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OrmoStamp mold fabrication via PBW for NIL

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ABSTRACT

Nanoimprint lithography (NIL) is a promising technology that can fabricate structures with high resolution and high throughput. To replicate patterns through NIL, a high quality master mold is needed. A UV patternable inorganic–organic hybrid polymer, OrmoStamp with high resolution is promising for the fabrication of NIL molds. Here, OrmoStamp molds were fabricated by proton beam writing (PBW) in resist followed by OrmoStamp casting. In this paper, different resists (HSQ, PMMA, SU-8 and SML) were evaluated by PBW for OrmoStamp mold fabrication. The results show that HSQ gives the smallest line width down to 30 nm. These lines have subsequently been successfully replicated in OrmoStamp. High aspect ratio structures in OrmoStamp and Ni were obtained from proton beam written resist samples, featuring an aspect ratio of ~7 and ~70, respectively. Finally thermal NIL has been demonstrated in PMMA using OrmoStamp molds.

1. Introduction

Proton beam writing (PBW) [1–3] has been demonstrated as a single step three dimensional (3D) direct writing technique for the fabrication of high resolution and high aspect ratio structures with straight side walls. In PBW, protons mainly interact with the substrate electrons and penetrate almost in a straight path except at the end of range. Since the mass of a proton is about 1800 times larger than the mass of an electron, the energy transfer in every collision is very small and thousands of collisions will occur before a proton comes to rest. Therefore a MeV proton beam can penetrate a resist very deep with minimal proximity effects. However, compared with masked techniques, PBW is relatively slow and inadequate for mass production of large-area high-density nanostructures. Nanoimprint lithography (NIL) [4–6] allows rapid replication of nanostructures on a mold with high quality, low cost and high throughput [7]. The resolution of NIL is primarily determined by the resolution of the features on the mold. Therefore direct PBW is chosen to fabricate high quality master molds for NIL.

Usually MeV protons are focused to pattern different resists at sub 100 nm dimensions [8]. The smallest features reported in PBW are 19 nm in HSQ [9]. Because resist molds are generally not strong enough for thermal NIL, the fabricated PBW patterns can be transferred to OrmoStamp (Micro Resist Technology GmbH) or Ni molds. OrmoStamp is a hybrid polymer with excellent mechanical properties and ultra-high resolution that can be used as a mold for thermal NIL [10]. In our experiments, different resists HSQ (XR1541), PMMA and SML 50 (EM Resist Ltd) were patterned by PBW to evaluate high resolution OrmoStamp fabrication. SML is a new positive tone resist designed for electron beam lithography (EBL) with very high resolution (5 nm) and ultra-high aspect ratios of more than 50:1. SML has 3 times higher sensitivity compared with standard PMMA resist [11,12]. Here we introduce SML as a powerful positive tone PBW resist capable of fabricating grooves down to 60 nm in width. SU-8 2005 and PMMA were used to fabricate high aspect ratio nanostructures, these nanostructures were successfully replicated in OrmoStamp and Ni. Finally HSQ written masters were used to create OrmoStamp molds for thermal NIL.

2. Fabrication process

In the first experiment, HSQ XR1541, PMMA A4 and SML 50 were spin coated on silicon substrates with a thickness of 200 nm, 200 nm and 50 nm, respectively. Then a 2 MeV proton beam focused down to 30 nm × 50 nm was used to write lines on the samples with different fluences. The lines were digitized to 4096 × 4096 pixels with a pixel size of 5 nm, using IonScan software [13]. Each line is one single pixel wide in X direction. The line fluence of HSQ is 6.3×10^3 protons/μm while PMMA and SML require a higher line fluence of 1.9×10^4 protons/μm. Below a width of 70 nm, a line fluence is chosen since the obtained line width is not constant and depends on the resist used as well as

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energy deposition profile in the resist [14]. After PBW, the HSQ sample was developed in a 2.38% tetramethylammonium hydroxide (TMAH) solution for 1 min. The PMMA and SML samples were developed in an IPA:DI water mixture (7:3 by volume) for 2.5 min. Finally, all the samples were rinsed in DI water for 1 min.

To fabricate taller nanostructures, another experiment was carried out with thick resists. In some of these experiments microlines were written to support high aspect ratio nanolines [3]. SU-8 2005, PMMA A4 and PMMA A11 were coated on silicon substrates with a thickness of 3.8 μm, 630 nm and 10 μm, respectively. Following that PBW was carried out for nanostructure fabrication. All samples were written using 2 MeV proton beams. The SU-8 was patterned using a 300 nm × 400 nm beam spot. The beam was scanned in single pixel wide lines over an area of 100 μm × 100 μm (pixel size 50 nm, fluence 40 nC/mm^2). After PBW, the structures were directly developed with SU-8 developer for about 2 min. The PMMA A4 structures were fabricated using a focused beam of about 80 nm × 200 nm. Single pixel wide lines were exposed over an area of 15 μm × 15 μm (pixel size 15 nm, fluence 100 nC/mm^2). The development time is about 1 min using the IPA/DI (7:3) developer. The PMMA A11 structures were fabricated using a focused beam of about 30 nm × 50 nm. Single lines were exposed over an area of 60 μm × 60 μm (pixel size 15 nm, fluence 5.6×10^4 protons/μm). The development time is about 10 min using the IPA/DI (7:3) developer. Then the sample was Ni electroplated (Technotrans AG, RD. 50 plating system) with a growth rate of 200 nm/min to yield a thickness of 5 μm.

The fabrication process (see Fig. 1) of OrmoStamp molds follows Fernandez-Cuesta et al. [15]. A glass slide was used as substrate for the OrmoStamp structure. The glass slide was first cleaned via plasma treatment (300 mTorr, 18 W for 0.5 min) and then coated with OrmoPrime 08 (Micro resist technology GmbH) at 4000 rpm for 1 min. The OrmoPrime coating was needed to guarantee good adhesion of OrmoStamp to the glass. Next, the glass slide was baked at 150 °C on a hot plate for 5 min. All the resist molds were coated with a thin layer of Teflon to protect them and facilitate demolding [16]. Following that, a drop of OrmoStamp was poured on the resist and spread by gently pressing the glass slide on the resist. Then, UV exposure (i-line 365 nm for 45 min) was conducted to crosslink the OrmoStamp. After UV exposure, the OrmoStamp was peeled off from the resist mold to obtain the reverse structure in OrmoStamp. A second generation working-stamp was made on demand by duplicating the first OrmoStamp copy on a glass substrate. Before the second generation OrmoStamp copy was made, a Teflon layer was coated on the first OrmoStamp copy to facilitate demolding of the two OrmoStamp structures. This second generation OrmoStamp copy carries the same geometry as the original resist mold.

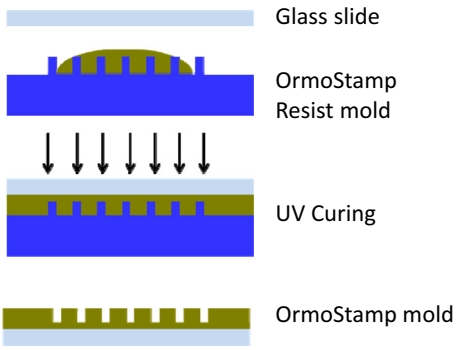

Fig. 1. Fabrication process for OrmoStamp structure: (1) prepare glass slide and resist mold; (2) UV curing of the OrmoStamp; (3) peel of OrmoStamp structure from the resist mold.

An OrmoStamp mold was tested with thermal NIL for PMMA imprinting. Here a 2 MeV proton beam was used to fabricate a HSQ resist mold (270 nm thick) which was subsequently twice replicated in OrmoStamp to form the NIL mold. The proton beam was focused to around 200 nm × 250 nm and exposed the nanolines using single pixel wide lines and 7 pixels wide lines (pixel size 78 nm) with a fluence of 200 nC/mm^2. Imprinting of the PMMA structure was conducted with a commercial nanoimprinter (Obducat Technologies AB, NIL-2-PI 2.5 in. nanoimprinter). The imprinting conditions (120 °C and 15 bar) were applied for 5 min. After the imprinting the sample was cooled down to below the glass transition temperature of PMMA and demolded.

3. Experimental results and discussion

For the first PBW experiment, HSQ, PMMA and SML were fabricated with dimensions (width × depth) of 30 nm × 200 nm, 70 nm × 200 nm and 60 nm × 50 nm, respectively (Fig. 2a–c left) using optimized fluences. The final dimension of the nanolines does not only depend on the resolution of the beam, but also depends on other factors like, energy deposition profile, resist contrast, resist resolution, developer type and development time [11,17]. Among these three resists, HSQ has the smallest line width (30 nm) which gives an aspect ratio of almost 7. The width of the SML groove (60 nm) is smaller than in PMMA (70 nm).

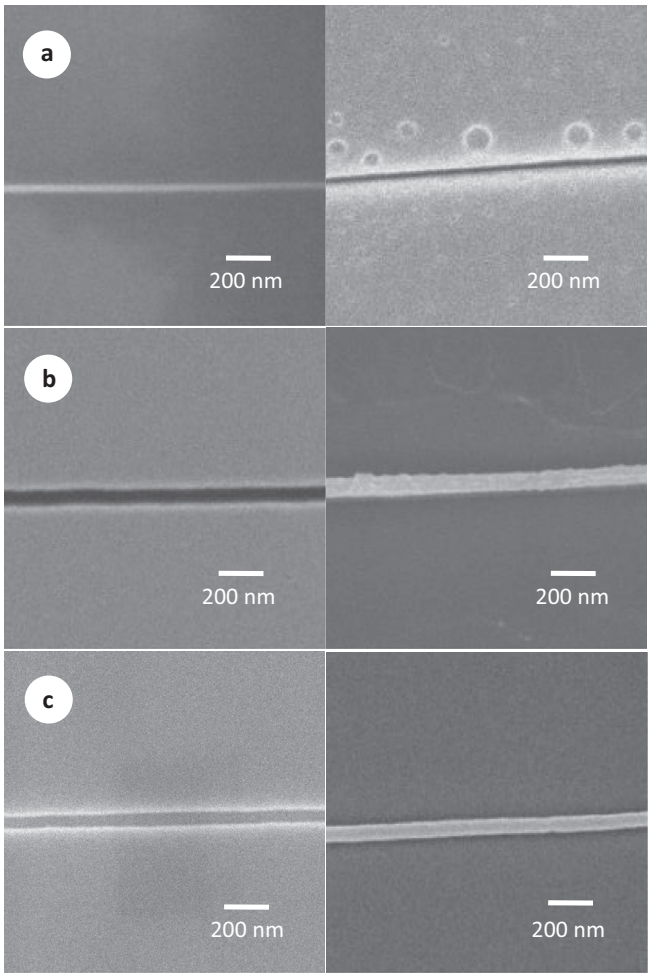

Fig. 2. SEM images of resist molds and OrmoStamp copies (a) HSQ ridge (left) and OrmoStamp channel (right); (b) PMMA channel (left) and OrmoStamp ridge (right); (c) SML channel (left) and OrmoStamp ridge (right).

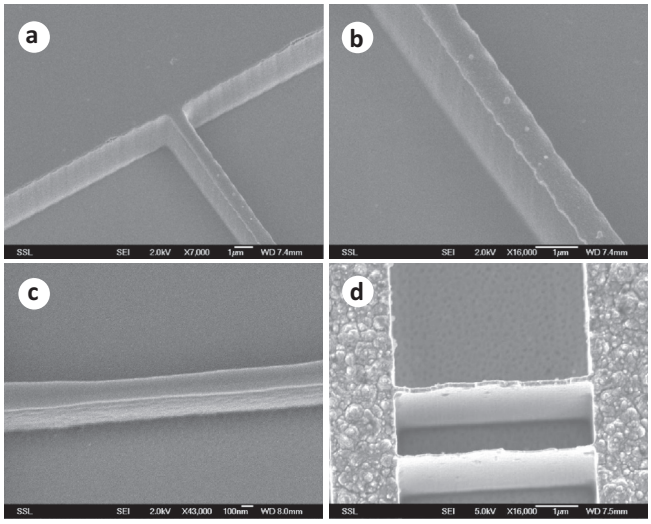

Fig. 3. (a) SEM image of 2nd generation OrmoStamp copied from a SU-8 master, (b) zoom in of (a). (c) OrmoStamp ridge copied from PMMA A4. (d) High aspect ratio nickel ridges, electroplated from the PMMA A11 master.

The OrmoStamp copy carries almost (±5 nm) the same dimension as the original resist. This means structures can be transferred with high fidelity in OrmoStamp at dimension of tens of nanometers. The ridge in the OrmoStamp copy, obtained from the groove in the PMMA, is a little bit rough (see Fig. 2b right), this could be attributed to the fact that the PMMA resist was probably not developed long enough or got damaged during the demolding process.

It is known that resist imaging using electron microscopes is challenging, especially when dealing with positive resist materials at sub 100 nm level. In case of negative resists this is less of a problem since negative resists typically crosslink further under electron beam exposure. Yang et al. [18] have reported SEM images featuring details down to 4.5 nm in HSQ. Therefore the results obtained with HSQ (Fig. 2a left) should be reasonably reliable. This is further supported by the fact that the replicated OrmoStamp features the same dimension (Fig. 2a right). All these samples were coated with ~2 nm of Pt (JFC1600 coater) and imaged in a JOEL GSM-6700F field emission scanning electron microscope.

Fig. 3a and b depict the 2nd generation OrmoStamp ridges, copied from the SU-8 sample with dimension of 800 nm × 3.8 μm (width × height). Another OrmoStamp mold (Fig. 3c) was fabricated using the PMMA A4 channel, which has a dimension of around 200 nm × 630 nm (width × height). Fig. 3d shows nickel walls electroplated from the PMMA A11 structure. The dimension of the nickel wall is around 72 nm × 5 μm, corresponding an aspect ratio of ~70. Comparing these images Ni seems more suitable for high aspect ratio mold fabrication.

Atomic force microscopy is challenging to perform on these structures. Comparing Fig. 3d to the nickel nanoline observed by Ansari et al. which feature a surface roughness of 7 nm RMS [19], we can conclude that the side wall smoothness of our Ni lines is comparable.

In the last experiment, an OrmoStamp mold was tested with PMMA nanoimprinting. A comparison of the resist mold, OrmoStamp molds and final imprinted PMMA structure are shown in Fig. 4. The HSQ nanolines (Fig. 4a) have a dimension of 250 nm × 270 nm (width × height). Fig. 4b and c depict the first and second generation OrmoStamp molds. Here we show that the second generation OrmoStamp mold can be copied successfully by coating a thin Teflon film. A SEM image of the imprinted PMMA film obtained using the second generation OrmoStamp mold is shown in Fig. 4d. We did not notice obvious OrmoStamp mold deterioration after a dozen imprints, confirmed by optical microscopy observation. The results indicate that OrmoStamp is suitable for PMMA nanoimprinting.

4. Conclusion

Different types of resists were tested by PBW for OrmoStamp mold fabrication. HSQ gives the best result with dimension down to 30 nm. A new SML resist was optimized for PBW featuring a dimension of 60 nm. Since it can be easily removed, it is expected to have great potential for Ni mold fabrication in combination with

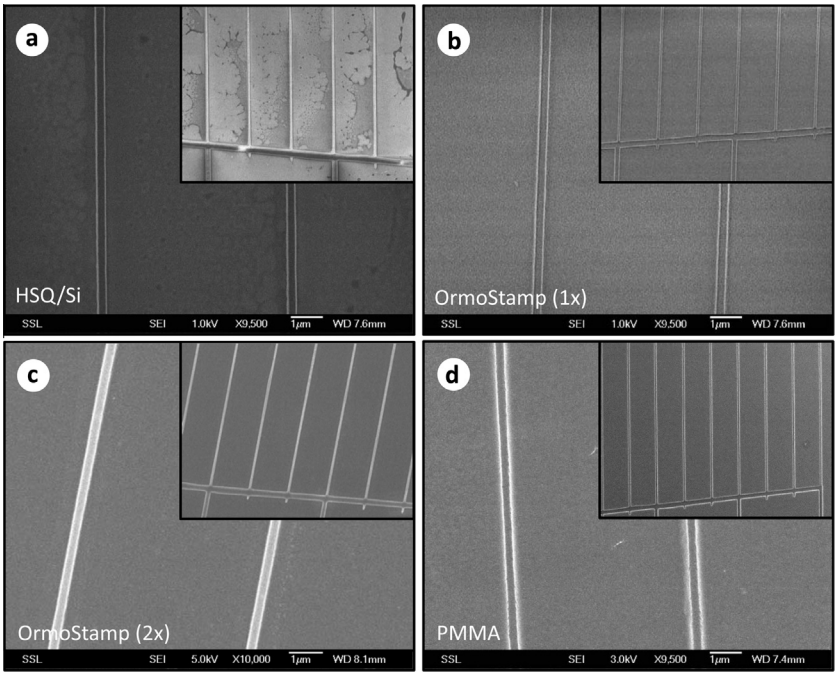

Fig. 4. (a) SEM image of a 270 nm thick HSQ master, patterned with a 2 MeV proton beam, (b) 1st generation OrmoStamp copied from the HSQ master in (a), (c) 2nd generation OrmoStamp copy, and (d) Imprinted PMMA obtained using the 2nd generation OrmoStamp from (c).

PBW. OrmoStamp structures fabricated from HSQ resist feature an aspect ratio up to 7, whereas Ni structures (72 nm width) obtained through electroplating on a PMMA sample show an aspect ratio of ~70. Finally, 2nd generation OrmoStamp copies obtained from a proton beam patterned HSQ master were fabricated successfully with the help of a Teflon release layer. This 2nd generation OrmoStamp mold has been used in thermal NIL to create nanochannels in PMMA. These imprinted PMMA nanochannels will be evaluated for nanofluidic lab on chip devices in the future.

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