

Simple fabrication of diffraction gratings by two-beam interference method in highly photosensitive hybrid sol-gel films

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Abstract: Sol-gel hybrid materials containing a large quantity of photoactive molecules exhibited large changes in both refractive index and volume by UV exposure. The materials were used for the fabrication of diffraction gratings using the two-beam interference method. With this technique, we could simply fabricate the diffraction gratings and easily control the grating periods. The diffraction effects and efficiencies of gratings rely heavily on the UV doses and the fabricated diffraction gratings showed a good diffraction performance.

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References and links

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1. Introduction

Diffraction gratings are the important component for wavelength dispersion, conversion, signal processing and modulation in integrated optics [1-3]. Thus, the study of fabricating diffraction gratings has been intensively performed using a variety of methods, including a photo-mask, electron beam lithography, etching techniques, and holographic interference [4-6]. Contact imprinting using a photo-mask is not suitable for the fabrication of gratings with a submicrometer period due to the diffraction limit between the mask and the samples. The lithography, which includes the etching process, is rather complex and needs several steps to reveal the precise surface structure. However, holography can produce fine patterns and it is easy to control the period of gratings. Thus, the interference method using beam holography has great potential for the fabrication of gratings with fine periods.

The materials as well as the fabrication processes are crucial factors in manufacturing the optical elements. Thus, the photo-polymers such as azo polymers [7, 8] and the sol-gel hybrid (SGH) materials [9-12] have received much attention because the patterns could be fabricated quickly. Recently, the photosensitive sol-gel hybrid (SGH) materials, doped with the large contents of photoactive molecule, were found to exhibit a larger refractive index and volume change by UV exposure [13-15]. The photosensitivity of these materials could be increased by the simple addition of photoactive molecules. Also, these materials have the advantage of simple single-step photo-patterning due to the simultaneous changes in both refractive index and volume. Thus, these photosensitive SGH materials are good candidates for the simple fabrication of diffraction gratings.

In this paper, we reported on the simple fabrication of diffraction gratings with various periods by two-beam interference method using highly photosensitive SGH materials. In particular, we investigated the effect of the UV doses on the photosensitivity of the SGH materials and the relationships between the photosensitive properties upon UV exposure, the diffraction effects and efficiencies of gratings.

2. Experiment

Photosensitive SGH films were prepared using methacryloxypropyl-trimethoxysilane (MPTS, Aldrich), perfluoroalkylsilane (PFAS, Toshiba) and zirconium n-propoxide (ZPO, Aldrich) chelated with methacrylic acid (MAA, Aldrich) as precursors, as described in previous reports on the fabrication of the diffraction gratings [11, 13-15]. All precursors are hydrolyzed with 0.01-N HCl. After 20 hour stirring for full sol-gel reaction, residual products such as alcohols were removed at 50°C using an evaporator. Benzyl dimethyl ketal (BDK, Aldrich) as a photoinitiator, and methylmethacrylic acid (MMA, Aldrich) as a photoactive monomer, were added into the hybrid solution prior to the coating. The contents of BDK and MMA were 15 wt% of the hybrid solution. In order to solve the large amount of solid state BDK, we added the same amount of liquid state MMA, which lead to the enhancement of the photosensitivity of SGH materials. After stirring the solution for 1 hour at room temperature, homogeneous photosensitive SGH solution was obtained. This solution was spin-coated on a cleaned glass substrate for 30 seconds with a spinning speed of 3000-rpm. The coated films were exposed by He-Cd laser with the wavelength of 325 nm for photo-induced reactions. The exposed time

was different for measuring the effects of the UV dose on the photosensitivity of the materials and on the diffraction effects and efficiencies of the gratings. The UV exposed films were characterized directly or after baking it at 150°C for 5 hours.

The changes in the refractive index and thickness of the films before and after illumination with the He-Cd laser were measured using a prism coupler (Metricon 2010) at a wavelength of 632.8 nm. The images of the fabricated diffraction gratings were investigated using optical microscopy and atomic force microscope (AFM, Park Scientific Instruments, Autoprobe 5 M). The diffraction effects were monitored using a CCD camera and the diffraction efficiencies were measured by the Littrow configuration using a He-Ne laser with the wavelength of 632.8 nm in transmission mode.

3. Results and discussion

Figure 1 shows the changes of refractive index (a) and thickness (b) depending on the UV doses of He-Cd laser with the power density of 0.55 mW/cm². In order to measure the changes of refractive index and thickness of UV exposed films, the films were baked at 150°C for 5 hours after UV exposure and then the changes in refractive index and thickness of the films were measured. The changes in the refractive index and the film thickness increase in proportional to the UV dose. When the UV dose increases, the refractive index and thickness changes continued to increase and then became saturated.

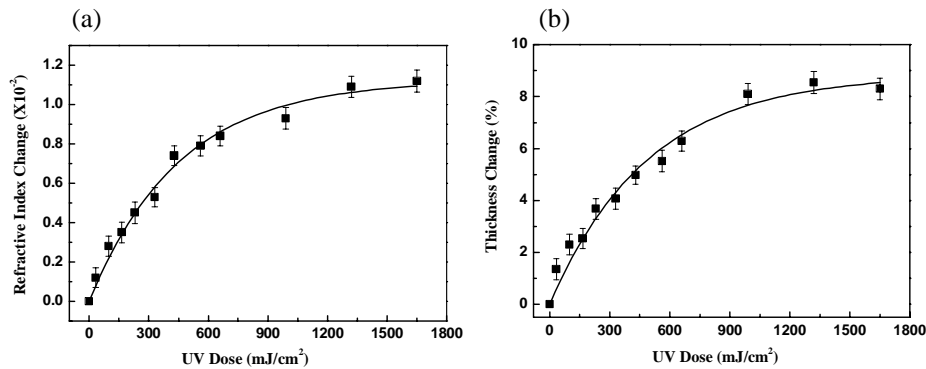


Fig. 1. Refractive index changes (a) and thickness changes (b) in UV exposed and baked SGH film depending on UV doses.

In the case of the SGH materials containing large quantities of photoactive molecules, it was reported that the photosensitive effects were related to various photoinduced reactions, such as photopolymerization of the radicals in the matrix and the photoactive molecules [13-15], a photolocking of photoinitiators into the matrix [13-15], and a photomigration of matrix and photoactive molecules [16] due to the concentration gradient between the unexposed and exposed areas. These photoinduced reactions occur in all UV ranges and lead to the increase in refractive index and thickness of the films. Besides above the photoinduced reactions, there is another photoinduced reaction, which is a photodecomposition of the matrix [11, 13]. This photodecomposition occurs in the UV ranges with the wavelength of around or below 250 nm and leads to the decrease in refractive index and thickness of the films due to the decomposition of the methacryl groups in the matrix [11, 13]. Thus, in this experiment, we could expect that BDK and MMA in the exposed areas were fixed with the SGH matrix by various photoinduced reactions besides photodecomposition and then not removed during heating and drying. On the other hand, BDK and MMA in the unexposed area were not involved in any photoinduced reactions. This means that the photoactive molecules in the unexposed area were not fixed with the SGH matrix. Therefore, BDK and MMA in the

unexposed area were volatile and could be easily removed by baking. After baking, these different phenomena of photoactive molecules between UV exposed area and unexposed area made the large changes in both refractive index and thickness. These differences became much larger with the increase of the UV dose. These highly photosensitive SGH materials are very good candidates for photo-patterning the diffraction gratings.

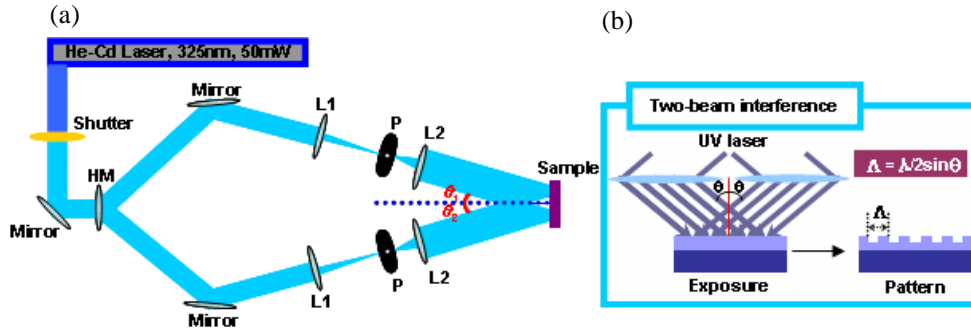


Fig. 2. Illustration of two-beam interference system (a) and the schematic illustration of the interference beam illuminated by the two-beam system (b).

Diffraction gratings were fabricated in photosensitive SGH films using the two-beam interference method. In order to use the high photosensitivity of SGH films, the wet films before heat treatment were used for the fabrication of diffraction gratings. Figure 2 shows the illustration of the two-beam interference system (a) and the schematic illustration of the interference beam illuminated by the two-beam system (b). The He-Cd laser is split into two beams by a half mirror (HM) and then the respective beam is condensed onto a sample surface to form straight interference fringes after passing through beam expander (L1), a 10 μm diameter pinhole (P) and collimating lens (L2). When this system is used for the fabrication of diffraction gratings, the grating period is represented by the equation $\Lambda = \lambda / 2 \sin \theta$, where λ is the wavelength of the He-Cd laser (325 nm), and θ is the incident beam angle on the SGH films. We can control the spacing of the fringe by changing the incidence angle of the two beams ($\theta = \theta_1 = \theta_2$), which can fabricate the diffraction gratings with the various periods in two-beam interference system.

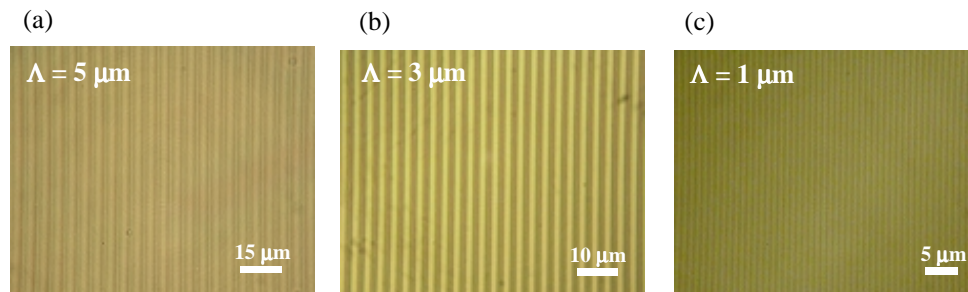


Fig. 3. Optical micrographs of diffraction gratings with periods of 5 μm (a), 3 μm (b), and 1 μm (c) fabricated with the two-beam interference system (photo-fabrication: before baking, optical micrographs investigation: after baking).

In order to investigate the images of the fabricated diffraction gratings on the wet films, the films with the fabricated diffraction gratings were baked at 150°C for 5 hours and then the images of the fabricated diffraction gratings on the films were investigated by using optical

microscope and AFM. Figure 3 shows the optical micrograph of the diffraction gratings with periods of 5 μm (a), 3 μm (b), and 1 μm (c) fabricated with the two-beam interference system in highly photosensitive SGH films. The diffraction grating patterns were very homogeneous regardless of the grating pitch.

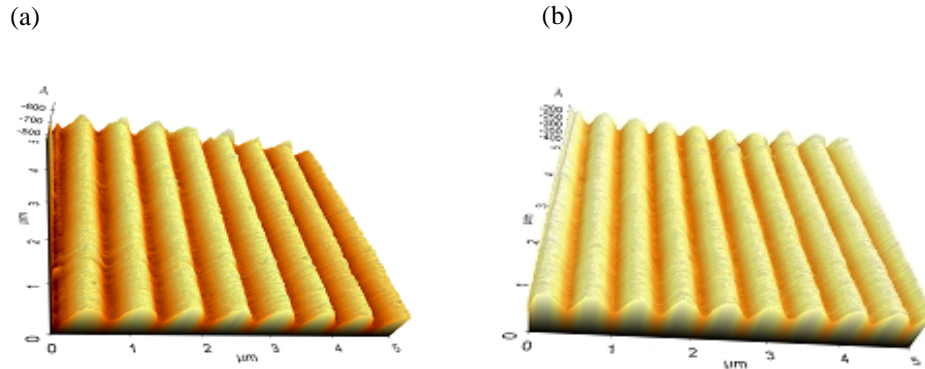


Fig. 4. AFM images of diffraction gratings with periods of 600 nm (a) and 500 nm (b) fabricated with the two-beam interference system (photo-fabrication: before baking, AFM investigation: after baking).

In particular, in the case of a contact patterning process such as a photo mask method, the fabrication of gratings with a submicrometer period was relatively difficult due to the diffraction limit between a sample and a mask. However, we could overcome this problem by using the two-beam interference method and fabricate the diffraction gratings with a submicrometer period. Figure 4 shows the AFM images of diffraction gratings with periods of 600 nm (a), 500 nm (b) fabricated with the two-beam interference system in highly photosensitive SGH films. The grating profile was a perfect sinusoid, which is related the precise control of UV doses including the intensity of the beam and the exposure time, as shown in Fig. 4. The intensity of each laser beam and the exposure time for obtaining the homogeneous and perfect sinusoidal diffraction gratings in SGH films were 0.55 mW/cm^2 and around 15 min, respectively.

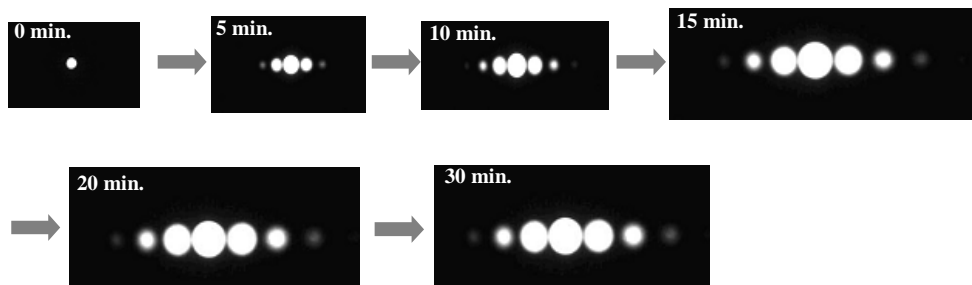


Fig. 5. CCD images of diffraction effects of the gratings with the period of 5 μm depending on exposure time (Diffraction effects in-situ measurement: before baking).

In order to investigate the effects of the UV doses on the diffraction of gratings, we measured in-situ the diffraction effects of gratings with increasing the exposure time of the photo-fabrication of the gratings. The diffraction of the gratings was measured by using the He-Ne laser beam ($\lambda = 632.8 \text{ nm}$) and a CCD camera. The He-Ne laser beam was located in

the front of samples and the CCD camera connected to a computer was placed at the back of the samples. Figure 5 shows the diffraction effects of the gratings with the period of $5\ \mu\text{m}$ depending on the exposure time from a CCD camera. As the exposure time increased, the diffraction effects were much clearer and the gratings showed the strongest diffraction effects in around 15 minutes. After the 15 min. irradiation, the diffraction effects were not enhanced.

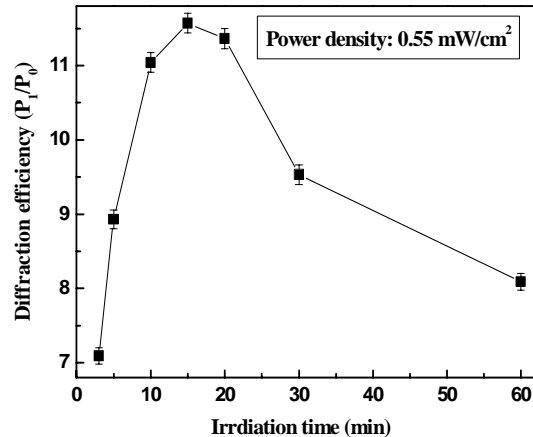


Fig. 6. Diffraction efficiencies of gratings with the period of $0.7\ \mu\text{m}$ depending on exposure time (Diffraction efficiencies measurement: after baking).

For the more detailed analysis of the relationship between the diffraction effects and the UV doses, the first-order diffraction efficiencies (η : ratio of diffracted power to incident power) of the gratings printed upon the photosensitive hybrid films were measured at a wavelength of $632.8\ \text{nm}$. The films with the fabricated diffraction gratings were baked and then the diffraction efficiencies of the fabricated diffraction gratings on the films were investigated. Figure 6 shows the diffraction efficiencies of the gratings with the period of $0.7\ \mu\text{m}$ depending on the exposure time in the transmission mode. The maximum diffraction efficiency of 11.57% was attained during the irradiation. The irradiation time of the maximum diffraction efficiency was around 15min., which agreed well with the optimum exposure time for obtaining the good-patterned gratings and the strongest diffraction effects shown in Fig. 4 and 5. The decrease in η was appeared since the maximum diffraction efficiency. One of the origins of this decrease in η at the irradiation time longer than 15 min could be due to the line width broadening of the gratings, which results in the decrease of the grating depth and the refractive index changes between the high lines and the low lines in the sinusoidal gratings. A long irradiation time could also cause the distortion of the grating shape or surface, which could be another reason for the decrease in η . Consequently, the diffraction effects and efficiencies of gratings were heavily dependent on the UV exposure time and would be decreased by much UV doses. Thus, the optimum UV doses in photo-fabrication of the diffraction gratings using photosensitive SGH materials are the most important factors for obtaining the stronger diffraction effects of gratings.

4. Conclusion

In conclusion, the photosensitive SGH materials containing the large contents of photoactive molecule exhibited very high photosensitivity with large changes in both the refractive index and the volume by UV exposure. With our high photosensitive SGH materials, we simply fabricated the diffraction gratings and easily controlled the grating periods using two-beam

interference method. The diffraction effects and efficiencies of gratings depended heavily on the contents of the UV dose and the fabricated diffraction gratings showed a good diffraction performance.

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