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Full Paper

Influence of MeV H^+ ion beam flux on cross-linking and blister formation in PMMA resist

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Abstract: In soft lithography, a pattern is produced in poly(dimethylsiloxane) (PDMS) elastomer by casting from a master mould. The mould can be made of poly(methylmethacrylate) (PMMA) resist by utilising either its positive or negative tone induced by an ion beam. Here we have investigated the irradiation conditions for achieving complete cross-linking and absence of blister formation in PMMA so that its negative characteristic can be used in making master moulds. PMMA thin films approximately 9 μm thick on Si were deposited by spin coating. The 2-MeV H^+ ion beam was generated using a 1.7-MV tandem Tandetron accelerator. The beam was collimated to a 500×500 μm^2 cross section using programmable proximity aperture lithography system with a real-time ion beam monitoring system and a high precision current integrator. The irradiated areas were investigated by a standard scanning electron microscope and a profilometer. It was found that both the ion beam flux and the stopping power of the ions in the polymer have a critical influence on the blister formation.

Keywords: soft lithography, H^+ ion irradiation, PMMA resist, blister formation

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INTRODUCTION

Numerous studies of ion-beam-induced modification of polymers have been performed in the last three decades because of its potential for technological applications [e.g. 1-3]. In recent years, ion beam lithography on a resist for the development of microfluidic devices has been extensively investigated [4-6]. The resist that has the tendency to form cross-linkage of the main polymer chains or pendant side chains during irradiation is of the negative type (also called negative tone). This is because the irradiated area becomes less soluble in developing solutions compared to an unirradiated region. On the other hand, the predominant modification in a positive resist (also called positive tone) is chain scissioning of the main and side polymer chains, which enhances the solubility rate in the exposed region [7]. Typically, the master mould for soft lithography is fabricated from either an ion-irradiated negative resist such as SU-8 [8] or a positive resist such as poly(methyl methacrylate) (PMMA) [5]. In addition, Licciardello et al. [9] found that the PMMA would undergo a changeover from a positive to a negative tone by the action of high fluence irradiation, but the utilisation of PMMA as a negative tone resist for master mould fabrication has been little used [10]. For both positive and negative resists, a good master mould used in a direct replica moulding technique must have smooth surfaces. However, blisters or craters have been observed on irradiated polymer surfaces [11-12]. These defects can spoil the mould since they may introduce blockages into poly(dimethylsiloxane) (PDMS) replicas for microfluidic networks. Consequently, blisters and craters must be avoided. This paper reports on an experimental study to control defects from 2-MeV H^+ ion irradiation until the dominance of cross-linking in PMMA has been achieved. Some effects of 1-MeV H^+ ion beam are also included for comparison.

PRINCIPLE

According to the stopping and range of ions in matter (SRIM) simulation program, version SRIM-2008 [13], for the projected range of 65 μm, the tracks of 2-MeV H^+ ions in PMMA is straight, especially in the first 10 μm. An individual ion loses about 200 keV of kinetic energy during its passage through the first 10 μm within 0.5 ps. For light incident ions with a velocity much greater than the Bohr velocity (2.2×10^6 m/s) in thin polymer targets, the energy deposited by the ion mainly results in the excitation and ionisation of atoms and molecules of the polymer in the ion-track zone. These initial physical processes of ion-solid interaction can cause chain scission, cross-linking and gas evolution [14]. In the case of PMMA, several simple low-mass gas products such as H_2, CO, CO_2 and CH_4 have been detected, with carbon monoxide as the dominant product [15-16]. This is indicative of bond breaking, which is a precursor of both the chain scission and cross-linking. There were reports that the gas yield from the polymers is strongly dependent on the linear energy transfer (LET) of the ions [17] and on the incident ion fluence [18]. Although the fundamental mechanism is still not fully understood, the proposed models [11-12] agree that blisters and craters on the surface of a polymer are formed by the gas products as they pass into the surrounding vacuum.

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MATERIALS AND METHODS

The PMMA used in this work had a molecular weight of 950 kDa (950 PMMA A11, MicroChem). All PMMA films were spin-coated on clean 1×1-cm^2 silicon substrates at a spin speed of 2,500 rpm for 45 sec. by using a self-made spin coater. Subsequently, the films were soft-baked on a hot-plate at 160^{o}C for 2 min. This process was repeated three times to attain a total film thickness of 8.8±0.1 μm as measured with a stylus profilometer (P-15 Profiler, KLA-Tencor, USA). The 1.7-MV tandem accelerator (1.7 MV high current Tandetron, High Voltage Engineering Europa B. V., the Netherlands) was used to irradiate the polymer with 1- and 2-MeV H^+ ion beams. The pressure during irradiation was about 5×10^{-6} mbar. The irradiated area was 500×500 μm^2 for all experiments and was defined by two computerised L-shaped blade apertures of the programmable proximity aperture lithography (PPAL) system [10]. The experimental set-up when utilising the PPAL technique is shown in Figure 1. The two L-shaped blades were made of copper plates 100 μm thick with well-polished edges. Each of the L-shaped blades was mounted on a computerised micro-stepper motor that independently moved with high precision in either vertical or horizontal direction. In this manner, the PPAL system could produce any rectangular pattern with dimensions between 1-1000 μm^2. The aperture was located at ~2 mm in front of the sample. The PMMA film on silicon substrate was mounted to the translation stage holder, which could move in both x and y directions with a resolution of 1 μm.

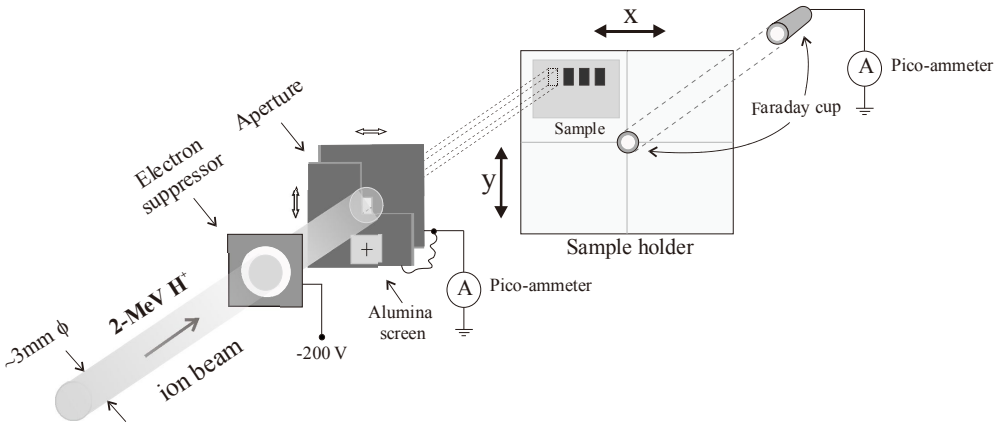

Figure 1. Schematic illustration of an experimental set-up using the PPAL technique for H^+ ion beam irradiation (not to scale)

The key parameters in this study were the values of ion beam fluence (ions/cm^2) and ion beam flux (ions/cm^2·s) at the irradiated areas. To ensure the accuracy of these measurements, the ion beam current at two different positions, as shown in Figure 1, was measured with high precision. A picoammeter with 4.8-pC resolution was specially designed for this purpose. To assure correctness in measuring, an electron suppressor with a 5-mm-diameter hole and a -200V potential was placed in front of the aperture to prevent secondary electrons from leaving the copper blades.

The picoammeter was used to measure the ion beam current detected by an 8-mm-inner-diameter, 65-mm-long Faraday cup. The Faraday cup was isolated and buried in the sample holder. The ion beam current was collected every second from start to stop. Together with the known hole area

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at the aperture, the ion beam fluence and flux could be easily calculated. Moreover, the major part of the incident ion beam blocked by the aperture was monitored also; this was used to fine-tune the accelerator for a stable ion beam current.

After irradiation, the surface morphology of the irradiated areas was investigated by an optical microscope and a scanning electron microscope (SEM) (JSM-5410LV, JEOL, Japan), while the shrinkage of the irradiated areas was measured by the profilometer.

RESULTS AND DISCUSSION

It was found that for 2-MeV H^+ ions, the cross-linking of PMMA within the entire pattern occurred when the fluence exceeded 3.5×10^{14} ions/cm^2, which is consistent with a previous report [19]. Therefore, all the incident fluences used in this work were above this value. Accordingly, in Figure 2 both a and d, b and e, and c and f patterns were irradiated by the 2-MeV H^+ ion beam with the same fluence, viz. 1.0×10^{15}, 1.25×10^{15} and 1.75×10^{15} ions/cm^2 respectively, while the ion beam flux used for patterns a-c and d-f was 4.7×10^{11} and 3.0×10^{12} ions/cm^2·s respectively. It was clearly seen that flaws on the PMMA surface were strongly dependent on the ion beam flux. For the same irradiation fluence but with small values of ion current, the flaws were absent. Figure 3(a) shows that the flaws are blisters and not craters. Each isolated blister has a common appearance of a round shape with about the same diameter.

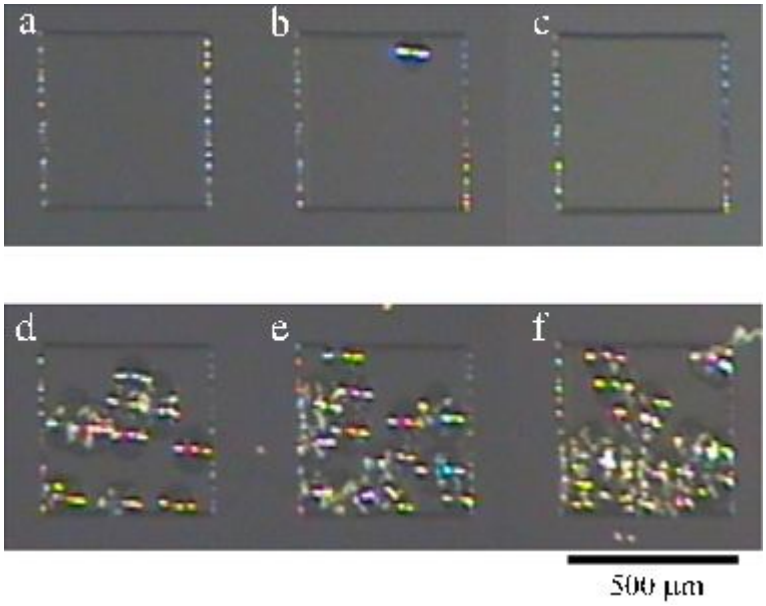

Figure 2. Optical microscope images (13×) of the six 500×500 μm^2 patterns of irradiated areas on the PMMA thin film

The surface profiles of patterns a, b and c in Figure 2 were measured by the profilometer. As shown in Figure 4, the surface regions modified by the 2-MeV H^+ ion beam are remarkably lower than those in the unirradiated regions. Also, the compaction or shrinking occurs even at the smooth patterns and increases with ion fluence. Hnatowicz and Fink [20] reported that the compaction of a polymer is initiated by cross-linking and tends to increase the material density. Experimental evidence from this study suggests that the gas evolution always occurs during irradiation even though no blister is

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observed, as shown in Figure 2 (a-c). However, the gas-release mechanisms for low-flux and high-flux irradiation may be different. More information can be found in a comparison of the smooth pattern a with the blister-filled pattern d, for example. Both of them experienced the same fluence but the irradiation duration of pattern a was 1.72 times longer than that of pattern d.

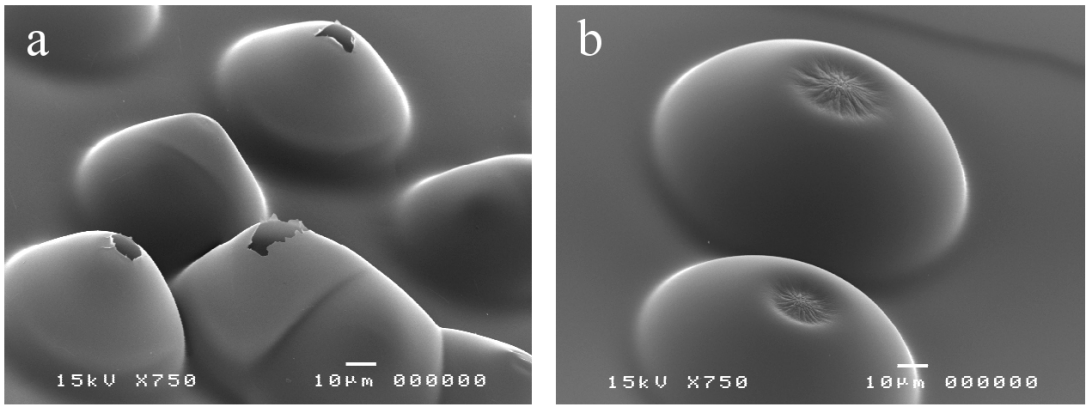

Figure 3. Tilted SEM images of the blisters created by (a) 2-MeV H^+ ions and (b) 1-MeV H^+ ions. The average blister diameters are (a) 61.0±5.8 µm and (b) 92.8±2.5 µm.

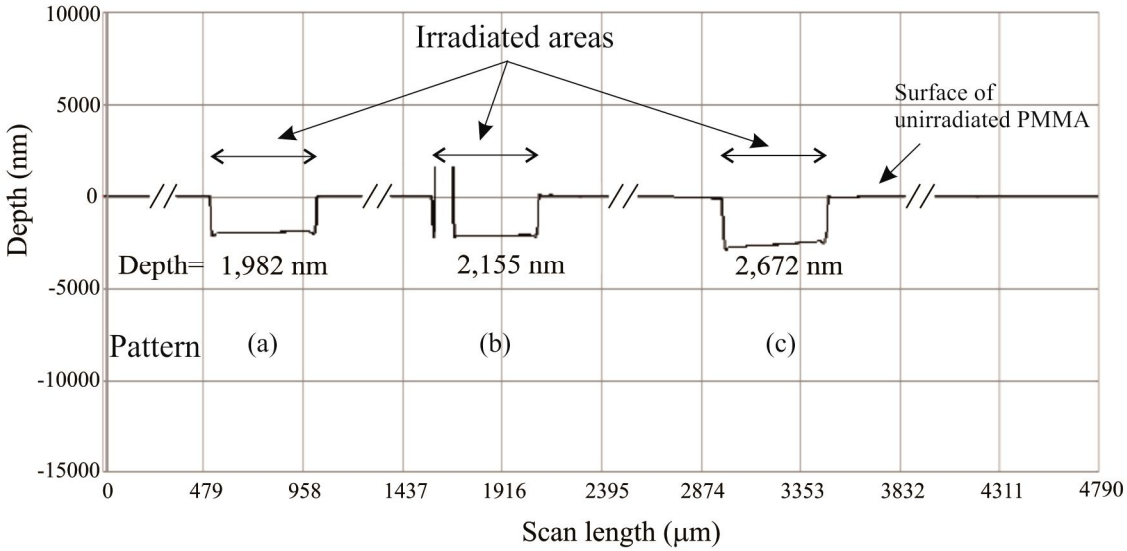

Figure 4. The surface profile of the 3 irradiated areas in the top row of Figure 2

It is reasonable to draw a conclusion that each ion track can be considered isolated in the case of low flux. Degassing due to the pressure gradient is thought to be the main mechanism. Moreover, the very thin PMMA film would allow the gases to leave the polymer easily without much build-up. On the other hand, in the high ion flux case, the temporal interval between the closely-spaced incident ion tracks would allow a build-up of dense low-molecular-weight fragments from intense main-chain scissions. This might nucleate gas bubbles in the whole irradiated volume of the polymer and accumulate gases which eventually converted it into a 'foamed' structure [21]. In this case, the gas bubbles that reached the polymer surface would form blisters.

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It was also found that a 1-MeV H^+ ion beam creates blisters at lower ion beam flux than does a 2-MeV H^+ ion beam. By comparing Figure 3(b) with Figure 3(a), we can see that although each isolated blister has the same shape, the blisters from 1-MeV irradiation are significantly larger in diameter than those from 2-MeV irradiation. From the SRIM code, the stopping power is 1.5 times and the displacement damage 2.4 times greater in 1-MeV than in 2-MeV proton irradiation.

CONCLUSIONS

At an ion irradiation fluence of 10^{14} ions/cm^2 of 2-MeV H^+ ions, the cross-linking process in PMMA started to overcome the chain scission process. The full cross-linking began at an ion fluence of 6.6×10^{14} ions/cm^2. The formation of blisters was strongly dependent on the ion beam flux and stopping power of the polymer for the ions. A 2-MeV proton flux of less than 4.7×10^{11} ions/cm$^2\cdot$s achieved a blister-free condition for the PMMA film ~9 μm thick. This work has confirmed that blisters are created by gas evolution due to chain scissions induced by the ion beams, especially in the early stage of irradiation.

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REFERENCES

1. T. M. Hall, A. Wagner and L. F. Thompson, "Ion beam exposure characteristics of resists: Experimental results", *J. Appl. Phys.*, **1982**, *53*, 3997-4010.
2. S. V. Springham, T. Osipowicz, J. L. Sanchez, L. H. Gan and F. Watt, "Micromachining using deep ion beam lithography", *Nucl. Instr. Meth. Phys. Res. B*, **1997**, *130*, 155-159.
3. F. Menzel, D. Spemann, S. Petriconi, J. Lenzner and T. Butz, "Proton beam writing of submicrometer structures at LIPSION", *Nucl. Instr. Meth. Phys. Res. B*, **2007**, *206*, 419-425.
4. P. G. Shao, J. A. van Kan, K. Ansari, A. A. Bettiol and F. Watt, "Poly(dimethylsiloxane) micro/nanostructure replication using proton beam written masters", *Nucl. Instr. Meth. Phys. Res. B*, **2007**, *260*, 479-482.
5. S. Gorelick, N. Puttaraksa, T. Sajavaara, M. Laitinen, S. Singkarat and H. J. Whitlow, "Fabrication of microfluidic devices using MeV ion beam Programmable Proximity Aperture Lithography (PPAL)", *Nucl. Instr. Meth. Phys. Res. B*, **2008**, *266*, 2461-2465.
6. C. Udalagama, E. J. Teo, S. F. Chan, V. S. Kumar, A. A. Bettiol and F. Watt, "Proton beam writing of long, arbitrary structures for micro/nano photonics and fluidics applications", *Nucl. Instr. Meth. Phys. Res. B*, **2011**, *269*, 2417-2421.

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7. M. J. Madou, "Fundamentals of Microfabrication: The Science of Miniaturization", 2nd Edn., CRC Press, Boca Raton, **2002**, pp.6-7.
8. V. Auzelyte, M. Elfman, P. Kristiansson, C. Nilsson, J. Pallon, N. A. Marrero and M. Wegdén, "Exposure parameters for MeV proton beam writing on SU-8", *Microelectron. Eng.*, **2006**, *83*, 2015-2020.
9. A. Licciardello, M. E. Fragalà, G. Foti, G. Compagnini and O. Puglisi, "Ion beam effects on the surface and on the bulk of thin films of polymethylmethacrylate", *Nucl. Instr. Meth. Phys. B*, **1996**, *116*, 168-172.
10. N. Puttaraksa, S. Unai, M. W. Rhodes, K. Singkarat, H. J. Whitlow and S. Singkarat, "Fabrication of a negative PMMA master mold for soft-lithography by MeV ion beam lithography", *Nucl. Instr. Meth. Phys. B*, **2012**, *272*, 149-152.
11. J. Kaur, S. Singh, D. Kanjilal and S. K. Chakarvarti, "Nano/micro surface structures by swift heavy ion irradiation of polymeric thin films on GaAs", *Digest J. Nanomater. Biostruct.*, **2009**, *4*, 729-737.
12. D. He and M. N. Bassim, "Atomic force microscope study of crater formation in ion bombarded polymer", *J. Mater. Sci.*, **1998**, *33*, 3525-3528.
13. J. F. Ziegler and J. P. Biersack, "The stopping and range of ions in matter", **2008**, http://www.srim.org.
14. M. E. Fragalà, G. Compagnini, A. Licciardello and O. Puglisi, "Track overlap regime in ion-irradiated PMMA", *J. Polym. Sci. B*, **1998**, *36*, 655-664.
15. Z. Chang and J. A. LaVerne, "The gases produced in gamma and heavy-ion radiolysis of poly(methyl methacrylate)", *Radiat. Phys. Chem.*, **2001**, *62*, 19-24.
16. M. E. Fragalà, G. Compagnini, L. Torrisi and O. Puglisi, "Ion beam assisted unzipping of PMMA", *Nucl. Instr. Meth. Phys. B*, **1998**, *141*, 169-173.
17. M. B. Lewis and E. H. Lee, "G-values for gas production from ion-irradiated polystyrene", *J. Nucl. Mater.*, **1993**, *203*, 224-232.
18. F. Schrempel and W. Witthuhn, "Deep light ion lithography in PMMA—a parameter study", *Nucl. Instr. Meth. Phys. B*, **1997**, *132*, 430-438.
19. N. Puttaraksa, R. Norarat, M. Laitinen, T. Sajavaara, S. Singkarat and H. J. Whitlow, "Lithography exposure characteristics of poly(methyl methacrylate) (PMMA) for carbon, helium and hydrogen ions", *Nucl. Instr. Meth. Phys. B*, **2012**, *272*, 162-164.
20. V. Hnatowicz and D. Fink, "Macroscopic changes in ion-irradiated polymers", in "Fundamentals of Ion-Irradiated Polymers" (Ed. D. Fink), Springer-Verlag, Berlin, **2004**, pp.349-375.
21. A. Chapiro, "Chemical modifications in irradiated polymers", *Nucl. Instr. Meth. Phys. B*, **1988**, *32*, 111-114.

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