Periodic structures in GeO$_2$-B$_2$O$_3$-SiO$_2$ glass films fabricated using ultraviolet laser pulses

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Abstract. We firstly observed the surfaces of periodic structures consisting of Ge nanoparticles in channel waveguide cores of GeO$_2$-B$_2$O$_3$-SiO$_2$ glasses. Such periodic structures were formed only by direct laser writing and subsequent annealing. Refractive index patterns were written in the glass films by irradiation with KrF excimer laser pulses. Then, the patterns were inverted by thermo-induced precipitation of Ge nanoparticles at unirradiated areas. Brown channel cores were obtained due to predominant precipitation of the nanoparticles in the cores. The periodic structures of 530 nm pitch and microchannels were directly observed by using wet-etched samples. The periodic structures were confirmed only inside the cores.

1. Introduction

Photonic band-gap (PBG) devices have been recognized as one of key components for integrated photonic systems. The PBG devices, which have artificial structures whose refractive index is periodically modulated, can control optical properties of propagation light. Due to their potential applications such as optical band-pass filters, high-Q resonators, integrated photonic sensors, display systems, and so on, PBG devices have been intensively studied in the last decade [1-3]. However, the fabrication of fine periodic structures which can work in optical communication wavelength is still a challenging topic.

Most PGB devices are produced by the semiconductor technology. To obtain submicron structures, we must use highly expensive electron-beam lithography system. In this system, electron beam exposure inside the vacuum chamber and complicated resist process are required.

On the other hand, direct laser writing techniques of photonic structures have attracted much attention. By these techniques, photonic devices such as optical filters and diffractive lenses can be directly written in glasses and polymeric materials [4-6]. Although this technique is highly flexible and does not require a vacuum chamber, laser-induced changes of refractive index are reported to be small and thermally less stable [7]. For example, the refractive index changes induced by ultraviolet laser exposure in optical fiber cores are as small as 10$^{-4}$ even though photosensitizing process is used. Furthermore, the index changes start to decay by annealing at 150ºC.

Recently, we have reported that crystalline Ge nanoparticles could be patterned in GeO$_2$-B$_2$O$_3$-SiO$_2$ (GBS) glass, which is often used as optical fiber and waveguide cores, by a combined process of
ultraviolet laser exposure and thermal annealing [5,8,9]. We also demonstrated the formation of periodic structures consisting of the nanoparticles in the cores of waveguide channels, which were fabricated by the semiconductor technology. The refractive index changes of such nanoparticle structures are approximately ten times larger than those of conventional direct laser writing technique. Furthermore, there are no changes of the refractive index changes even after annealing at 500ºC [8].

In the present paper, we firstly report the observation of the surfaces of PBG elements consisting of Ge nanoparticles inside channel cores, which are formed only by direct laser writing and subsequent annealing.

2. Experimental
GBS thin glass films with SiO$_2$ upper cladding layers were deposited on 1-mm thick SiO$_2$ substrates at 400ºC by the plasma-enhanced chemical vapor deposition method. Respective thickness of GBSs and upper layers were approximately 4 and 1 µm. Liquid sources of Si(OC$_2$H$_5$)$_4$, Ge(OCH$_3$)$_4$ and B(OC$_2$H$_5$)$_3$ were used as raw materials for SiO$_2$, GeO$_2$ and B$_2$O$_3$, respectively. Photoinduced periodic refractive index changes were written by irradiation with KrF excimer laser of 248 nm wavelength through the phase mask of 1060 nm pitch at room temperature. Refractive indices of the films were measured by the prism coupling method using 632.8-nm light source. Thermal annealing was carried out in a tube furnace with nitrogen atmosphere. The sample surfaces were observed by FE-SEM.

3. Results and discussion
Figure 1 shows changes of refractive indices of the GBS films by annealing at 600ºC. Here, we used two films; an as-deposited GBS film and a homogeneously irradiated GBS. The laser fluence and pulse number were 180 mJ/cm$^2$ and 27000, respectively. The refractive index increased by $3.1 \times 10^{-3}$ after this irradiation. The index difference between both films was remarkably decayed by annealing only for 10 min by thermal relaxation. However, refractive indices increased by annealing longer than 10 min. The amount of increase for the unirradiated film was larger than that of the irradiated one, resulting in inversion of the refractive index between both films. The inverted refractive index difference was highly stable and no changes were observed even after further annealing at 500ºC. Irradiation of higher fluence enhanced the difference of refractive index induced by the inversion.

We previously reported that periodic refractive index changes formed in GBSs by the direct laser writing technique were drastically enhanced by annealing at 600ºC [8]. In the films, crystalline Ge nanoparticles of 20–40 nm diameters are precipitated by annealing at 600ºC. This precipitation can be suppressed by laser exposure prior to the annealing. Due to this suppression, Ge nanoparticles, which have high refractive indices, were periodically precipitated, resulting in large refractive index modulation [8]. The inversion of refractive index in Fig. 1 is most likely due to this suppression effect of the nanoparticles by laser exposure.

![Figure 1. Changes of refractive indices of unirradiated films and homogeneously irradiated films as a function of annealing time at 600ºC. The refractive indices were measured using 632.8 nm light source.](image-url)
Figure 2 presents the fabrication processes for periodic structures in channel waveguides. These photonic structures consist of Ge nanoparticles and work as PGB devices. We also indicate the expected cross-sectional distributions of refractive index at each step. First, 5-mm-long periodic structures are written by laser exposure through a phase mask. The period of the periodic structures is 530 nm. Then, homogeneous exposure is performed through a Cr mask with a straight line pattern of 7 µm width on a SiO₂ substrate. The laser fluence and pulse number are 180 mJ/cm² and 27000, respectively. As a final step, annealing at 600ºC is carried out for 20 min. We can expect that the refractive index patterns are inverted by this annealing, resulting in the formation of periodic structures in 4-µm-high and 6-µm-wide channel cores.

An optical microscope image of the waveguide structures is shown in Fig. 3(a). We can see that a brown straight line was induced in the film. The line width was approximately 7 µm, which was consistent with the width of the Cr line mask. In our films, intense absorption bands are induced in ultraviolet-visible wavelength ranges by annealing at 600ºC. According to previous studies, these...
absorption changes are originated from Ge nanoparticles [10]. As the diameter of the nanoparticles decreases, the absorption edge remarkably shifts to shorter wavelength due to the size effect. The edge of our GBSs is located at about 300 nm wavelength, and absorption shoulder spreads to visible wavelength. The laser exposure suppresses the precipitation of the nanoparticles. Therefore, we can consider that the concentration of the nanoparticle at the straight line area became higher than that of the surroundings, and brown-colored straight line appeared due to the absorption shoulder of the Ge nanoparticles. Figures 3 (b) and (c) present SEM images of top view and overall view of the samples after HF wet etching treatment. Although it was difficult to recognize individual nanoparticle by this SEM observation because the annealing time was as short as 20 min, the channel core and periodic structures in the films were visible. We could not confirm as-fabricated structures because their surfaces were smooth. The width of channel core and period of the structures were 7 µm and 530 nm, respectively, which were identical with those of the photoimprinted patterns in Fig. 2. Bright lines in the periodic structures are likely to be aligned aggregated nanoparticles. Note that the periodic structures at clad areas (outside areas of the cores in the film) disappeared. This erase is most likely due to exposure with higher fluence in Fig. 2(c) than that in Fig. 2(a). By this exposure, photoinduced refractive index contrast in Fig. 2(a) decayed because larger refractive index changes can be induced by higher fluence. This confinement of the periodic structures in the core areas can avoid coupling of propagation light to clad and leaky modes, which is important for practical applications. The PBG properties of the periodic structures were reported in our previous works [5]. These structures exhibited high diffraction efficiencies and no changes of their optical properties were observed even after further annealing up to 500ºC. Our laser-assisted patterning technique of the nanoparticles is useful for the fabrication of more complicated functional photonic structures.

4. Conclusions
We firstly observed the periodic structures consisting of Ge nanoparticles in microchannels formed only by direct laser writing and subsequent thermal annealing. These photonic structures were induced by the inversion of photoimprinted patterns during the annealing. Brown-colored channel cores of 7 µm widths were observed, indicating that Ge nanoparticles were mainly precipitated in the core areas. By using HF etching of sample surfaces, we could see the periodic patterns of 530 nm pitch and microchannel directly. The periodic structures were induced only inside the cores.

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