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Fabrication of a negative PMMA master mold for soft-lithography by MeV ion beam lithography

Nitipon Puttaraksa^{a,b,*}, Somrit Unai^a, Michael W. Rhodes^c, Kanda Singkarat^a, Harry J. Whitlow^b, Somsorn Singkarat^{a,d}

^a Plasma and Beam Physics Research Facility, Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

^b Department of Physics, P.O. Box 35 (YFL), FIN-40014 University of Jyväskylä, Finland

^c Science and Technology Research Institute, Chiang Mai University, Chiang Mai 50200, Thailand

^d Thailand Center of Excellence in Physics, CHE, 328 Si Ayutthaya Road, Bangkok 10400, Thailand

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ABSTRACT

In this study, poly(methyl methacrylate) (PMMA) was investigated as a negative resist by irradiation with a high-fluence 2 MeV proton beam. The beam from a 1.7 MV Tandetron accelerator at the Plasma and Beam Physics Research Facility (PBP) of Chiang Mai University is shaped by a pair of computer-controlled L-shaped apertures which are used to expose rectangular pattern elements with 1–1000 µm side length. Repeated exposure of rectangular pattern elements allows a complex pattern to be built up. After subsequent development, the negative PMMA microstructure was used as a master mold for casting poly(dimethylsiloxane) (PDMS) following a standard soft-lithography process. The PDMS chip fabricated by this technique was demonstrated to be a microfluidic device.

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1. Introduction

Poly(methyl methacrylate), or PMMA, is well-known as a lithographic "positive" resist due to the predominant main-chain scission reactions upon exposure to ionizing radiation [1]. As a resist material, it has many useful features such as high insulation, good resolution, good etch resistance, and acceptable sensitivity and adhesion. Because of this. PMMA is one of the most commonly used polymers as a mask in the semiconductor fabrication process and in LIGA applications [2,3]. However, because of this positive behavior, PMMA has not been considered to be a practical resist for particle beam writing of master molds for casting poly(dimethylsiloxane) (PDMS) microfluidic structures. For this application, a SU-8 "negative" resist is favored; but its shorter shelf life, high sensitivity to UV/ambient room light, and very hard-to-remove contamination from equipment makes it difficult to handle in some workplaces. Recently it was found that a PMMA resist has a twoin-one characteristic. At a sufficiently intense fluence of radiation, PMMA can also undergo cross-linking which allows it to be used as negative resist [4,5]. This condition makes possible the fabrication of molds with ridges that can be used for casting channels using an ion beam. In this work, utilization of the negative tone of PMMA

E-mail address: nitipon@fnrf.science.cmu.ac.th (N. Puttaraksa).

was investigated for making a micropatterning mold by using 2 MeV H^+ beam programmable proximity aperture lithography (PPAL) [6,7] for microfluidic application. The results obtained for protons constitute useful basic information for using beams of heavier ions. There is evidence that higher linear energy transfer (LET) ions induces higher cross-linking in polymers [8,9] so that lower fluence is expected for the same level of chemical modification.

2. Experimental

2.1. Ion beam irradiation

The experimental arrangement for ion beam irradiation when using the PPAL technique is shown in Fig. 1. A PMMA film was prepared by spinning PMMA A11 solution of 950 kDa (MicroChem, Newton, MA) [10] onto a silicon substrate at 2500 rpm for 45 s; this was followed by soft-baking on a hot plate at 160 °C for 2 min. The procedure was repeated three times to reach a PMMA total thickness of $8.8 \pm 0.1 \,\mu\text{m}$ as measured by an ellipsometer [11]. For ion irradiation, a 1.7 MV Tandetron accelerator at the Plasma and Beam Physics Research Facility (PBP) of Chiang Mai University was used to produce a 2 MeV proton beam. Two L-shaped aperture blades, each independently mounted on computerized MM-3M-F-1 Motorized MicroMiniTM stages (National Aperture, Salem, NH) [12], were used to shape the proton beam into a rectangle of variable width and height between 1 μ m and 1 mm. In combination with X–Y micro-step translation of the

^{*} Corresponding author at: Plasma and Beam Physics Research Facility, Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand. Tel.: +66 53 222973; fax: +66 53 222776.

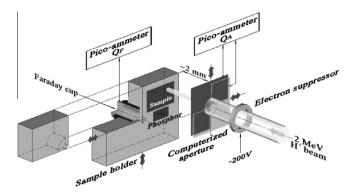


Fig. 1. Simplified schematic diagram of the experimental system (not to scale).

sample holder, a large-area complex pattern can be drawn on the sample by stitching together the rectangular subpatterns. For observation of the transformation mechanism and to determine the cross-linking fluence threshold (in ions cm⁻²), the sample was separately irradiated with several single-square areas of different ion fluences, followed by developing in a 7:3 mixture (by volume) of isopropyl alcohol (IPA) and deionized (DI) water to remove PMMA that had undergone scission. Part of the result is shown in Fig. 2. To make the master mold, the designed pattern must be drawn at the cross-linking fluence on the PMMA layer through a serial writing method, as mentioned above. Final development with acetone revealed the master mold, as shown in Fig. 3(a).

2.2. Fluence monitoring

For the reproducibility of the process mentioned above, a sensitive and reliable ion fluence monitoring system is very important. Here, the accumulated charges were measured by a purpose designed current integrator with a resolution of 4.8 pC.

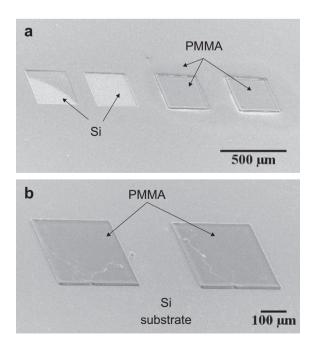


Fig. 2. (a) SEM image of patterns exposed to 2 MeV H^{*} beams at four ion fluences of, from left to right, 2.67×10^{13} , 1.08×10^{14} , 1×10^{15} and 1.14×10^{15} ions cm⁻² after developing in a mixture of IPA + DI water in 7:3 by volume at 25 °C for 4 min. (b) SEM image of the sample after developing in acetone at 25 °C for 5 min.

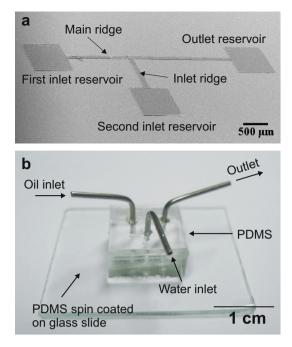


Fig. 3. (a) SEM micrograph of the T-junction pattern of the negative master mold made by the method of this work and (b) its microfluidic chip fabricated via soft-lithography.

The front end is battery operated, with an isolated grounding system to reduce sensitivity to noise and ground loop issues. The calibration curve for the setup shown in Fig. 1, is the relationship between the total charges of the incident beam on the aperture blades (Q_A) and of the beam passing through the aperture (Q_F) . This must be determined first, which was done by integrating the currents measured on the aperture blades and a faraday cup behind the aperture for a fixed aperture size and different times and assuming the beam current density is constant over the area of the aperture. The measurement was performed by moving the faraday cup (65 mm long, 8 mm inner diameter, made of copper) to the irradiation position so that its opening was centered on the beam passing through the aperture. The ion fluence at the PMMA was calculated from Q_F. This was estimated (by using the calibration curve) from the measured Q_{A} , which was also an in situ ion beam monitor, and the known area of the rectangular aperture. In this system; to prevent secondary electrons, from escaping, an electron suppressor made of a copper ring with a 5 mm diameter hole biased at -200 V, was mounted in front of the aperture.

2.3. Device fabrication

Soft-lithography is commonly used for fabricating microfluidic devices from PDMS because the process is simple, fast and inexpensive [13]. Typically, a microfluidic channel in the PDMS is transferred from a micro-ridge of a master mold. Here, a 10:1 ratio (by volume) of base to curing agent of PDMS from a Sylgard 184 silicone elastomer kit (Dow Corning, Midland, MI) was mixed together. The mixture was degassed under coarse vacuum to remove air bubbles, poured over the negative PMMA master mold, and then placed on a hot plate for curing at 70 °C for 1 h. Subsequently, the embossed PDMS layer was peeled off. After that the PDMS replica was sealed with a PDMS film prepared by spin coating the PDMS mixture onto a clean glass slide pre-cured at 70 °C for 6 min. To achieve full hardening of the PDMS film, the microfluidic chip was cured again at 70 °C for 45 min. The device is shown in Fig. 3(b).

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