviolet-imprinting or thermal-imprinting processes.^{8)–10)} However, the mechanical strength and the long-term chemical durability of the resin are sometimes insufficient for practical use as high-quality optical devices. Inorganic glasses have mechanical strength, chemical durability and thermal stability higher than resins, and therefore, the fabrication of SWSs on glass surfaces has been attempted by the nanoimprint process.^{11)–17)}

In a previous study, one-dimensional (1D) periodic SWS with a period of 300 nm and a groove depth of 210 nm was fabricated on a glass surface by the nanoimprint process, which exhibited a phase retardation of 0.08λ at a wavelength of 400 nm between transverse electric (TE)- and transverse magnetic (TM)- polarized beams due to form birefringence.^{16),17)} Higher phase retardation is, however, required for the application of 1D periodic SWS to quarter wavelength plate. Higher phase retardation can be attained by the use of materials with a higher refractive index and/or by the fabrication of higher-aspect-ratio (deeper groove) structure. It is, however, still difficult to fabricate high-aspect-ratio structure on glass surfaces by the nanoimprint process. One

of the solutions to overcome this difficulty is the fabrication of SWSs on both surfaces of a glass plate, which doubles the phase retardation. In the present study, a borate glass with a high refractive index and low deformation temperature has been developed. A 1D-SWS with 300 nm period has been fabricated on both surfaces of the glass.

2. Introduction experimental procedures

2.1 Preparation of glass for nanoimprint

Glasses used in the present study must have a low deformation temperature for glass nanoimprint, a high refractive index for form birefringence and high transmittance in the near ultraviolet ray region for the application to several optical appliances such as Blu-ray disc drives. It is expected that $\text{Bi}_2\text{O}_3\text{--GeO}_2\text{--B}_2\text{O}_3$ glass fulfills the properties required in the present study, since it is known that $\text{Bi}_2\text{O}_3\text{--B}_2\text{O}_3$ glasses have a high refractive index and low deformation temperature¹⁸⁾ and it is expected from the optical basicity that the addition of GeO_2 to $\text{Bi}_2\text{O}_3\text{--B}_2\text{O}_3$ glass improves the transmittance in the near ultraviolet ray region.¹⁹⁾ Therefore, the glass formation and properties of glass were studied in $\text{Bi}_2\text{O}_3\text{--GeO}_2\text{--B}_2\text{O}_3$ system, particularly, in the composition of $(40\text{--}0.5y)\text{Bi}_2\text{O}_3\cdot y\text{GeO}_2\cdot (60\text{--}0.5y)\text{B}_2\text{O}_3$ along the compositional line between $40\text{Bi}_2\text{O}_3\cdot 60\text{B}_2\text{O}_3$ and $80\text{GeO}_2\cdot 20\text{B}_2\text{O}_3$. The glass used for the glass nanoimprint was sought around this compositional line.

The mixture of reagent grade of Bi_2O_3 , GeO_2 and B_2O_3 was melted in a Pt crucible at temperatures from 1000 to 1200°C in air, and was poured onto a carbon plate to form a 50 g glass. The glass formation was confirmed by the naked eye. The thermal expansion coefficient was measured with a thermo-mechanical analyzer (Seiko Instrument Inc., TMA/SS6300) under a load of 0.1 N using samples with 10 mm length. Refractive indexes were measured at 404.7 (Hg-h line), 435.8 (Hg-g line), 546.1 (Hg-e line), 587.6 (He-d line), and 656.3 nm (H-C line) with a precision

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refractometer (Shimadzu Co., KPR-2000) and at 632.8 (He-Ne laser) and 831.8 (semiconductor laser) nm with a prism coupling instrument (Metricon, prism coupler Model 2010). Optical absorption spectra were measured with a spectrophotometer (Hitachi, Ltd., U4000 spectrophotometer).

2.2 Fabrication of one-dimensional periodic structures in SiC molds

SiC plates of $25 \times 25 \times 2$ mm with an optically flat surface (YW; Adomap, Inc.) were used for the molds, since it has been reported that SiC has heat-resistance and a high mechanical strength and also has micro-workability.²⁰⁾ A W-Si film with 120 nm thickness was deposited by DC sputtering and an EB resist (ZEP520A; Zeon Co.) was spin-coated on the SiC plates. Then, a grating pattern with 300 nm period and 150 nm grating width was drawn with an EB direct writing apparatus (ELS-7500EX; Elionics, Inc.) on the SiC plates in 6×6 mm area, followed by the development of resist with o-xylene. The grating pattern was transferred to the W-Si mask layer by inductively coupled plasma reactive ion etching (ICP-RIE, RIE-200iP; Samco, Inc.) with SF_6 gas. The SiC plate was etched through the patterned W-Si mask by ICP-RIE with a gas mixture of CHF_3 and O_2 .²¹⁾ The SiC plates with one-dimensional periodic grooves obtained were used as molds for the glass nanoimprint.

2.3 Glass nanoimprint

Glass nanoimprint was carried out using a pressing machine (GMP-311V; Toshiba Machine Co., Ltd.). The two SiC plates with one dimensional periodic grooves were set as the upper and lower molds in the pressing machine. The grooves of the upper and lower SiC molds were parallel to each other. A glass preform of 12 mm diameter and 2 mm thickness was set between the SiC molds. In this study, the imprinting temperature, pressure, and time were 488°C , 8 MPa, and 120 s, respectively. Adhesion between the SiC molds and the glass occurred during glass-imprinting at a temperature beyond 488°C , pressure beyond 8 MPa, and time longer than 120 s. Before imprinting, the pressing chamber was filled with N_2 gas and subsequently evacuated to pressures lower than 0.4 Pa in order to minimize the residual O_2 gas. The upper mold was removed from the glass after pressing at an elevated temperature and the glass was removed from the lower mold after cooling. The surface of the glass was observed with a scanning electron microscope (Hitachi, Ltd., S-4800) and an atomic force microscope (Shimadzu, Co., SFT-3500).

2.4 Phase retardation measurement

The phase retardation between TE- and TM-polarized beams transmitted through the one-dimensional periodic structures was measured with a rotating analyzer (RETS-100; Otsuka Electronics Co., Ltd.).

3. Results and discussion

3.1 $\text{Bi}_2\text{O}_3\text{-GeO}_2\text{-B}_2\text{O}_3$ glass

Deformation temperature, refractive index at 587.6 nm, internal transmittance (3 mm thick) at 400 nm wavelength of the $(40-0.5y)\text{Bi}_2\text{O}_3\cdot y\text{GeO}_2\cdot(60-0.5y)\text{B}_2\text{O}_3$ glasses were plotted against the GeO_2 content in Fig. 1. Glass was formed in the region from $y = 0$ to 55. Glass was partially devitrified at $y = 60$. The deformation temperature showed a maximum at 40 mol% GeO_2 . Such an anomaly have been reported in the $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ and $\text{Bi}_2\text{O}_3\text{-GeO}_2$ glass systems.^{22),23)} The refractive index decreased gradually with the GeO_2 content, but was higher than 1.7. The internal transmittance at 400 nm wavelength increased with the GeO_2

content. Based on these experiments, we chose $17.5\text{Bi}_2\text{O}_3\cdot 50\text{GeO}_2\cdot 32.5\text{B}_2\text{O}_3$ glass for the following glass nanoimprint process. That is, Bi_2O_3 was substituted for B_2O_3 by 2.5 mol% for $15\text{Bi}_2\text{O}_3\cdot 50\text{GeO}_2\cdot 35\text{B}_2\text{O}_3$ glass to increase the refractive index to higher than 1.8 with maintaining the deformation temperature lower than 470°C and the internal transmittance higher than 80%. Properties of this glass are summarized in Table 1. The glass had a refractive index of 1.82 at 587.6 nm wavelength, an internal transmittance higher than 80% (3 mm thickness) at a wavelength of 400 nm, and a deformation temperature of 468°C .

3.2 Glass nanoimprint

Figure 2 shows a scanning electron microscope (SEM) photograph and an atomic force microscopic (AFM) depth profile of grooves of the one-dimensional periodic structure fabricated on the SiC molds. The period and groove depth of grooves fabricated on SiC were 300 and 220 nm, respectively, according to the AFM measurement. The cross-sectional groove structure was not

Fig. 1. Deformation temperature, refractive index at 587.6 nm wavelength and internal transmittance at 400 nm wavelength (3 mm thickness) against GeO_2 content (mol%). Open circles, open squares and closed squares represent deformation temperature, refractive index and transmittance, respectively. Curves are shown for the guide of eyes.

Table 1. Properties of $17.5\text{Bi}_2\text{O}_3\cdot 50\text{GeO}_2\cdot 32.5\text{B}_2\text{O}_3$ Glass

T_g $^\circ\text{C}$	A_t $^\circ\text{C}$	α 10^{-7}K^{-1}	n_b	n_g	n_e	n_d	n_{633}	n_c	n_{832}	τ_{400} %
425	468	75.7	1.846	1.839	1.823	1.816	1.811	1.807	1.795	85

T_g , A_t , α and τ_{400} represent glass transition temperature, deformation temperature, average linear thermal expansion coefficient (30– 400°C) and internal transmittance at 400 nm (3 mm thickness), respectively. n_b , n_g , n_e , n_d , n_{633} , n_c , n_{832} represent refractive indexes at 404.7, 435.8, 546.1, 587.6, 632.8, 656.3 and 831.8 nm, respectively.

Fig. 2. (a) SEM photograph and (b) AFM depth profile of grooves of SiC mold surface.

Fig. 3. SEM photographs of (a) upper and (c) lower surfaces, and AFM height profiles of (b) upper and (d) lower surfaces of glass after glass nanoimprinting.

rectangular in shape but a tapered shape, which was suitable to fabricate high-aspect-ratio structures by the glass nanoimprint.²⁴⁾

Figure 3 shows the SEM photographs and the AFM height profiles of the upper and lower glass surfaces after imprinting. It can be seen that one-dimensional periodic structures were formed on both the upper and lower surfaces of the glass. It was confirmed by the SEM observation that the structures were formed in the area of 6×6 mm on both sides of the glass. Since the glass was removed from the lower mold after cooling in the present study, the mismatch of the thermal expansion coefficient between the glass and mold ($43 \times 10^{-7} \text{ K}^{-1}$ ²⁵⁾) below the glass transition temperature should cause the shrinkage difference of about $1.2 \mu\text{m}$ at the end of the periodic structure, which is greater than the period of the structure. However, the glass was removed from the lower mold without breakage of the structure. It is unclear yet why the structure was not broken during cooling. We speculated that the tapered shape of grooves caused the self-demolding of glass during cooling, which prevented the structure from breaking.

The grating heights of the upper and lower surfaces were 170 and 150 nm, respectively, according to the AFM measurement. The grating height on the glass was lower than that of the groove depth of the SiC mold. Further improvement of imprinting conditions is currently underway to realize the greater grating height.

3.3 Phase retardation of the glass

Figure 4 shows the relationship between the phase retardation obtained empirically and the wavelength. The phase retardation of 0.23λ was obtained at 400 nm wavelength. The phase retardation expected for a model structure was calculated numerically using commercially available software (GSOLVER 4.20: Grating Solver Development Co.) based on a rigorous coupled wave analysis.²⁶⁾ The model had rectangular cross-sectional grooves, a line/space ratio of 1:1, and grating heights of 170 and 150 nm on each surface. The calculated values, as shown by solid squares in Fig. 4, agree fairly well with the experimental values, showing that the phase retardation observed in the present study was due to form birefringence. The small difference between the experimental and calculated values might be due to the difference between the model structure and fabricated structure. Finally, it

Fig. 4. Relationship between wavelength and phase retardation between TE-polarized and TM-polarized beams transmitted through periodic structures. The open circles and solid squares represent the experimental and the calculated values, respectively.

should be stressed that the quarter wavelength plate is expected to be produced by the glass nanoimprint process.

4. Conclusion

One-dimensional periodic sub-wavelength structures were simultaneously fabricated on both sides of a newly developed bismuth germano-borate glass plate by a direct glass nanoimprint method using SiC molds. The structure with a period of 300 nm and height of a few hundred nanometers were successfully formed on both sides of the glass surfaces in an area of 6×6 mm. The glass showed a phase retardation of 0.23λ at 400 nm wavelength, which originated from the form birefringence.

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