

Single-step photopatterning of diffraction gratings in highly photosensitive hybrid sol-gel films

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Abstract: Inorganic-organic hybrid materials prepared by a sol-gel process showed a large photoinduced negative refractive-index change (2×10^{-2}) and a volume change. Diffraction gratings were made directly by irradiation with a KrF excimer laser (248 nm) through a phase mask without any etching process. The dependence of diffraction efficiency on irradiation conditions was investigated. The maximum diffraction efficiency, measured by the Littrow configuration with a He-Ne laser (633 nm), was 3.4% in reflection mode.

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1. Introduction

Diffraction gratings with a period comparable to an optical wavelength are important for wavelength dispersion, conversion, and modulation, which are used for optical interconnection [1] and optical signal processing [2,3] in optical integrated circuits [4] and optical data-storage systems. Diffraction gratings can be classified into two groups depending on their structure, the refractive-index modulation type, and the surface-relief types. A typical example of the refractive-index modulation gratings is the waveguide filter, in which a periodic change in refractive index is formed in the core of the waveguide by laser irradiation [5]. Surface-relief gratings (SRGs), in contrast, are typically fabricated by mechanical, chemical, and optical processing, and their combinations [6-8]. However, these processes are rather complex if our aim is to reveal the precise surface structure. Thus, many studies have recently concentrated on simplifying the fabrication steps of SRGs. In particular, the facile, single-step photopatterning of azo polymers [9,10] and inorganic-organic hybrid materials [11-16] made by the sol-gel technique have received much attention because the SRG could be fabricated quickly.

Recently, inorganic-organic hybrid materials were found to exhibit a large modulation of refractive index on the surface of various hybrid materials by UV exposure [16]. It was discovered that a fluorinated hybrid material was a large negative change by UV lamp exposure (200-260 nm) [16]. One of the advantages of this material was the potential for simple single-step photopatterning. The fluorinated hybrid materials were also recently found to be highly photosensitive to KrF excimer laser light (248 nm).

In this paper we report on direct fabrication of SRGs by irradiation with a KrF laser through a phase mask and on SRG characterization.

2. Experiment

Fluorinated hybrid materials were synthesized by use of methacryloxy-propyl-trimethoxysilane (MPTS, Aldrich) and perfluoro-alkyl silane (PFAS, Toshiba) as precursors. MPTS and PFAS were mixed with water in the presence of 0.01 N hydrochloric acid (HCl), which acted as a catalyst for the sol-gel reaction. MPTS was reacted with PFAS in a molar ratio of 3:1 to avoid a viscous solution, which would not be coated on the substrate. After stirring for 24 h, the totally transparent filtered solution was coated on Si substrate by use of the spin-coating method. The coated film was then thermally cured at 150 °C for 10 h. Prism coupling was employed to measure the refractive index of the film before and after irradiation with a KrF laser. The optical energy density, shot number, and repetition time of the laser were 33 mJ/cm², 1.5×10⁴, and 10 Hz, respectively.

3. Results and discussion

Figure 1 shows the refractive index and film thickness as functions of the irradiation time of the KrF excimer laser. The refractive index and the thickness decreased exponentially with the laser exposure time. The decreases in refractive index and thickness were similar to that observed after irradiation with a 1000-W Hg/Xe lamp (Oriel 82511, 220-260 nm). However,

the saturation time was shorter than with the lamp illumination because the optical power density of the KrF laser light was higher than that of the lamp (0.045 J/cm^2 , 70 V).

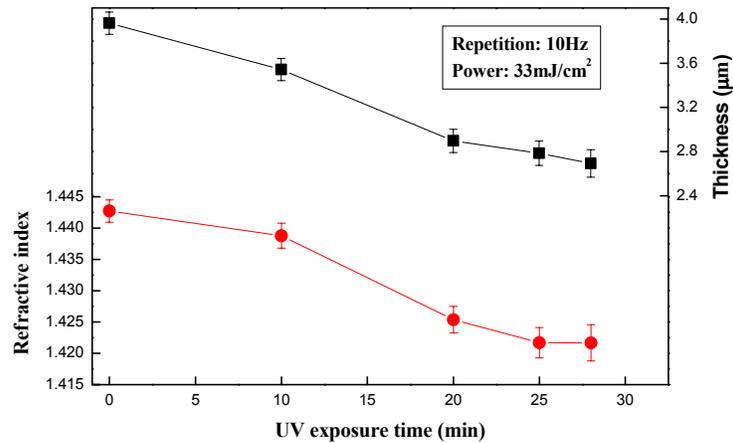


Fig. 1. Changes in refractive index and film thickness versus irradiation time by a KrF excimer laser at room temperature and an ambient atmosphere.

The decomposition of methacryl groups upon UV exposure has been known to reduce the refractive index, and the photoinduced densification in an inorganic framework decreases the film thickness in fluorinated hybrid materials [16]. Generally, carbonyl groups in the methacryl group are very polar, and hence materials with the methacryl group have high refractive indices. During the decomposition of methacryl chains in the hybrid material, the carbonyl groups are decomposed, which causes a large decrease in the refractive index upon UV irradiation. Therefore the diffraction gratings would be patterned on the hybrid films by use of these photosensitive phenomena on a KrF laser exposure. These unique photosensitive characteristics of the material are different from those of other sol-gel materials, which appear only as the change of refractive index or the thickness of films upon UV exposure. Also, this photopatterning mechanism resulting from the decomposition of methacryl chains is different from the fabrication mechanism, owing to photopolymerization with a photoinitiator.

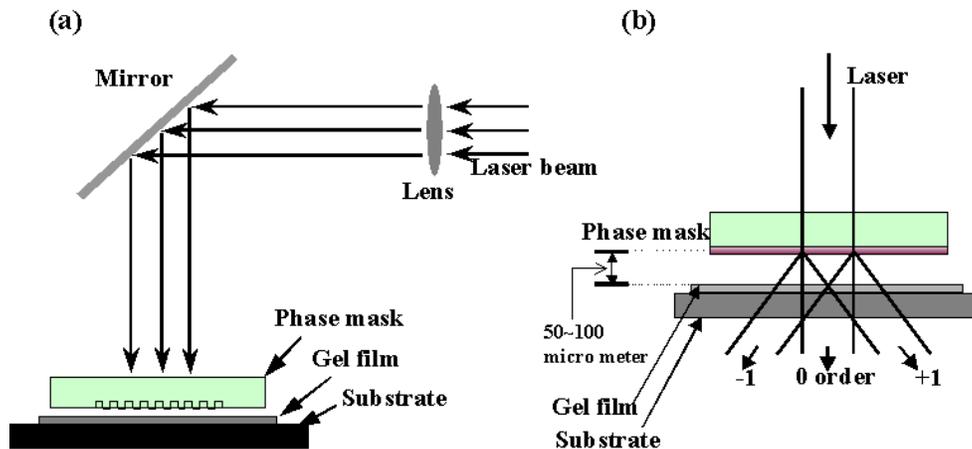


Fig. 2. (a) Illustration of the system of an excimer laser and (b) the schematic illustration of the interference beam diffracted by a phase mask.

SRG was formed in the hybrid gel films by irradiation with the KrF excimer laser (248 nm) through a phase mask with a 1050.50-nm pitch. Figure 2 shows (a) an illustration of the system of an excimer laser and (b) a schematic illustration of the interference beam diffracted by a phase mask. The optical energy density, shot number, and repetition rate were 33 mJ/cm^2 , 1.5×10^4 , and 10 Hz, respectively. SRG can be fabricated directly upon the photosensitive hybrid films, and this presents a number of interesting possibilities. In general, SRG fabrication requires treatments, such as developing and dry or wet etching processes, after irradiation. However, the photosensitive hybrid gel films used in this study did not require such additional steps.

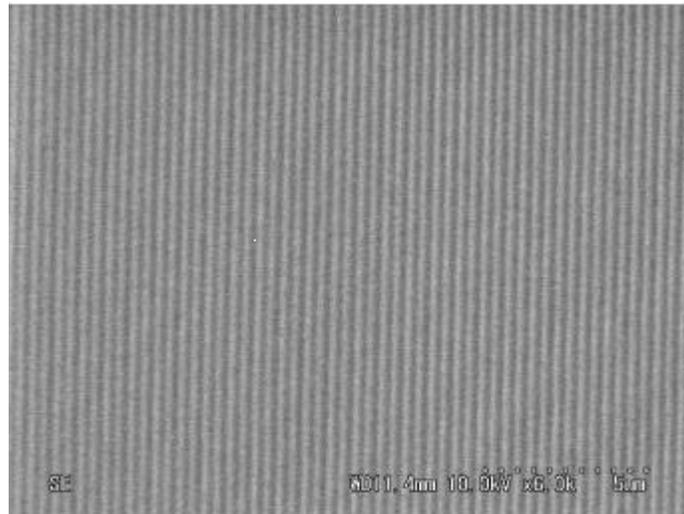


Fig. 3. Perspective SEM view of a $0.5 \mu\text{m}$ grating printed upon an inorganic-organic hybrid gel film.

Figure 3 shows the surface-relief modulation obtained by single-step KrF laser exposure. The grating period identified from scanning electron microscope (SEM) photography was nearly 500 nm , which almost agreed with half the phase mask pitch. The grating groove depth of $\sim 200 \text{ nm}$ was characterized by atomic force microscopy. The precise period (Λ) was determined by the equation $\Lambda = \lambda / 2 \sin \theta_d$, where λ is the wavelength (633 nm) of a He-Ne laser. A Littrow configuration was used for the measurement. The measured Littrow angle (θ_d) was 36.8° with the period of 528.36 nm , which agreed well with the phase mask pitch. These results showed the experimental conditions such as the irradiation time, and the contact conditions were almost ideal.

The first-order diffraction efficiencies (η : ratio of diffracted power to incident power) of SRGs printed upon the photosensitive hybrid films were measured at a wavelength of 633 nm . Figure 4 shows the dependence of the diffraction efficiency on KrF laser exposure time in reflection mode. A maximum diffraction efficiency of 3.41% was attained during irradiation. To obtain a higher η , the irradiation time and the distance between the thin film and the phase mask must be controlled precisely. The latter is an important parameter for making an excellent interference pattern on the thin film. During the formation of the diffraction grating, the power of the zero-order light had to be minimized, and the power of the first-order light had to be maximized. In the case of fiber Bragg gratings, the optimum distance between the phase mask and the films should be $50\text{-}100 \mu\text{m}$. A similar distance was secured in this experiment. As shown in Fig. 4, there was an optimum irradiation time for attaining the high η . The irradiation time of the maximum diffraction efficiency was $\sim 37 \text{ min}$, which is longer

than the saturation time of the refractive-index change in Fig. 1. Normally, the first-order laser power irradiated on the film through the phase mask should be approximately 75-80 % of the original laser power. That is why there is the difference in irradiation time between Figs. 1 and 4. The decrease in η appeared because of the maximum diffraction efficiency. One of the origins of this decrease in η at the irradiation time longer than 40 min could be the effect of zero-order light, which was approximately 4%. A long irradiation time could also cause the distortion of the grating shape or surface ablation, which could be another reason for the decrease in η .

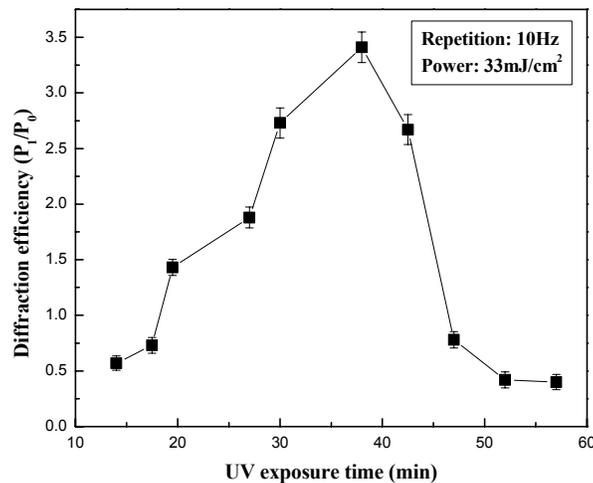


Fig. 4. Relation between the diffraction efficiency and the irradiation time of a KrF excimer laser.

4. Conclusion

The inorganic-organic hybrid materials made by a sol-gel process resulted in a large photoinduced refractive-index change and a thickness change by KrF excimer laser irradiation. The diffraction gratings were directly patterned on the hybrid films solely by laser irradiation through a phase mask. The quality of the interference pattern formed below the phase mask depended on the distance between the mask and the film. Irradiation time was also important in optimizing the diffraction efficiency. These photopatterns fabricated directly because of the concurrent photosensitive phenomena on UV exposure appeared to be promising not only for applications using wavelength multiplexing devices for integrated optical devices but also for enhancing the efficiency of optical elements such as antireflection coatings and microlenses.

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