Direct Photo-Imprinting in High Photosensitive Organically Modified Germanosilicate (ORMOGSIL) Glasses

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ABSTRACT

Direct photo-imprinting of both surface relief pattern and refractive index modulation upon the organically modified germanosilicate (ORMOGSIL) glass using its large volume change was performed by ultraviolet exposure. A large refractive index increase up to $10^{-2}$ is induced by ultraviolet-induced densification in the ORMOGSIL glasses. The photosensitivity in the ORMOGSIL glass was enhanced by introducing a photo-polymerizable methcrylate group in the glass structure. Also, a surface AFM scans and optical microscope images of unetched sample show that the volume compaction in the ultraviolet illuminated region is associated with periodic pattern inscription.

INTRODUCTION

Light-induced surface relief gratings have attracted attention because of their potential application for optical data storage, integrated optics or LC devices fabrication. Surface relief gratings are typically fabricated by mechanical, chemical, optical processing, and their combinations [1,2]. Since these processes are rather complex to reveal the precise surface structure, intensive research on the direct formation of surface relief gratings have been carried out in many research groups and companies all around the world in recent years [3-6]. Germanium doped silica glasses have received much attention because of the ultraviolet-induced refractive index change [7]. In this case, refractive index changes through defect reaction within the glass, but surface relief grating is rarely found [8-10]. However, recent our research on organically modified germanosilicate (ORMOGSIL) glasses fabricated by sol-gel method shows that the large refractive index change in ORMOGSIL glasses is predominantly due to the glass density increase induced by ultraviolet exposure rather than a defect chemistry [11].

In the present study, we report on the direct photo-inscription of both surface relief pattern
and refractive index modulation upon the organically modified germanosilicate (ORMOSIL) glass using its large volume change induced by ultraviolet exposure. The shorter photo-imprinting time and the higher photosensitivity can be obtained by introducing photopolymerizable organic units such as methacrylates into ORMOSIL glass structure.

EXPERIMENTAL DETAILS

Organically modified germanosilicate glasses with Ge contents of 10, 15 and 20 mol% were prepared by the sol-gel method. Germanium Isopropoxide (GI, Aldrich) of 97%, Diethoxydimethylsilane (DMDES, Aldrich) of 97% and 3-(Trimethoxysilyl)propylmethacrylate (MPTMS, Aldrich) of 98% purity were used as the starting material. Since hydrolysis reaction of germanium isopropoxide was very fast compared with those of DMDES and MPTMS, DMDES and MPTMS were each prehydrolyzed and then germanium isopropoxide was added to the solutions. 2-Benzl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (Irgacure369, Aldrich) was used as photoinitiator in MPTMS/GI system. This photoinitiator undergoes a photocleavage to yield benzoyl radicals which initiate the photo-polymerization in the ORMOSIL glass. The ORMOSIL(I) and ORMOSIL(II) glasses denote the DMDES/GI (unreactable organic) and MPTMS/GI (photo-polymerizable organic) system, respectively.

The ORMOSIL glasses were illuminated by UV lamp (1KW Hg/Xe lamp, 220–260nm, Oriel 82521), which gave a power density of 45 mJ/cm². The refractive index of the glasses was measured at 632.8nm with a prism coupler (Metricon 2010). The density was measured by the Archimedes method using a Sartorius LA120S balance. Patterning of ORMOSIL glass was carried out by ultraviolet fluence at 2500 J/cm² through a quartz contact mask. The surface morphology of the samples was observed with an Atomic Force Microscope (AFM, Park Scientific Instruments, Autoprobe 5M) and optical microscope.

RESULTS AND DISCUSSION

Figure 1 shows the refractive index change of the ORMOSIL(I) glasses as a function of UV illumination. For all compositions of ORMOSIL(I) glass, the refractive index increased linearly with UV fluence up to 2500 J/cm² and then approached a saturated level. The refractive index change of the 10 mol% Ge-doped ORMOSIL(I) glass was about $10^{-2}$. This is comparable with that seen with cold high pressure hydrogen soaking, which has led to germanium-doped fibers with the highest observed photosensitivity. Contrary to our expectation, for the
Figure 1. Changes in refractive index of 10, 15 and 20 mol% Ge-doped ORMOGSIL(I) glasses with UV fluence of a 1000W Hg/Xe lamp.

ORMOGSIL(I) system, the refractive index change of 10 mol% Ge-doped ORMOGSIL glass was larger than that of 20 mol% Ge-doped ORMOGSIL glass. This result shows that the color-center model is not sufficient to explain large refractive index change in ORMOGSIL(I) glass. Figure 2 shows the density change of 20 mol% Ge-doped ORMOGSIL(I) glass with UV fluence. Density increases linearly with the UV fluence, the same behavior as observed in the refractive index change behavior. In addition, we have found recently that the refractive index change in ORMOGSIL(I) glass is mainly due to the structural densification by reduction of the average intertetrahedral bonding angle $\theta$ from the shifts in frequency of the Raman bands with the UV illumination [11].

Certain monomers, notably styrene and methyl methacrylate and some strained-ring cycolalkenes, undergo photoinduced chain polymerization. This polymerization also induces refractive index increase [12]. Thus, we fabricated the organic-inorganic hybrid silica glasses having higher photosensitivity by introduction of methacrylates instead of methyl groups. Figure 3 shows the refractive index change and thickness of ORMOGSIL(II) glass as a function of UV illumination. The ORMOGSIL(II) glass reacts more quickly to the UV light and produces higher saturated index changes rather than that in figure 1. And the gradual decrease in glass thickness with UV exposure indicates that the refractive index change in ORMOGSIL glass is associated with volume compaction induced by UV exposure.

The ORMOGSIL glasses are direct photopatternable without any developing steps such as wet etching. Figure 4 shows AFM and optical microscope image of direct photo-imprinted
Figure 3. Refractive index change in 10 mol% Ge-doped ORMOGSIL(II) glass with UV fluence of a 1000W Hg/Xe lamp.

pattern written in the ORMOGSIL(I) glasses. The three-dimensional view of AFM revealed that a periodic pattern of a sinusoid wave with a 6 µm period spacing and 65 nm changes in depth from the original surface was formed upon the ORMOGSIL(I) glass. A photoinduced direct densification occurs in the UV illuminated regions. This regular surface modulation has attracted attention for optical device applications such as diffractive optical elements, optical switching, optical recording, channel waveguides, microlens and antireflection coatings, etc. Figure 5 shows

Figure 4. Optical microscope and AFM image of illustrated and line pattern written in the ORMGOSIL(I) glass, respectively.

Figure 5. Optical microscope and AFM image of an array of microlenses written in the ORMGOSIL(II) glass, respectively.
Figure 6. Change in refractive index of the 10 mol% Ge-doped ORMOGSIL glasses with the aging time at (a) 100 °C and (b) room temperature.

an array of microlenses, each with a diameter of 5 µm, inscribed on the ORMOGSIL(II) glass. The depth change from the original surface is about 400 nm, which is larger than that in the ORMOGSIL(I) glass. This result also indicates that the direct photo-patterning in the ORMOGSIL(II) glass is more efficient rather than that in the ORMOGSIL(I) glass.

To examine the thermal stability of the ORMOGSIL glass, we measured the refractive index of UV-exposed ORMOGSIL glass with aging time at 100 °C and room temperature. As shown in figure 6, no changes in refractive index of the ORMOGSIL glasses with UV exposure were detected. This result indicated that the photosensitivity in the ORMOGSIL glass is thermally stable up to 100 °C and also permanent at room temperature.

No doubt refractive index modulations based on GeO₂ doped silica glasses have many attractive and unique features. Nevertheless they have also their limits. Most apparent limitation seems to be their limited wavelength tenability and stress responsivity. This could be a fundamental limit that restricts silica glasses from being used in some of the important applications. Wavelength tenability will be a crucial feature required for future broadcasting and reconfigurable dense wavelength division multiplexer(DWDM) systems. The main reason for the poor tenability is clearly linked to the high rigidity of silica glass. Likewise the poor stress responsivity is related to its relatively large Young’s modulus. Therefore, the high photosensitive ORMOGSIL glass is attractive for its good flexibility, low cost and ease of handling.

CONCLUSIONS

This study reports a direct photoinduced inscription of both surface relief pattern and
refractive index modulation upon the organically modified germanosilicate (ORMOGSIL) glass fabricated by sol-gel method. The refractive index modulation in ORMOGSIL glass with UV exposure is accompanied with large volume change induced by the structural densification. The shorter photo-imprinting time and the higher photosensitivity can be obtained by introducing polymerizable organic units such as methacrylates into ORMOGSIL glass. In addition, photosensitivity in ORMOGSIL glass is thermally stable.

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REFERENCES