Nuclear Instruments and Methods in Physics Research B 267 (2009) 2376–2380

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

# Proton beam writing and electroplating for the fabrication of high aspect ratio Au microstructures

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ARTICLE INFO

*Article history:*
Received 17 February 2009
Received in revised form 30 March 2009
Available online 8 April 2009

*PACS:*
07.78.+s
85.40.Hp
81.16.Nd
81.15.Pq

*Keywords:*
Proton beam writing
High aspect ratio
Electroplating
Au microstructure

ABSTRACT

We present an approach to fabricate tall high aspect ratio Au microstructures by means of proton beam direct writing. Combining proton beam direct writing and electroplating, we successfully produced gold structures with sub-micrometer lateral dimensions, structure heights in excess of 11 μm, and aspect ratios over 28. Sidewall quality of the Au structures was improved by lowering the process temperature to 20 °C when developing PMMA patterns with GG developer. The application of such structures as X-ray masks for deep X-ray lithography with synchrotron radiation was demonstrated.



## 1. Introduction

Many new fields, such as microelectromechanical systems (MEMS), photonic crystals and meta-materials, require metallic microstructures which feature high aspect ratios and large thickness. Structure heights of multiples of 100 μm up to more than 1 mm can be achieved by deep X-ray lithography with synchrotron radiation [1–4]. This implies exposure of a suitably thick resist such as SU-8 or PMMA through an X-ray mask that features patterned gold absorber structures of typically 20 μm thickness. Such structures are usually first written into a suitable resist by either electron beam or laser beam as primary pattern generators. Upon wet development, voids are either filled with gold by electroplating or sputter deposition to form a soft X-ray mask or they are used to etch the chromium layer in case of a UV lithography mask. As the e-beam-written mask has a typical thickness of about 1 μm [5] it cannot be used directly for deep lithography with hard X-rays since the contrast would not be high enough. Indeed, it is commonly copied into a sufficiently thick resist of typically 20 μm by either UV or soft X-ray exposure. Alternatively, laser beam direct writing into AZ resists up to 30 μm thick has been found to yield strongly concave and bumpy sidewalls when a single writing process was used. Multiple writing significantly improved sidewall straightness and smoothness, but did not completely solve the problem [6]. Obviously, the common techniques for primary pattern generation have limitations when it comes to producing X-ray masks thick enough to provide sufficient contrast for deep X-ray lithography [7,8].

On the other hand, proton beam writing (PBW) seems an ideal tool for fabricating such microstructures in a single exposure, thus reducing process complexity and times as well as promising improved pattern accuracy and sidewall smoothness.

PBW is a direct-writing technique capable of pattering 3D high aspect ratio nanostructures. A 2 MeV proton beam which is highly focused is used to irradiate resist material. The kinetic energy of the protons is transferred to the resist, which leads to the formation of a latent image, by chain scission in the case of positive resist (such as polymethylmethacrylate (PMMA)) or by crosslinking in the case of negative resist (e.g. SU-8™ or hydrogen silsesquioxane (HSQ)). A high energy proton beam can penetrate deeply into resist in a very straight path, more than 60 μm in the case of a 2 MeV proton beam into PMMA resist. Previous works have shown that PBW can fabricate high aspect ratio structures with critical lateral dimension at micrometer and nanometer scale [9–11]. Therefore,

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doi:10.1016/j.nimb.2009.03.103

high aspect ratio, tall microstructures can be fabricated with PBW. PMMA as a commonly used positive resist has exhibited sub 100-nm features and extremely smooth sidewalls in the case of thin layer [10]. However, with an increase of the PMMA thickness (>5 μm), the problem of PMMA stress cracking is encountered when the PMMA patterns are developed [12]. The stress cracking significantly influences metallic structures subsequently formed by electroplating. The objective of this work was to fabricate high aspect ratio tall Au microstructures, by a combination of PBW and electroplating. Efforts were made to improve sidewall quality of tall Au microstructures. As an application, the method was used to fabricate high quality X-ray masks for deep X-ray lithography with synchrotron radiation.

## 2. Experiment

### 2.1. Fabrication process

The fabrication process is schematically illustrated in Fig. 1. Cleaned Si wafers were first sputter coated with a 10 nm layer of Cr (as adhesion layer) and then a 40 nm thick Au layer (as electroplating seed layer). Then, PMMA (950 PMMA A11, Micro Chem) was spin coated on the sputtered wafers to obtain layers more than 10 μm thick. Finally, microstructures were written with PBW in the PMMA resist.

The PBW experiments were performed at the Centre for Ion Beam Applications (CIBA), National University of Singapore, using a focused beam of 2 MeV protons to write structures in PMMA resists. Details of the lithography endstation and the accelerator facility can be found elsewhere [13]. The proton beam was typically focused to a spot size of about 300 nm with a beam current of around 0.30 pA. The latent images written in the PMMA resist were then developed using IPA–water (7:3) mixture or GG developer, a mixture of 15 vol% water, 60 vol% butoxyethoxyethanol, 20 vol% tetrahydro-oxazine and 5 vol% aminoethanol.

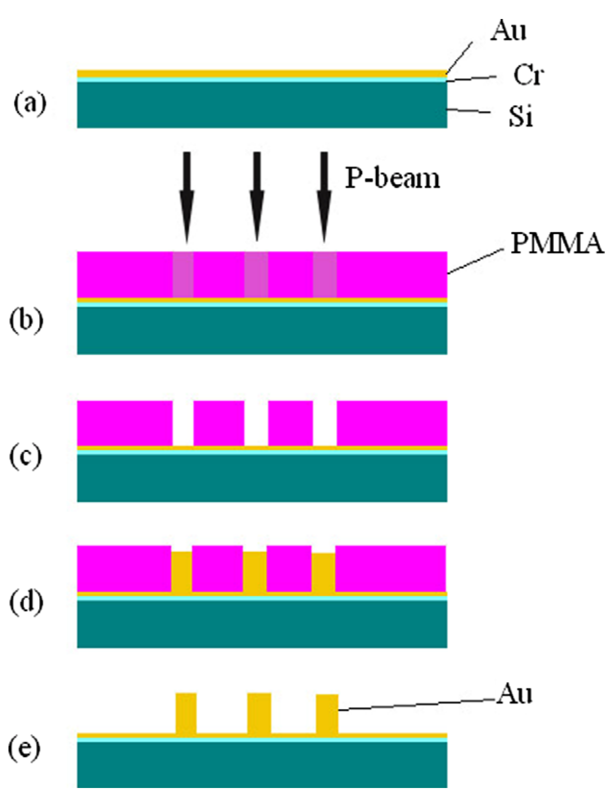


**Fig. 1.** Schematic illustration of fabrication process. (a) Seed layer coating, (b) PMMA spin-coating and proton beam writing, (c) development of PMMA latent patterns, (d) Au electroplating and (e) PMMA removal.

After the development, the PMMA channels were filled with gold by electroplating. The gold electrolyte used was MICROFAB Au 100 (from Enthrone Pte. Ltd.). Plating was carried out at a constant temperature of 60 °C and a plating current density of 2.5 mA/cm$^2$. A rotary-stirrer was adopted to improve the uniformity of the solution and to reduce air bubbles generated during plating process. After the gold electroplating process, the residual PMMA was chemically removed by means of toluene at 40 °C.

### 2.2. Development of PMMA structures

IPA–water (7:3) mixture and GG developer are commonly used for developing PMMA resist. GG developer is normally used at 30–35 °C and IPA–water is used at room temperature (20–25 °C). We developed the PMMA structures with IPA–water (7:3) at room temperature and GG developer at 30–35 °C and 20 °C, respectively. For GG developer at 30–35 °C, we used a standard beam dose of 90 nC/mm$^2$, which was sufficient to completely expose the resist using a 2 MeV proton beam. When GG developer was used at a lower temperature (20 °C), 2–3 times the standard beam dose was required for the exposure of submicron size structures. The developing time for GG developer at 20 °C was 40 min, which was much longer than the time of about 5 min used at 30–35 °C.

## 3. Results and discussion

### 3.1. Au structures fabricated by PBW

Some Au structures are shown in Fig. 2. In Fig. 2(a), lateral dimensions of the pillars are 0.4 μm and their heights are 11.5 μm, resulting in aspect ratios of over 28. As far as we are aware, these are the largest aspect ratio metallic structure made by direct-writing techniques. Fig. 2(b) shows circular shape pillars with diameter of 1 μm and height of 11.3 μm. Arrays of metallic pillars are of great research interest because of their unusual optical and electromagnetic properties. Applications can be found in plasmonics devices and photonics [14,15]. Fig. 2(c) shows gold parallel lines with different line width. The smallest line width is 1 μm and the largest is 10 μm. Fig. 2(d) shows concentric circles. The outermost line width is 0.5 μm and thickness is 4.5 μm. This kind of concentric metallic circles may be used as Fresnel Zone Plate (FZP) for focusing hard X-rays [16]. PBW has an ability to fabricate structures down to 20 nm size [10]. So, once a smaller beam size is used, a high aspect ratio FZP with outermost line down to 100 nm can be fabricated in this way.

### 3.2. Improvement of sidewall quality

In a microfabrication process, sidewall quality is an important consideration. As mentioned above, with increase of PMMA thickness, cracking in sidewall of PMMA structure becomes increasingly a problem that influences the quality of subsequent metallic microstructure. Efforts were made to improve sidewall qualities by optimizing development conditions. Conventionally, IPA–water (7:3) of room temperature and GG developer of 30–35 °C are used to develop PMMA microstructures. However, we found that these normal development conditions of GG developer and IPA–water caused a few stress cracks in the developed PMMA structures which resulted in protruding structures on the sidewalls of Au structures which follows the morphology of the cracking. Fig. 3(a) shows this kind of protruding structures on Au microstructures. The PMMA template for these structures was developed with GG developer at a conventionally used temperature (30 °C). We varied the developing temperature of GG developer and found

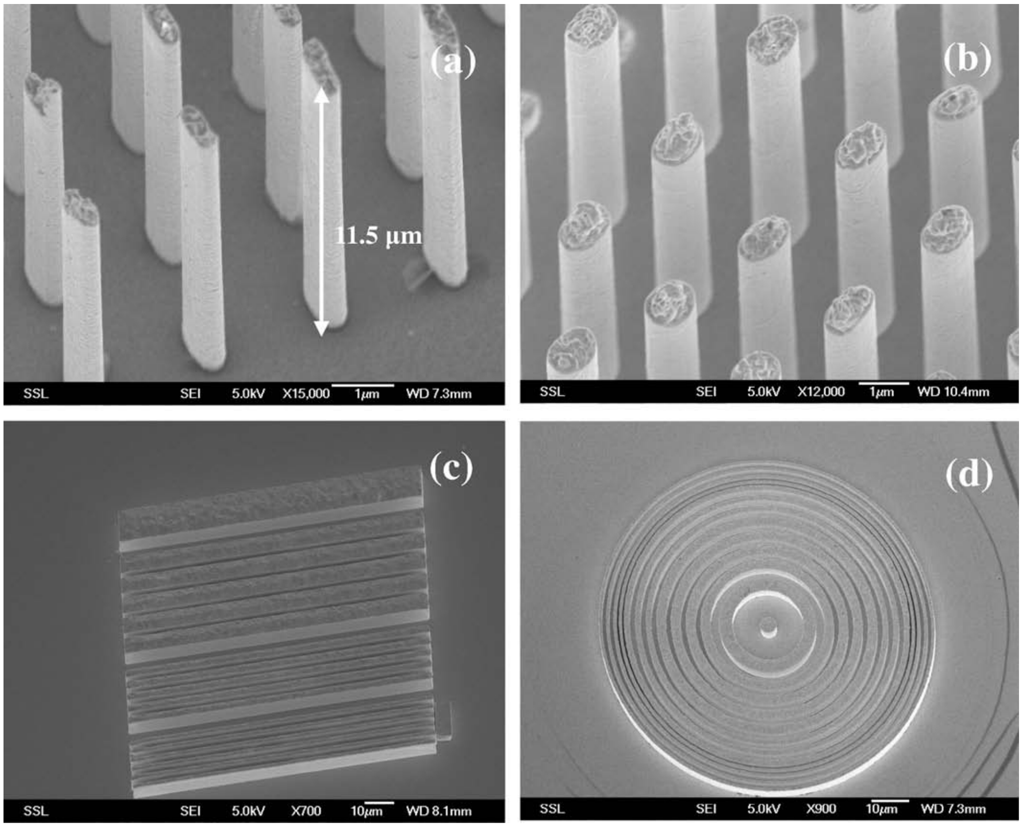


**Fig. 2.** 20° tilted view of gold structures. (a) Au pillar with aspect ratio of over 28; (b) circular Au pillar; (c) parallel lines with different line width and (d) concentric circles.

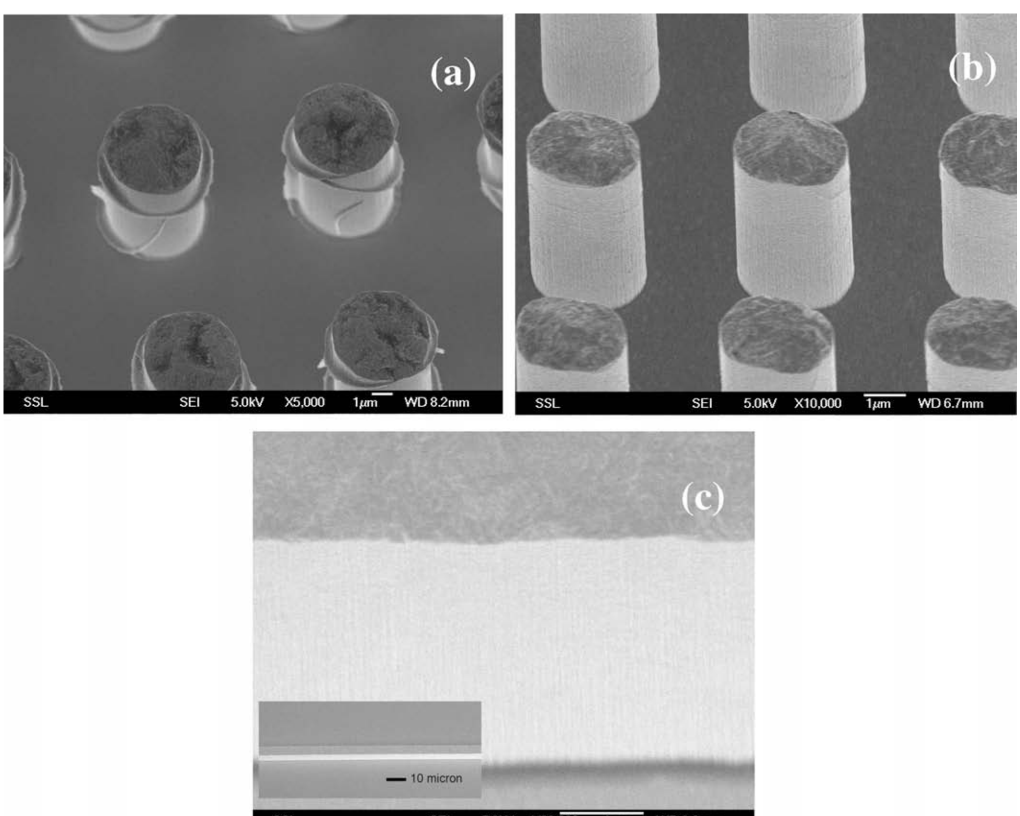


**Fig. 3.** Sidewall of Au microstructures formed through PMMA templates developed under different conditions. (a) GG developer at 30 °C; (b) GG developer at 20 °C; (c) GG developer at 20 °C. Inset in (c) is a low magnification view.

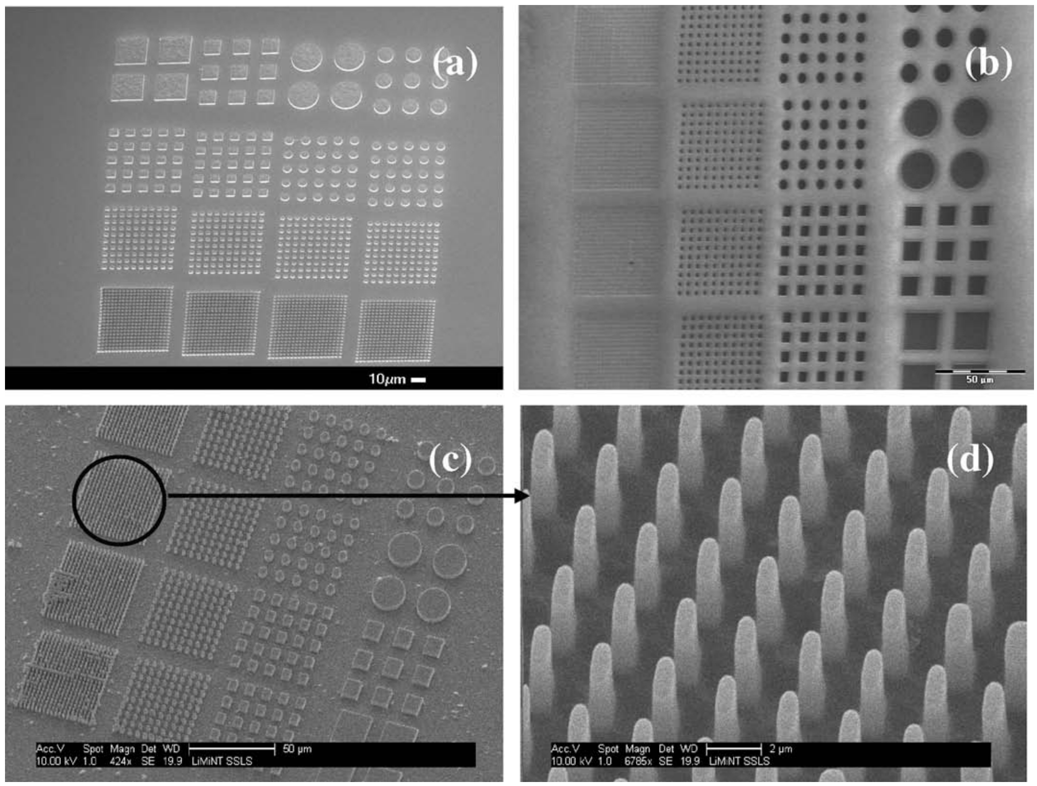


**Fig. 4.** SEM images of Au absorbers on $Si_3N_4$ membrane (a) and corresponding structures produced with X-ray lithography through the absorbers: SU-8 holes (b), PMMA microstructures (c and d). (d) is a magnified view of the 1 μm size pillars in (c).

that sidewall the qualities were improved when the development was carried out at lower temperatures. Fig. 3(b) and (c) is Au microstructures with improved sidewalls. The PMMA patterns for these structures were developed with GG developer at 20 °C. Fig. 3(c) is a magnified view of a line wall. It shows a smooth and vertical sidewall. The Au microstructures shown in Fig. 2 are also the results of development optimization, with obviously much better sidewall. Conventionally, because GG developer is more viscous than IPA–water and thus its diffusivity is less than that of IPA–water, IPA–water mixture is sometimes preferred as when developing high aspect ratio structures [17]. However, we found that with increased developing times, GG developer was also capable of fully developing submicron structures to a full depth of more than 11 μm (Fig. 2(a)). These longer development times appear to have very limited effect on unexposed resist. Thus, by developing of PMMA patterns with GG developer at a lower temperature, sidewall qualities of corresponding Au structures formed by electroplating were improved. This result is consistent with reports of Pantenburg et al., who studied sidewall cracking of PMMA microstructures fabricated with deep X-ray lithography [18]. However, it should be noted that extremely low temperature of GG developer is not desirable, because the sensitivity of GG developer decreases significantly with decreasing of temperature, and too low sensitivity may cause insufficient development of PMMA microstructures, even with increased developing time.

### 3.3. Application to X-ray mask fabrication

From the above discussion, we can see that the Au microstructures fabricated with PBW in this work have characteristics of high aspect ratio, large thickness, sharp edge and smooth sidewall. Au microstructures with these features are well suitable to be used as absorbers of X-ray masks for hard X-ray lithography. Therefore, PBW provides an alternative method for X-ray mask fabrication [19]. Using our technique, an X-ray mask with absorbers up to 10 μm can be fabricated in only one writing step without conventional intermediate mask making steps. An X-ray mask is typically composed of an absorber, a membrane and a substrate. Au patterns were fabricated on a 1-μm thick silicon nitride membrane which was supported by a Si frame. The silicon nitride membrane was highly transparent to X-rays because it is thin and consisted of low-*Z* elements. Thus, the gold structures, silicon nitride membrane and Si frame formed an X-ray mask. In this work, the absorbers had a thickness of nearly 11 μm. The masks were used for X-ray lithography tests at the LiMiNT station of SSLS [20]. SU-8 resist and PMMA resist were exposed with white X-rays of 2–10 keV through the mask. Fig. 4 is SEM images of Au absorbers on $Si_3N_4$ membrane (Fig. 4(a)) and microstructures of SU-8 (Fig. 4(b)) and PMMA (Fig. 4(c) and (d)) produced by means of deep X-ray lithography. In Fig. 4(a), the largest and smallest dimension size of the patterns was 20 μm and 1 μm. For the SU-8 exposure, resist layers of 17 μm and 28 μm thickness were exposed. SU-8 microstructures produced using X-ray lithography through the mask are shown in Fig. 4(b). Except for the 1 μm size, all the absorber patterns were well duplicated in the X-ray lithography process. In the case of 1 μm structures, we observe formation of the well known skin at the top of the nominally unexposed surface of SU-8. This is due to a lacking contrast of the mask for the given spectrum of the Helios 2 storage ring, since, at 11 μm thickness of the Au absorber, the contrast is <200 for photon energies >7.3 keV, spectral range in which Helios 2 is producing copious flux. There are two options to improve upon this problem, first, to increase absorber thickness and, thus contrast, and, second, to cut off the harder part of the incident spectrum by means of a mirror. Both options are being pursed in current work.

We also exposed 20 μm thick PMMA resist through the mask. Fig. 4(c) is an SEM image of the resulting PMMA microstructures. It shows that all the absorber patterns in Fig. 4(a) are well duplicated, even the 1 μm size pattern. Fig. 4(d) is a magnified view of the 1 μm size PMMA pillars, showing exposure results in more detail. The reason for the better pattern transfer into PMMA is that PMMA needs less contrast than SU-8.

In summary, the results showed that proton beam direct writing enables manufacturing of high-quality X-ray masks without intermediate mask step. This technique is also promising to improve pattern transfer accuracy because the process sequence is simplified to only include one direct writing step followed by development and electroplating. X-ray lithography test showed that pattern transfer from the mask to PMMA resist layer worked well for all the patterns. Pattern transfer from the mask to an SU-8 resist layer by means of X-ray deep lithography was demonstrated to work well for structures of 2 μm size and above. In the case of 1 μm structures, skin formation becomes visible. To avoid it, either the absorber thickness must be increased and/or the X-ray spectrum made softer.

## 4. Conclusion

An approach to fabricate Au microstructures featuring high aspect ratio as well as smooth vertical sidewalls was developed, by a combination of the proton beam writing and electroplating. We successfully fabricated gold structures with aspect ratio over 28 and thickness more than 11 μm. The work showed that cool temperature development of PMMA latent image using GG developer helps to reduce PMMA cracking and thus helps to improve sidewall quality of subsequently formed Au microstructures. X-ray masks with absorber patterns of nearly 11 μm thick were fabricated with the process without intermediate mask making steps.

## Acknowledgements

We acknowledge financial support from the MOE Academic Research Fund under the grant R-144-000-130-112. Work partly performed at SSLS under NUS Core Support C-380-003-003-001, A*STAR/MOE RP 3979908 M and A*STAR 12 105 0038 grants.

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