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Resist evaluation for Ni mold fabrication and proton beam writing

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ABSTRACT

In our experiments, we use different photoresists for proton beam writing and mold fabrication. We have fabricated Ni mold with structures down to 500 nm. We first use a fine focused proton beam to expose different photoresists, Polymethyl Methacrylate (PMMA), AR-P 3250 and ma-N 2410. After development and nickel sulfamate electroplating, the structures were faithfully transferred from the photoresists to Ni molds.

1. Introduction

Proton beam writing (PBW) is a promising new direct-write lithographic technique which employs a focused MeV proton beam to pattern suitable resists [1,2]. The process, although similar in many ways to direct writing using electrons, nevertheless offers some interesting and unique advantages. Protons, being more massive, have deeper penetration in materials while maintaining a straight path, enabling PBW to fabricate high aspect ratio nanostructures with smooth and vertical sidewalls [3–7]. Essentially no proximity effects have been observed in PBW experiments [4].

In the rapid development of nanotechnology, the demand for low cost high-through–put technologies of fabricating nanometer structures is increasing. There are many techniques like injection molding and nano-imprinting which enable low cost and high throughput replication of polymer structures with features on the micro- as well as on the nano-scale. However, first of all we need a metal mold with nanostructures which can be used in these techniques. As a result, we first need to make the mold. For mold fabrication, electroplating is a good technique for deposition of metal by an electrochemical reaction. The electroplating is a suitable technique for fabricating microstructures [8]. Here we will need suitable photoresists that can be patterned with PBW to get the nanostructures which can be transferred to the mold. Three kinds of photoresists are tested—PMMA, AR-P 3250 and ma-N 2410.

PMMA is a high quality positive resist with its high resolution, high contrast and low sensitivity [9]. PMMA is the first discovered polymer material working as an e-beam resist [10]. It also works very well with PBW. van Kan et al. succeeded to fabricate parallel lines with a width of 50 nm in a 350 nm-thick PMMA layer using a focused 2 MeV proton beam [4]. In addition, PMMA is easy to remove with acetone after exposure, therefore it is suitable for making metallic Ni mold [11].

AR-P is a relatively high sensitive photoresist to UV [12]. AR-P 3250 (ALLRESIST GmbH) is an interesting photoresist because it is a positive photoresist to UV, i.e., the molecular chains are scissioned. Under proton exposure the molecular chains cross link, i.e., it shows negative resist behavior. Before development, the photoresist should be exposed to UV. The photoresist that is exposed to UV becomes soluble to the photoresist developer. The resist can be easily removed with the developer after UV exposure. However, UV will also impact the structures that are patterned by proton beam. UV can break the molecular chains that have been crosslinked by proton exposure. There is a delicate balance between the UV and proton exposure. It requires us to optimize the dose of each of them.

Ma-N (Micro Resist Technology GMBH) is a negative tone photoresist series. The photoresist allows high tolerance in resist process control and also has good resolution. Eighty-nanometer lines and space patterns have been obtained using electron beam writing with ma-N 2400 at 20 kV acceleration voltage [13]. Menzel et al. also have shown Ni grids faithfully replicated from PBW fabricated ma-N 440 resist structures [14]. Here we introduce ma-N 2410 in combination with PBW, according to the supplier this resist is able to support finer details in combination with electron beam writing compared to ma-N 440 [15].

In this paper, we evaluate the above mentioned photoresists with PBW for Ni mold fabrication. The Ni mold can be used for nano-imprinting as well as injection molding [16]. However, it was suggested that the surface roughness of the mold features has a major effect on the cavity filling and demolding [17]. Since PBW is capable of producing very smooth side walls with roughness

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down to sub-10 nm RMS in Ni molds [18] and a resolution of sub-100 nm, it is a promising technique for the fabrication of molds with micro- and nano-meter features [4,19].

2. Experimental procedures

Fig. 1 shows a schematic overview of the mold fabrication process for negative photoresist at CIBA using PBW. This process involves several steps. In this section a more detailed description will be given for PMMA, AR-P 3250 and ma-N 2410.

For PMMA, The process starts with coating of 20 nm Cr and 60 nm of Au using magnetron sputtering on a Si wafer, this layer acts as a seed layer for Ni electroplating. Next a layer of PMMA 950 A11 is spincoated on the wafer at 6000 rpm for 30 s. The thickness of PMMA 950 A11 is about 1 μm. The PMMA layer is exposed using a 1 MeV proton beam focused down to a spot size of $130 \times 150\ nm^2$ using a dose of $100\ nC/mm^2$. During the exposure, we use the focused beam to draw a circle whose diameter is 300 nm. After PBW the sample is developed in a mixture of IPA and DI water (7:3) for 120 s, rinsed with DI water for 3 min and air dried. To guarantee a smooth formation of the Ni stamp during the electroplating process, a 6 nm Ti layer is coated on the sample as a secondary seed layer for the Ni electroplating using the filtered cathodic arc vacuum deposition method ($<10^{-5}$ mbar). Then the sample was mounted on a 6" Ti plate using conductive Cu tape to cover the edge of the sample which is then covered with isolation tape. The Ti plate is mounted in a Technotrans RD.50 plating machine and electroplating is carried out. During electroplating, Ni is first plated in the holes. When Ni grows up to the top of the holes and touches the Ti on the surface of the PMMA, Ni will be electroplated on the whole surface of the sample. Ni is electroplated at a plating rate of $1681\ A/dm^2$ for 1000 min reaching 500 μm. Then we put the whole sample into the acetone for about 10 min to separate the Si and resist from the Ni mold.

For AR-P 3250, after Cr and Au were coated onto the Si wafer, a layer of AR-P 3250 is spincoated on the wafer at 6000 rpm for 30 s. The thickness of AR-P 3250 is about 4 μm. Then the AR-P 3250 layer is exposed using a 1 MeV proton beam focused down to a spot size of $120 \times 150\ nm^2$ using a dose of $50\ nC/mm^2$. After the PBW, the AR-P 3250 is exposed with UV (365 nm using a 100 W lamp) for 7 min. The sample is developed in a mixture of AR-300-26 and DI water (1:1) for 60 s, rinsed in DI water for 2 min and air dried. To guarantee a smooth formation of the Ni stamp during the electroplating process, a 6 nm thick Ti layer is coated onto the AR-P 3250. During electroplating, Ni starts to grow from Ti/Au/Cr/Si surface, after Ni reaches the top of the photoresist and connects the Ti on the top of AR-P 3250, Ni will be electroplated on the whole sample. Ni is electroplated in the Technotrans RD.50 plating machine at a plating rate of $1528\ A/dm^2$ for 600 min to reach a total thickness of 300 μm. Then we put the sample into AR 300-73 remover to remove any leftover AR-P 3250 resist from the Si/Ni interface, this process results in delamination of the Si wafer from the Ni mold. To remove any remaining resist the Ni mold is rinsed in acetone for 40 min.

For ma-N 2410, a layer of ma-N 2410 is spincoated at 8000 rpm for 30 s, this yields a layer of 1 μm thick on a Si wafer which is also coated with Cr and Au (20 nm and 60 nm respectively). The ma-N 2410 layer is exposed using a 1 MeV proton beam focused down to a spot size of $100 \times 120\ nm^2$ using a dose of $70\ nC/mm^2$. After PBW the sample is developed in ma-D 525 for 130 s, rinsed with DI water for 3 min and air dried. A 6 nm Ti layer is coated on the sample as a secondary seed layer for the Ni electroplating. Ni is also electroplated in the Technotrans RD.50 plating machine at a plating rate of $52.08\ A/dm^2$ for 100 min reaching 10 μm followed by $520.8\ A/dm^2$ for 41.5 h reaching 2490 μm, yielding a total thickness of 2.5 mm. We first cut the back of the Ni to get a really flat surface. Then a square sample is cut out from the Ni/resist-Si sample (Fig. 1(f)) plate with the structures in the center. The Ni is cut using wire spark erosion cutting. To separate the Ni mold from the resist-Si interface the square cut out sample stack is placed in acetone for 30 min.

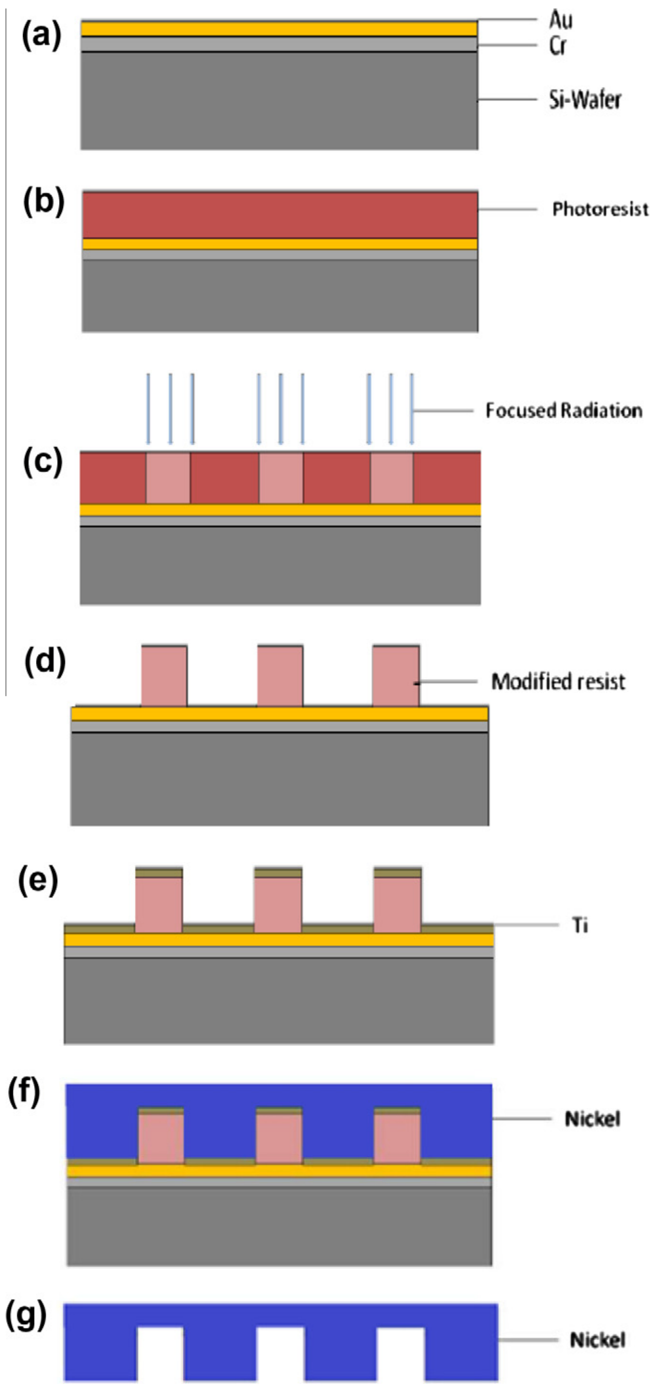

Fig. 1. A schematic overview of the process steps in Ni mold fabrication using PBW, (a) Coating the Si wafer with Cr and Au as seed layer for electroplating, (b) Resist coating, (c) PBW using 1 MeV protons, (d) Resist development, (e) Ti coating as a second seed layer for Ni electroplating, (f) Ni electroplating and (g) Mold release.

3. Results

In PMMA photoresist, we fabricated holes using PBW. The thickness of the PMMA is about 1 μm and the size of the holes is about $300 \times 500\ nm^2$. During PBW, the beam was focused down to

$130 \times 150\ nm^2$. The holes are not perfectly circular. This is because when we use the focused beam to draw a circle, the beam spot in X and Y is not the same size, also in the Y direction there is more beam scattering giving rise to lager features in Y direction. However, more experiments will be done to fabricate smaller and more circular nanoholes [8].

The patterned PMMA is then coated with 6 nm of Ti as a second seed layer for electroplating. Fig. 2 shows a replication in Ni of the original PMMA structure, the Ni nano-pillars are 1 μm tall and have a width down to 300 nm. As we can see, the sidewall of the nano-pillars is very smooth. In addition, all the PMMA has successfully been removed with acetone. This indicates that PMMA is a high quality positive photoresist for both proton beam writing and subsequent mold fabrication.

For the evaluation of AR-P 3250, three samples were prepared and exposed by PBW with the same dose. We fabricate a grid structure using a 1 MeV proton beam in AR-P 3250. In a next step the samples were exposed to UV at 365 nm for 5 min, 7 min and 10 min respectively, and after that, the samples were developed for 80, 60 and 60 s respectively. UV exposure for 5 min is not enough to expose the 4 μm thick AR-P 3250, a longer exposure of 10 min results in a concave shape on the top of the grid lines. Prolonged UV exposure can counteract the cross linking by proton irradiation, as a result the parts exposed by proton will become soft and not hard enough to stand. A 7 min UV exposure gives the best results. Fig. 3(a) shows a SEM photograph of the grid featuring lines down to about 500 nm in width in 4 μm thick AR-P 3250 written with a proton dose of $50\ nC/mm^2$ and UV exposure for 7 min. The width of the lines matches with the designed file. Fig. 3(b) is a high magnification SEM photograph of the horizontal line marked in Fig. 3(a). As can be seen from Fig. 3(a) and (b), the structures are well defined with sidewalls of high smoothness and verticality, which is important for fabricating high quality molds.

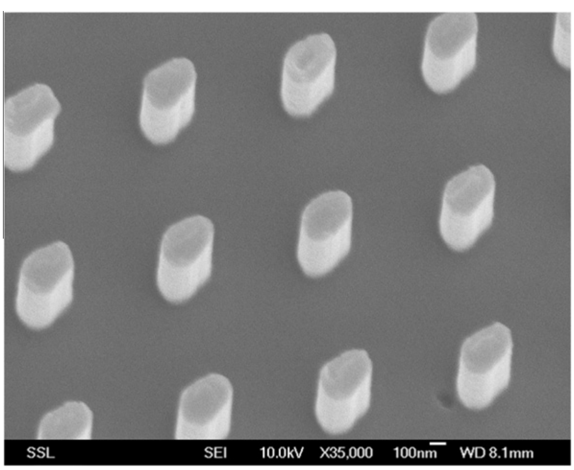

Fig. 2. Ni electroplated mold featuring 300 nm wide and 1 μm high pillars plated in a 1 μm thick PMMA resist layer written with a 1 MeV proton beam.

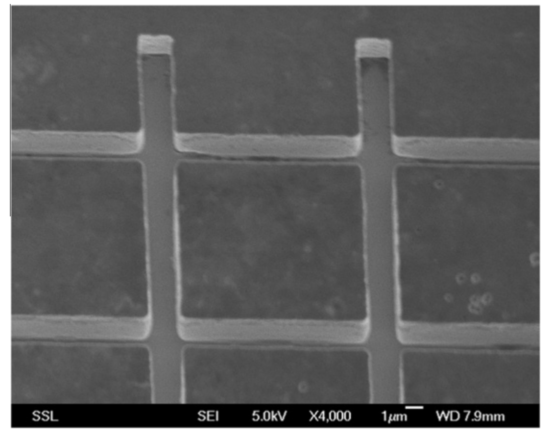

Fig. 4. Ni mold with grooves about 1.4 μm wide and 4 μm deep plated in a 4 μm thick AR-P 3250 resist layer.

After coating 6 nm Ti as electroplating seed layer and electroplating, we have the Ni mold with micron-sized grooves (Fig. 4). As shown in Fig. 4, the photoresist is completely removed in the 1.4 μm wide grooves. The depth of the groove is 4 μm nicely matching the height of the original AR-P 3250 resist layer. If the aspect ratio of the grooves is very high, the photoresist cannot be easily removed. The removal after electroplating needs to be optimized for even finer features. The experimental results show that AR-P 3250 is potentially a powerful negative tone photoresist for PBW when used in combination with UV lithography.

We fabricated micro- and nano-lines using PBW on a ma-N 2410 resist layer coated on a silicon wafer as shown in Fig. 5. The resist layer is 1 μm thick and the width of the lines ranges from 500 nm to 2 μm. During PBW using 2 MeV protons, the beam was focused to a 100 nm × 120 nm spot. As can be seen, the fabricated structures are vertical and have reasonable smooth side walls but the smoothness is not as good as for AR-P, the ma-N2410 resist exposure needs more optimization to achieve higher quality structures.

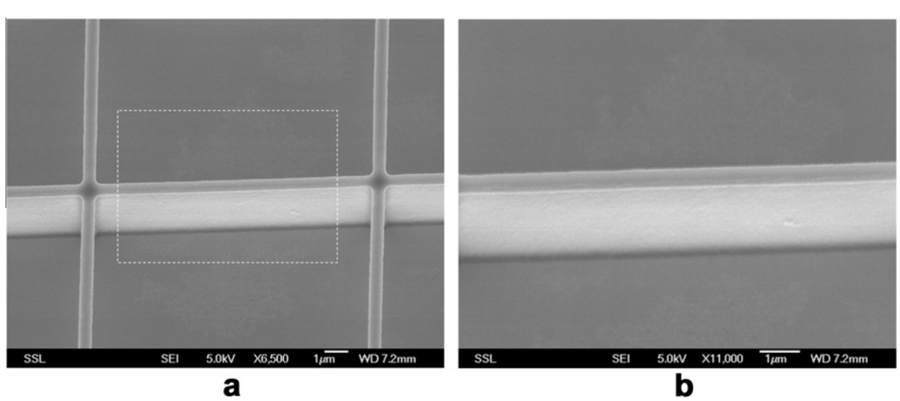

Fig. 3. (a) Electron microscope image of AR-P 3250 grids in 4 μm thick layer featuring 500 nm wide lines. (b) A high magnification SEM image of the 500 nm wide line in 4 μm thick AR-P 3250.

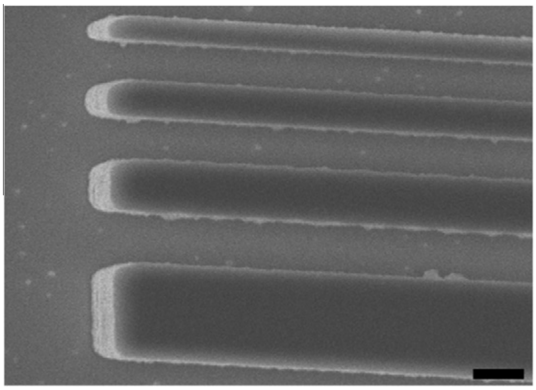

Fig. 5. Electron microscope image of ma-N 2410 structures written with a 1 MeV proton beam in a 1 μm thick resist layer (scale bar: 1 μm).

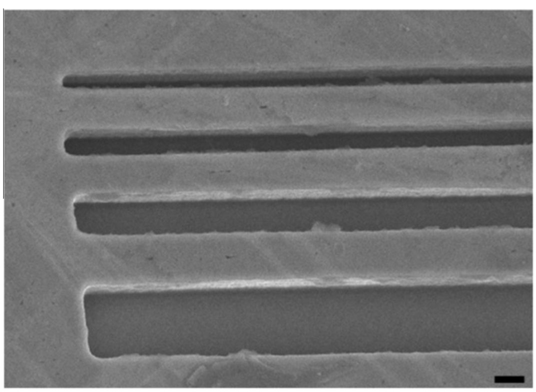

Fig. 6. Ni electroplated mold featuring 500 nm wide and 1 μm deep lines plated in a 1 μm thick ma-N 2410 resist layer (scale bar: 1 μm).

The sample was then coated with a 6 nm thick Ti layer acting as a second seed layer for electroplating, followed by electroplating. Fig. 6 shows a SEM photo of the Ni mold replicated using the polymer structure featuring 1 μm deep grooves down to 500 nm in width. As can be seen, the structures were transferred from the ma-N resist pattern to the Ni mold accurately and the resist was completely removed with Acetone.

Normally patterned negative resist, e.g. SU-8 is very difficult to be removed from the electroplated metal replica, which is the main obstacle in the fabrication of metal molds with details down to the micro- and nano-scale, especially when the aspect ratio of the pattern is high. Our experiments indicate that patterning AR-P 3250 and ma-N 2410 resist with PBW is a promising process for making high quality Ni metal molds with high aspect ratio featuring details at the micro- and nano-scale.

4. Conclusion

We fabricated integral Ni molds featuring nano-pillars in Ni with PMMA and PBW. The Ni pillars have smooth sidewalls and have an aspect ratio of 3 which is challenging to achieve in integral Ni molds used for nano-imprinting technique. In addition, we have demonstrated the suitability of PBW in AR-P 3250 and ma-N 2410. Structures down to 500 nm in width were well fabricated in 4 μm and 1 μm thick resists respectively. AR-P 3250 resist is special since it requires a flood UV exposure after PBW to guarantee resist removal during development. Optimized balance between proton dose and UV exposure results in well defined resist structures with smooth and vertical sidewalls. In the future for PBW, we will focus our proton beam size even smaller to pattern the photoresist. Our recent experiments show that the size of the structure can be reduced further. Structures in the photoresist smaller than 100 nm can be fabricated using PBW. We will try to transfer the structures to Ni with electroplating. In addition, higher aspect ratio structures can be fabricated. The PBW patterned resist structures were successfully transferred to Ni using electroplating and all the resists can be easily removed from the Ni replica after plating, which enables the fabrication of a high quality Ni mold with high aspect ratio and highly vertical and smooth sidewalls.

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