Excimer Laser Microphotoetching of Electro-responsive Poly (2-acrylamido-2-methylpropane sulfonic acid) Gels

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1. Introduction

Various kinds of polymer gels have been studied as chemomechanical energy-conversion materials. [1] Many polymeric hydrogels undergo abrupt changes in volume in response to external stimulation such as solvent composition, [2] pH, [3] temperature [4] and electric field. [5–11] Among responsive gels, electro-responsive gels are one of the most promising soft materials for microactuators, because the electric field is easily controlled. Since the electromechanical phenomena in synthetic polymer gels were first observed in 1982 by Tanaka et al. [5], several workers have been studying the volume changes and the deformation behavior of polymer gels in an applied electric field. [5–8] Applications such as artificial muscles, [9,10] actuators, [6,8] and controlled drug delivery [11] have been investigated for polymer gels. Polyacrylic acid [7,9,11] or poly (2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) [6,8,10] has been well used for preparing electro-responsive hydrogels. For several potential applications such as microactuators, a fast response is needed. The rate of volume change is inversely proportional to the square of a characteristic length of the gel. [7, 12] However, the processing of the polymer gels with dimensions on the micrometer scale and arbitrary forms is difficult because of their weak mechanic strength.

Since Kawamura et al. [13] and Srinivasan et al. [14] reported that the pulsed irradiation of intense ultraviolet (UV) lasers is efficient to etch polymer

films, laser ablation has been applied to various fields as a new method of processing solid materials. [15] From the viewpoint of spatial resolution and depth control, laser processing with UV lasers is superior to those with a Nd:YAG (1.064 μm) or a CO₂ laser ($\sim 10\ \mu\text{m}$), because the UV lasers bring about etching with minimal thermal damage. Direct photoetching by UV laser ablation is suggested for microfabrication of the polymer gels. This method is a fast, single, and totally dry process, compared with conventional lithography and, in principle, can be applied to various kinds of polymer gels.

This paper is concerned with investigation of the ablation behavior of PAMPS gel in swelled and dried states and the fabrication of three-dimensional gel structure by direct photoetching with an ArF excimer laser.

Fig. 1 Schematic diagram of the optical system

2. Experimental

2-(Acrylamido)-2-methylpropanesulfonic acid (AMPS) (Tokyo Chemical Industry Co., Ltd.), N,N'-methylene bisacrylamide (MBAA) (Nacalai Tesque, Inc.) of a cross-linking agent, and potassium peroxodisulfate (Kanto Chemical Co., Inc.) of a radical initiator were purified by recrystallization. [16] PAMPS gel was prepared by radical polymerization of the AMPS monomer (3.5 M) in the presence of 4.0×10^{-2} M MBAA and 2.7×10^{-2} M potassium peroxodisulfate in aqueous solution. The polymerization was carried out at 333 K for 12 h under a nitrogen atmosphere. After polymerization, the gel was immersed in a large amount of distilled water until the size was equilibrated. Dried PAMPS gels were prepared by drying the immersed gels at 333 K for 24 h. Swelled PAMPS gels were prepared by swelling the dried PAMPS gels in a large amount of distilled water until the size was equilibrated. Laser irradiation was carried out using an excimer laser system, LEXTRA50 (Lambda Physik), operated at 193-nm. The pulse duration was 17 ns in FWHM. The repetition rate was kept at 1 Hz in order to avoid any effects arising from cumulative heating of the sample. The laser beam was homogenized with a combination of cylindrical lenses and

passed through an aperture to obtain a region of uniform intensity. Laser irradiation was demonstrated with the optical system in Fig. 1. The laser beam was directed to the gel surface by a mirror. PAMPS gels on the quartz plates were placed perpendicular to the laser beam and irradiated through a mask placed on the gels at contact. The mask used was a nickel mesh with $30 \mu\text{m} \times 30 \mu\text{m}$ square apertures. AFM images of the irradiated surfaces were observed with NanoScope III (Digital Instruments). The AFM was operated in the contact mode using cantilevers, NP (Digital Instruments).

3. Results and Discussion

Figures 2 (a), (b) show AFM image and the cross-sectional profile of a swelled PAMPS gel irradiated at a fluence of 0.16 J/cm^2 with ten shots. The square hole was created in the surface, and the size of the hole was bigger than that of the original mask ($30 \mu\text{m} \times 30 \mu\text{m}$). The structures fabricated by direct photoetching at various fluences are slightly different from the original mask shape. Figures 3 (a), (b) show AFM image and the cross-sectional profile of a swelled PAMPS gel irradiated at a fluence of 1.0 J/cm^2 with one shot. The irradiated surface of the swelled PAMPS gel was

Fig. 2 AFM image (a) and the cross-sectional profile (b) of a swelled PAMPS gel irradiated by the 193-nm laser at a fluence of 0.16 J/cm^2 with ten shots.

Fig. 3 AFM image (a) and the cross-sectional profile (b) of a swelled PAMPS gel irradiated by the 193-nm laser at a fluence of 1.0 J/cm^2 with one shot.

irregular, and the size of the hole was bigger than that of the original mask, even though the total irradiated energy was smaller than the experimental condition in Fig. 2. The difference in the surface structures in Fig. 2 and Fig. 3 is inferred to come from the difference in the degree of temperature jump through photo-thermal conversion. Therefore the irregularity of the surface structure in Fig. 3 is attributed to enormous heat through photo-thermal conversion and/or vaporization of water in the gel matrix. Several researchers also observed similar irregularity of the irradiated region in the IR-laser irradiation of gel and tissue. [17,18] In these cases, the cause of the irregularity was explained in terms of the collapse of a bubble induced by water evaporation. These results indicated that the fabrication of the swelled gels was difficult, and the quality of the shape was not good.

Figures 4 (a), (b) show AFM image and the cross-sectional profile of a dried PAMPS gel irradiated at a fluence of 0.17 J/cm^2 with ten shots. A well-defined periodic structure was created in the irradiated region. This periodic structure was observed specifically on non-fused materials such as polythiophene films. [19] This periodic structure is ascribed to a Fresnel diffraction of the

Fig. 4 AFM image (a) and the cross-sectional profile (b) of a dried PAMPS gel irradiated by the 193-nm laser at a fluence of 0.17 J/cm^2 with ten shots.

Fig.5 Cross-sectional profiles of a dried PAMPS gel irradiated by the 193-nm laser at a fluence of 0.43 J/cm^2 with one shot before (a) and after swelling (b).

Fig.6 Optical microscope images of the three-dimensional gel structure fabricated by the 193-nm laser at a fluence of 0.60 J/cm^2 with 2000 shots before (a) and after swelling (b).

laser beam at the edge of the aperture. [19]

Figure 5 shows cross-sectional profiles of a dried PAMPS gel irradiated at a fluence of 0.43 J/cm² with one shot before (a) and after swelling (b). The etch depth of the swelled state was 5 times deeper than that of the dried state. The periodic structure which was observed on the irradiated region of the dried gel was maintained on the swelled state. The minimum top-to-top distance of the periodic structure was about 2.0 μm. This value might correspond to a maximum resolution for the microfabrication of swelled PAMPS gels by excimer laser.

In order to investigate the etching behavior of dried PAMPS gels, we estimated the threshold fluence. The linear relationship was in good agreement with the well-known relationship between the etching rate (d) and the fluence (F):

$$d = \frac{1}{\alpha_{\text{eff}}} \log \frac{F}{F_{\text{th}}} \quad (1)$$

where α_{eff} is the effective absorption coefficient, and F_{th} is the threshold fluence for the etching to occur. By extrapolating $d \rightarrow 0$, the threshold fluence was estimated to be approximately 80 mJ/cm². It should be noted that the etching rate was easily controlled by the fluence, and further, the etch depth consistently increased with shot number. We applied multi-shot irradiation technique to fabricate a three-dimensional gel structure.

Figure 6 shows the optical microscope images of a three-dimensional gel structure fabricated by direct photoetching at a fluence of 0.60 J/cm² with 2000 shots before (a) and after swelling (b). The shape was maintained after swelling. The swelled fabricated gel worked on electric field with a fast response rate, and therefore, expected to be in practice applied to a microactuator

4. Conclusions

In conclusion, it has been demonstrated that PAMPS gel can be fabricated by direct photoetching using 193-nm excimer laser irradiation. The polymer gel, which is generally regarded as not processable, can be fabricated into three-dimensional structures with micrometer scale. The three-dimensional gel structure was obtained

by swelling the dried gel structure. From AFM observation, the maximum resolution with this technique was about 2.0 μm. The swelled fabricated gel worked on applied electric field with a fast response rate, and therefore expected to be in practice applied to microactuator

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