Fabrication of Micro-Optical Devices by Holographic Interference of High Photosensitive Inorganic-Organic Hybrid Materials (Photo-HYBIRMER)

Dong Jun Kang, Jin-Ki Kim and Byeong-Soo Bae
Laboratory of Optical Materials and Coating (LOMC), Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Korea

ABSTRACT

Sol-gel derived photosensitive inorganic-organic hybrid materials (Photo-HYBIRMER) containing a large quantity of photoactive molecules exhibit the large changes in both refractive index (over $10^{-2}$) and volume (over 30%) on UV exposure. The materials could be used for direct fabrication of micro-optical devices using holographic interference. With the change of the beam number for holographic interference (1-beam, 2-beam, 3-beam and 4-beam interference), various typed micro-optical devices (Fresnel-type lens, 1D- and 2D-typed diffraction gratings) could be easily fabricated. Importantly, the fabricated micro-optical devices exhibited the very homogeneous surface structures and good optical performance.

INTRODUCTION

Micro-optical devices are the important component for beam dispersion and conversion, optical signal processing and modulation in compact and complicated optical data storage systems and optical integrated circuits [1-3]. Thus, the study of fabricating micro-optical devices has been intensively performed using a variety of methods, including a photo-mask, beam lithography, etching techniques, holographic interference. Contact imprinting using a photo-mask is not suitable for the fabrication of devices with a submicrometer period due to the diffraction limit between the mask and the samples. The beam lithography, which includes the etching process, is rather complex and needs several steps to reveal the precise surface structure. These disadvantages of a photo-mask and lithographic techniques cause limitations to easy fabrication and obtaining higher performance of micro-optical devices. However, the holography can produce fine and precise patterns easily. Thus, the holographic interference has great potential for the direct fabrication of micro-optical devices with high performance.

The materials as well as the fabrication processes are crucial factors in fabricating the micro-optical devices with high performance. In order to achieve higher performance in optical devices,
materials must have high photosensitivity, meaning a large refractive index, and undergo a volume change upon light irradiation, because the direct photo-fabrication and the performance of an element depend on the photosensitivity of the materials used. In recent years, sol-gel hybrid materials (HYBRIMERs) [4-6] and photosensitive polymers [7,8] have been used as potential materials for fabricating highly efficient micro-optical elements. In particular, the photosensitive hybrid materials (Photo-HYBRIMERs) doped with large amounts of photoactive molecules were found to exhibit larger refractive index and volume change on UV exposure [9-11]. The photosensitivity of these materials could be increased by the simple addition of photoactive molecules. Also, these materials have the potential to be used in simple single-step photo-patterning due to the simultaneous changes in both refractive index and volume. Thus, these Photo HYBRIMERs are good candidates for highly efficient micro-optical devices.

In the present study, we report on the effect of UV dose and the functionality of the photoactive molecules on photosensitivity in HYBRIMERs, with a focus on increasing the photosensitivity. We make the various interference fringes by changing the beam number of holography for direct photo-fabrication of micro-optical devices. Finally, with both surface relief structures and refractive index modulation of HYBRIMERs, we manufactured directly well shaped micro-optical devices with different types and good optical performance by using various holographic interference fringes without any etching treatment. In addition, we investigated the effects of UV dose on the optical performance of fabricated micro-optical devices.

EXPERIMENTAL DETAILS

Transparent photo-HYBRIMERs were prepared using methacryloxypropyl-trimethoxysilane (MPTS, Aldrich), perfluoroalkylsilane (PFAS, Toshiba) and zirconium n-propoxide (ZPO, Aldrich) chelated with methacrylic acid (MAA, Aldrich) as precursors. All precursors were hydrolyzed with 0.01-N HCl. After 20 hour stirring for full sol-gel reaction, any residual products such as alcohols were removed at 50°C with an evaporator. Benzyldimethylketal (BDK, Aldrich) as a photoinitiator, and mono-, di-, and three-acrylate monomer (Aldrich) as a photoactive monomer, were added into the HYBRIMER solution prior to the coating. After stirring the solution for 1 hour at room temperature, a homogeneous photosensitive HYBRIMER solution was obtained. This solution was spin-coated on a cleaned glass substrate with 3000-rpm spinning speed. The coated films were exposed by a Hg UV lamp (wavelength 350-390nm) and a He-Cd laser (wavelength 325 nm) for photo-induced reactions and holographic interference. The exposed time was different for measuring the effects of the UV dose on the photosensitivity of the materials and then consolidated by baking at 150°C for 5 hours.
The changes in the refractive index and thickness of the films before and after illumination with the Hg lamp were measured using a prism coupler (Metricon 2010) at a wavelength of 632.8 nm. Holographic interference using a He-Cd laser was used for the fabrication of micro-optical devices. The images of the fabricated micro-optical devices were investigated using optical microscopy and atomic force microscope (AFM, Park Scientific Instruments, Autoprobe 5 M). The diffraction effects of micro-optical devices were monitored using a CCD camera.

RESULTS AND DISCUSSION

Figure 1 shows the refractive index and thickness changes of photo-HYBRIMERs as a function of UV dose and the acrylate functionality in the photoactive molecules. Most changes in refractive index and film thickness occurred during short UV doses and the photosensitivity was enhanced with the increase of acrylate functionality in photoactive monomers. Also, photo-HYBRIMERs with large amounts of photoactive molecules exhibit excellent photosensitivity, that is, the large changes in both refractive index (over $10^{-2}$) and volume (over 30%) on UV exposure as shown in Fig. 1. These high photosensitivity are closely related to the various photo-induced mechanisms, which are photo-polymerization between sol-gel matrix and decomposed radicals of photoinitiator and photo-locking of photochemical species with UV exposure. Upon UV illumination, photochemical species, such as photo-initiators and photoactive monomers, are decomposed and are locked inside the sol-gel hybrid matrix or are dimerized themselves. Moreover, during space controlled UV illumination, these photo-HYBRIMERs undergo the

![FIGURE 1](attachment:image.png)

**FIGURE 1.** Refractive index (a) and thickness changes in Hg UV lamp (wavelength 350-390nm) exposed and baked photo-HYBRIMERs depending on UV dose and functionality of photoactive molecules.
photo-migration due to the concentration gradient of photoactive molecules between unexposed and exposed areas, which derives large changes in refractive index and volume between unexposed and exposed areas. Therefore, we can apply these photo-HYBRIMERs with high photosensitivity to direct photo-patterning for high-efficiency micro-optical devices. In particular, we used holographic interference for the fabrication of various type micro-optical devices.

Figure 2(a) shows an optical micrograph of a Fresnel-type lens patterned by 1-beam pinhole interference on photo-HYBRIMERs. The Fresnel type lens exhibited the higher odd zones and lower even zones by the negative-type sensitivity depending on the spatially controlled exposure of pinhole interference. Figure 2(b) and 2(c) show the focusing property and diffraction effects of a Fresnel type lens from a CCD camera. The diffracted laser beams exhibited the intensified focusing effect and the expanded diffraction effects were also strong, which lead to a very high efficiency approaching 85% of Fresnel type lens. This high-efficiency Fresnel type lens would be potentially useful for application in compact optical systems.

**FIGURE 2.** (a) Optical microscope, (b) CCD images of focusing effect and (c) diffraction beam of a patterned Fresnel-type lens by 1-beam interference.

Figure 3 shows (a) AFM image and (b) CCD images of diffraction effects of 1D diffraction gratings with periods of 1000 nm fabricated with the 2-beam interference on photo-HYBRIMERs. 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. Importantly, the fabricated diffraction gratings exhibited a good diffraction performance. In addition, in order to investigate the effects of the UV doses on the diffraction efficiency of gratings, we measured the diffraction efficiency of gratings with increasing the exposure time of the photo-fabrication of the gratings. The maximum diffraction efficiency of 1D diffraction gratings was around 11.57 % and highly dependent on UV doses related to the intensity of the beam and exposure time. The exposure time for obtaining maximum diffraction efficiency agreed well with the optimum exposure time for obtaining the good-patterned gratings and the strongest diffraction effects. This UV exposure time dependence on diffraction efficiencies 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 diffraction efficiency. 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 photo-HYBRIMERs are the most important factors for obtaining the stronger diffraction effects of gratings.

![Figure 3](image1.png)

**FIGURE 3.** (a) AFM image and (b) CCD image of diffraction effects of 1D diffraction gratings fabricated by 2-beam interference.

Figure 4 shows optical microscope of (a) 2D hexagonal type diffraction gratings fabricated by 3-beam interference and (b) 2D rectangular type diffraction gratings fabricated by 4-beam interference. For forming the 3-beam interference, diffraction optical element with a triangle type lines was used and the laser beam through this element divided into three diffraction beams. These diffraction beams focused on one plane, where 3-beam interference is formed. The fringe shape of 3-beam interference is hexagonal type. Thus, 2D hexagonal type diffraction gratings were patterned on focal plane of three diffraction beams. In case of 4-beam interference, we used diffraction optical element with rectangular type lines. The principle of 4-beam interference formation is same as 3-beam interference. With the triangle and rectangular type diffraction optical elements, 3- and 4-beam interference could be easily formed and 2D type diffraction gratings with homogeneous surface structures could be fabricated precisely. Moreover, these well

![Figure 4](image2.png)

**FIGURE 4.** (a) Optical microscope of 2D hexagonal type diffraction gratings fabricated by 3-beam interference and (b) optical microscope of 2D rectangular type diffraction gratings fabricated by 4-beam interference
shaped 2D type diffraction gratings also showed 2D strong diffraction effects. 2D hexagonal and rectangular type diffraction gratings exhibited hexagonal and rectangular typed diffraction patterns, respectively.

CONCLUSIONS

The photo-HYBRIMERs containing large amounts of photoactive molecule exhibited very high photosensitivity with large changes in both refractive index and volume on UV exposure. With the high photosensitivity of photo-HYBRIMERs, various typed micro-optical devices (Fresnel-type lens, 1D- and 2D-typed diffraction gratings) could be fabricated easily by changing the beam number of holographic interference (1-beam, 2-beam, 3-beam and 4-beam interference). The diffraction effects and efficiencies of micro-optical devices depended heavily on UV doses related to the exposure time and the beam intensity. Importantly, the fabricated micro-optical devices exhibited the very homogeneous surface structure and good optical performance.

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REFERENCE