Fabrication of silica-based three-dimensional structures by changing fluence using proton beam writing

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We performed micromachining of relatively thick siloxane films by proton beam writing (PBW) with beam energy of 1 MeV. The polydimethylsiloxane (PDMS) prepolymer films with a thickness of about 13 μm were spin-coated onto silicon substrates. After exposure to the 1-MeV proton beam ($\sim 1\text{ }\mu\text{m}$ in diameter), the samples were developed. The PDMS shows the behavior of negative resist and can be regarded as analog resist where the thickness of the structure gradually increases as a function of the proton beam (PB) fluence. Using this feature of the PDMS, we manufactured micro lenses with diameter of 40 μm by changing PB fluence. Micro-patterning of the PDMS films using scanning proton beam can offer a possibility of making three-dimensional structures for silica-based devices without baking and mask process.

Key word: siloxane, proton beam writing, polydimethylsiloxane, micro lens

1. INTRODUCTION

In recent years, rapid progress has been made in the development of optical devices for memory and interconnect. In the field of the optical devices, we need decreasing coupling loss and downsizing of devices. Up to now, several ideas to produce optical devices such as micro lenses were reported [1-4]. Generally, silica is a material of choice for these devices due to the high transparency and good mechanical properties. However, because of the fact that conventional prototyping techniques for silica-based optical devices require several processes including photolithography, dry etching etc., the cost is expected to be high.

We have previously reported a micro-patterning of a relatively thin organic and inorganic siloxane films such as Methyl Silsesquioxane (MSQ) and Hydrogen Silsesquioxane (HSQ), both exhibiting the characteristics of negative resists [5]. However, since the thickness of these films was limited to less than 1 μm , the deep micromachining feature of the proton beam writing (PBW) was not fully utilized for potential optical applications, such as micro lenses and planar waveguides.

In this paper, we performed micromachining of relatively thick siloxane films of more than 10 μm by PBW with beam energy of 1 MeV to simplify the processing steps and to produce flexible silica-based optical devices.

PBW is a promising method for micro-fabrication by

direct writing using a focused beam of MeV protons, since the MeV-order proton beam has several advantages over other sources such as electrons and photons. First, the scattering of the proton is small when compared with electrons penetrating into the same depth. Secondly, the projected range of the protons can be controlled with the beam energy. It is useful for the fabrication of high aspect ratio structures and prototyping of devices [6-8].

Siloxane refers to chemical compounds composed of Si-O-Si bonds. Since the siloxane is sensitive to irradiation by energetic particles of electrons and ions, micro-patterning of the siloxane film by these irradiation is promising technique to fabricate silica-based optical devices [9, 10].

In this study, we use PDMS (polydimethylsiloxane) to obtain thick prepolymer films suitable for PBW. Fig.1 shows the structure of PDMS. Due to the fact that PDMS is optically clear, chemically inert and stable, non-toxic

Fig.1. Structure of PDMS

and biocompatible material it is usually used for the production of numerous active and passive implant devices and optical waveguides or microlenses.

2. EXPERIMENTAL

We used PDMS prepolymer for fabrication silica-based three-dimensional structures using PBW. The PDMS (Dow Corning: Sylgard184) consists of base liquid (prepolymer) and curing agent for polymerization. In this study, we used only the base prepolymer liquid spin coated on a substrate to expose for polymerization by PBW.

The PDMS films with a thickness of about 13 μm were spin-coated onto 10 x 10 mm^2 silicon substrates for 60 sec at 8000 rpm. After exposure to PB, PDMS films were developed with a solution of tetrahydrofuran (THF)- CH_3CN (8:2) mixture for 2 min.

The PBW was performed using a proton beam writer (Kobe Steel Corp., MB-S1000) at beam energy of 1.0 MeV. After development, these samples were observed by the Scanning Electron Microscope (SEM, Shimadzu, SSX-550) and Confocal Laser Microscope (OLYMPUS, LEXT OLS4000). We also measured micro-Raman and FT-IR spectra on the PB-exposed area to analyze change in the local chemical bonding.

SRIM^[11] calculations show that the projected range of 1.0 MeV protons is $\sim 29 \mu\text{m}$ into PDMS. Although the range is larger than the thickness of 13 μm PDMS film on silicon substrate, no deformation of the silicon surface due to implanted protons was observed by SEM at the present PB fluence.

3. RESULTS AND DISCUSSION

3.1 Raman and FT-IR measurements

Figs. 2 (a) and (b) show Raman and FT-IR spectra obtained before and after exposure to 1.0 MeV PB for PDMS films up to the fluence of 1.0 $\mu\text{C}/\text{mm}^2$. The Raman spectra show decreasing peaks at 2910 cm^{-1} and 2960 cm^{-1} , which correspond to $-\text{CH}_3$ bond in $\text{CH}_3\text{-Si}$. The FT-IR spectra show increase of the peak at 1015 cm^{-1} and decrease of the peak at 1075 cm^{-1} which indicate the decrease of Si-O-Si short chain and increase of Si-O-Si long chain, respectively. Both changes in the local chemical bonding show the scission at Si- CH_3 bonds by PB in the PDMS film and formation of Si-O-Si networked structure^[12, 13].

Based on these observations, we expect the following reaction in Fig.3, where $-\text{CH}_3$ bonds were broken by irradiation with PB and react with H_2O to form Si-O-Si network. The role of H_2O in the scheme of Fig.3 is to drive the methyl group out of the Si-O-Si network in the form of methyl alcohol. Since the reaction requires H_2O in the PDMS films, it is suggested that the H_2O uptake into the PDMS prepolymer must be important to control the reaction scheme in Fig. 3.

(a) Raman spectra

(b) FT-IR spectra

Fig. 2. Raman and FT-IR spectra obtained before and after exposure with 1.0 MeV proton beam at the fluence of 100 nC/mm^2 and 1.0 $\mu\text{C}/\text{mm}^2$ for PDMS films.

Fig. 3. The reaction of PDMS prepolymer exposed to PB involving H_2O .

3.2 Fluence modulation of PBW on PDMS

Fig. 4 shows a SEM image obtained for PDMS films which was scanned with 6 x 6 arrays of squared patterns with 1.0 MeV PBW at various fluences from 1.0 nC/mm² to 300 nC/mm².

(a) SEM image after development

(b) Squared patterns scanned by PBW

Fig. 4. (a) SEM image of a PDMS film after development which was scanned with (b) 6 x 6 arrays of squared patterns by PB.

The squared pattern was produced at fluences starting from 4 nC/mm². The curved surfaces observed at low fluence were changed to cubic structures with upright side surfaces around 12 nC/mm².

Fig.5 shows the thickness of the remaining structures in Fig. 4 plotted as a function of the fluence of PB. The thickness of the PDMS structures gradually increases

Fig. 5. Remaining film thickness of PDMS films as a function of the fluence of 1.0 MeV PB.

with increasing PB fluence from 1.0 to 300 nC/mm². Contrast γ , which is defined by $\gamma = [\ln(F_{100}/F_{50})]^{-1}$ is estimated to be 1.34 from the values of F_{100} : 20 nC/mm² and F_{50} : 9.5 nC/mm² obtained from Fig. 5. The F_{100} and

Fig. 6. The method of changing fluence to produce curved PDMS surface by PBW.

(a) Overall image

(b) Magnified image

Fig.7. The SEM images of a curve surface after development for the PDMS film by PBW under the condition shown in Fig.6.

F_{50} represent, respectively, the fluence at which the film is fully insoluble to developer and the one at which the thickness is 50% of the original thickness. The value of γ is comparable to that reported for siloxane films exposed to EB^[14]. Therefore, we can conclude that the PDMS prepolymer shows the behavior of an analog resist.

The analog resist feature of PDMS prepolymer shown in Fig. 5 suggests that the height of the PDMS structure can be controlled by PB fluence. We can apply the feature to produce silica based optical elements with curved surface structure such as micro lens. The curved surface can be obtained by increasing the PB fluence gradually from the outer edge to the center of circles, as shown in Fig. 6.

Fig.7 shows the SEM image obtained by PBW with changing fluence shown in Fig. 6. A smooth curved surface aimed for micro lens with a height of 10 μm and diameter of 40 μm was obtained.

4. SUMMARY

A 13 μm thick PDMS prepolymer film was studied for micro-patterning using 1-MeV proton beam. Raman and FT-IR spectra measurements show the PDMS prepolymer was cross-linked to form Si-O-Si network by exposure to PB. The PDMS exhibits a feature of a negative resist with gradually changing thickness as a function of PB fluence. Using this feature, a smooth curved surface has been obtained for PDMS. We demonstrated that application of the PDMS prepolymer for PBW is useful in prototyping silica-based optical device.

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