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TECHNICAL PAPER

J. A. van Kan · P. G. Shao · K. Ansari
A. A. Bettiol · T. Osipowicz · F. Watt

Proton beam writing: a tool for high-aspect ratio mask production

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Abstract P-beam writing (proton beam writing), a direct write 3D nano lithographic technique has been employed for the production of X-ray masks in a single step fabrication process, with high aspect ratios and extremely smooth absorber edges. P-beam writing employs a focused MeV proton beam scanned in a predetermined pattern over a resist (e.g. PMMA or SU-8), which is subsequently chemically developed. P-beam writing in combination with electroplating appears ideally suited to directly write X-ray masks with nano sized features, high aspect ratios, small lateral feature sizes, and smooth and vertical sidewalls. Sub 100 nm resist structures with aspect ratios up 160 have been produced, as well as metallic (nickel) structures down to the 100 nm level. Preliminary tests on p-beam written X-ray test masks show that Ni stencils can be fabricated with a thickness of 2–20 μm, smooth side walls, feature details down to 1 μm, and aspect ratios up to 20.

1 Introduction

A number of processes have been developed for the production of X-ray masks (Menz et al. 2001). Because of the large thickness required, typically a two step process is carried out, where first an intermediate and relatively thin mask is produced either by electron beam writing (e-beam writing) or by a photolithographic process, e.g. laser direct writing or UV lithography. This intermediate mask is then used in a (soft) X-ray lithographic step to transfer the features onto the final thick mask without significant loss of structural quality. Obtaining deep sub micron resolution in X-ray lithography requires features down to several hundred nanometer in a metal absorber mask, featuring high aspect ratios.

Proton beam writing is a new direct write lithography technique for fabricating high aspect ratio structures (van Kan et al. 2003a). The slowing-down and ensuing energy deposition of energetic charged particles (e.g. MeV protons) impinging on and penetrating into solids is governed by the Coulomb interaction of the incident particle with the electrons and nuclei of the target. In e-beam writing as well as p-beam writing the stopping is dominated by substrate electrons. Unlike the high energy secondary electrons generated during e-beam writing, the secondary electrons induced by the primary proton beam have low energies, typically less than 100 eV, and therefore a limited range, resulting in minimal proximity effects. Low proximity effects coupled with the characteristic straight trajectory and high penetration of the proton beam enables the production of high density 3D micro and nano structures with well defined smooth side walls to be directly written into resist materials. Recent results (van Kan et al. 2003a) indicate there is no noticeable proximity effect in the p-beam writing process, allowing the production of high density and high aspect ratio nano-structures. Work carried out at CIBA (Centre for Ion Beam Applications) recently resulted in an exceptional result: the demonstration that p-beam writing (combined with electroplating) can be used to produce metallic (nickel) structures down to the 100 nm level, with very smooth and near vertical sidewalls (Ansari et al. 2004). These results show the potential of p-beam writing as a way to produce high quality X-ray masks, and therefore we will concentrate in this paper on Ni plating of stencil masks for X-ray lithography.

2 Experimental procedures

P-beam writing has been carried out at the CIBA using a 3.5 MV HVEE Singletron™ accelerator coupled to a

J. A. van Kan (✉) · P. G. Shao · K. Ansari
A. A. Bettiol · T. Osipowicz · F. Watt
Centre for Ion Beam Applications (CIBA),
Department of Physics, National University of Singapore,
2 Science Drive 3, Singapore 117542, Singapore
E-mail: phyjavk@nus.edu.sg
Tel.: +65-6516-2638
Fax: +65-6777-6126

dedicated p-beam writing set-up (Watt et al. 2003; van Kan et al. 2003b). This system is unique, since it is dedicated to p-beam writing on a micron as well as on a nano scale. In this system proton beams are focused down to sub 100 nm spot sizes and scanned over suitable resist materials. Both SU-8 and PMMA exhibit sub 100 nm features and extremely smooth sidewalls when p-beam writing is utilised (van Kan et al. 2003a). PMMA and SU-8 molds have been investigated as templates to electroplate metallic X-ray absorbers. Using a focused 2 MeV proton beam structures were written in two SU-8 resist coated Si wafers. Resist thicknesses of 2 and 10 μm were used, corresponding to the final thickness range in which we expect to produce X-ray masks with sub-100 nm details. The ultimate resolution is compromised if a post exposure bake is applied (van Kan et al. 2003b), therefore the SU-8 resist is developed directly after the proton beam exposure. Figure 1 shows lines of 130 nm width in the 2 μm thick layer and in Fig. 2 an array of hollow circular pillars connected via nano walls are shown, here an aspect ratio of 160 is obtained for the 60 nm wide walls in the 10 μm thick SU-8 layer. Earlier results have shown that accurate high aspect ratio nanostructures can be produced in PMMA using p-beam writing, with a typical RMS sidewall roughness for both PMMA and SU-8 of less than 3 nm (van Kan et al. 2003a). As well as smooth sidewalls it is important to have perfect side wall verticality. SRIM (Biersack and Haggmark 1980) calculations show that a parallel incoming proton beam will spread less than 8.0 nm (90% of the beam) after penetrating 2 μm in PMMA. Secondary electron excitation calculations (Waligorski et al. 1986) show that 90% of the energy will be deposited within 3.0 nm of the proton track using a 2 MeV proton beam in 2 μm thick PMMA. Taking these two facts into consideration we can expect a sidewall verticality of about 89.7° if we write structures in a 2 μm thick resist layer.

After the resist mold fabrication it is important to generate a high quality negative metal copy of the structured resist. Electroplating requires the sample to have an adequate metallic seed layer. Since protons are not affected by the underlying substrates (van Kan et al. 2004a) and no proximity effects have been observed (van Kan et al. 2003a), we can choose any metallic layer as substrate. Recently an isolated 100 nm wide Ni wall was electroplated in 2 μm thick Ni featuring very smooth and nearly 90 degree sidewalls (Ansari et al. 2004). In Fig. 3 we show that it is also possible to Ni plate high density structures, where we have produced a regular grating with lines and spaces of 180 nm and a height of 200 nm. The Si substrate was coated with Au as a plating base and Cr as an adhesive layer to the Si wafer followed by spinning a 200 nm thick PMMA layer. After p-beam writing the sample was development in iso-propyl alcohol (IPA) and water (7:3) for 1 min. We have observed previously that it is better to use this less viscous developer compared to the conventional GG developer (Springham et al. 1997) for the production of high aspect ratio nano structures (van Kan et al. 2003a; van Kan et al. 2004b). To produce a nanostructure surface for use as a metallic stamp for nano imprinting, we continue the plating process until the sample reaches a total Ni thickness of around 1 mm. This gives added strength to the stamp rendering it suitable for nano imprinting. The plating was performed in a Technotrans AG, RD.50 plating system.

Only electroplating results in combination with PMMA resist will be presented here, since we have found that the difficulties involved in the SU-8 removal process can damage the stencil mask (van Kan et al. 2005). For the production of a stencil mask there are different requirements to the metallic seed layer. Since the Ni structure has to be released from the substrate after plating, two different seed layers which can be etched as a sacrificial layer were evaluated (e.g. Cu and

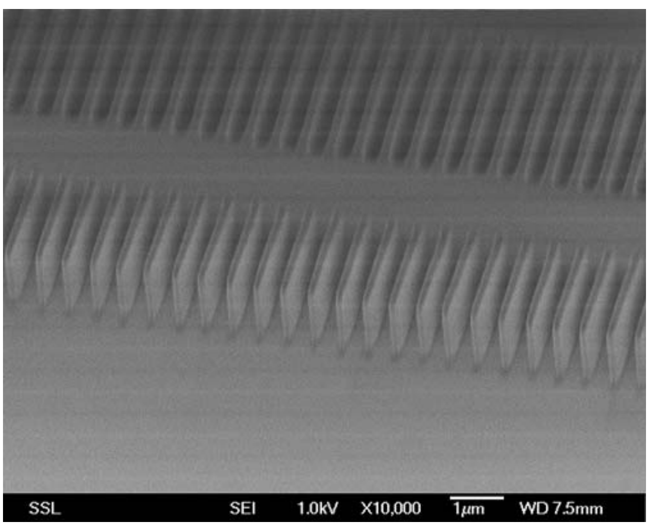

Fig. 1 SEM of p-beam written 130 nm lines in 2 μm thick SU-8

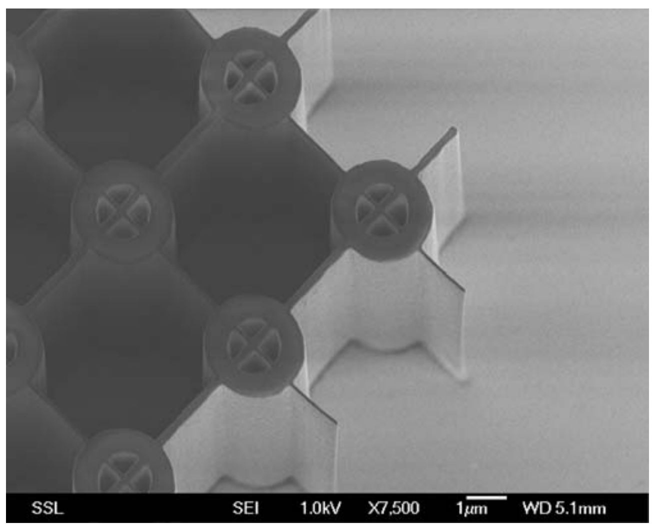

Fig 2 SEM of p-beam written high aspect ratio structures in 10 μm thick SU-8 featuring 60 nm walls

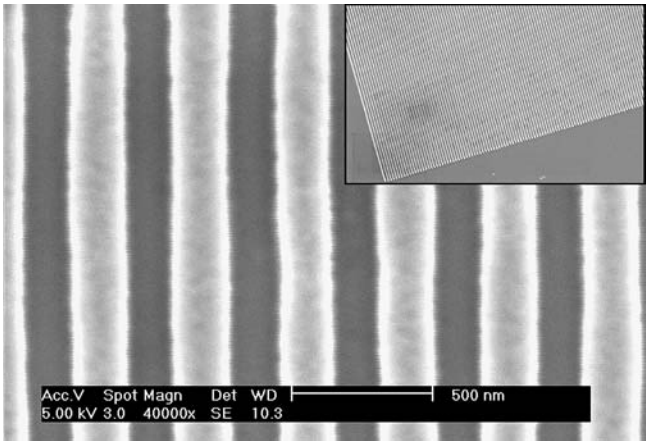

Fig. 3 SEM of a Ni stamp featuring 180 nm lines and spaces, 200 nm deep, the stamp has a total thickness of 1.1 mm. The inset shows an overview of the grating

Cu/Ta). For the first experiments we chose a Cu coated Si wafer to produce a Ni stencil mask. The Si wafer was cleaned and dry baked at 180°C for 1 h. Next a 200 nm Cu layer was coated followed by spincoating of a 3 μm thick PMMA layer. P-beam writing was performed with 2 MeV protons. After development in IPA and water (7:3) the sample was electroplated up to a thickness of 2 μm. The PMMA was removed in toluene at 40°C for 1 to 2 h. Finally the Cu etching was performed in a H3PO4/HNO3/CH3COOH solution at room temperature. Almost immediately the Ni grid delaminated from the substrate, the sample was left in the Cu etch solution for a total time of 3 min to completely dissolve the Cu. In Fig. 4 a SEM photograph is shown of the 2 μm thick Ni stencil mask featuring smooth vertical sidewalls and 3 μm lateral details.

Next high aspect ratio stencil masks will be discussed. High aspect ratio PMMA structures on a substrate require good adhesion of PMMA to the substrate. It turned out the adhesion of the PMMA/Cu layer to the Si substrate is not good enough to successfully produce high aspect ratio PMMA structures on the Si wafer. Similar adhesion problems of high aspect ratio PMMA structures on Si have been reported by Achenbach (2004). Using Ta as an adhesive layer between the Si substrate and the Cu layer, good adhesion was observed between the PMMA and the substrate. A 25 μm PMMA layer was spin coated in three consecutive coating steps on a Cu/Ta coated Si wafer. P-beam writing was performed using 2 MeV protons. The stencil mask is designed to include square openings of 2, 2.5 and 4 μm, separated by Ni walls with a minimum width of 1 μm, this requires the production of closely packed high aspect ratio freestanding PMMA pillars. After development the sample was Ni plated up to a thickness of 20 μm. The PMMA was removed under similar conditions as for the thin sample. The improved adhesion requires a much longer Cu etching time before the Ni stencil mask is released from the substrate. In order to

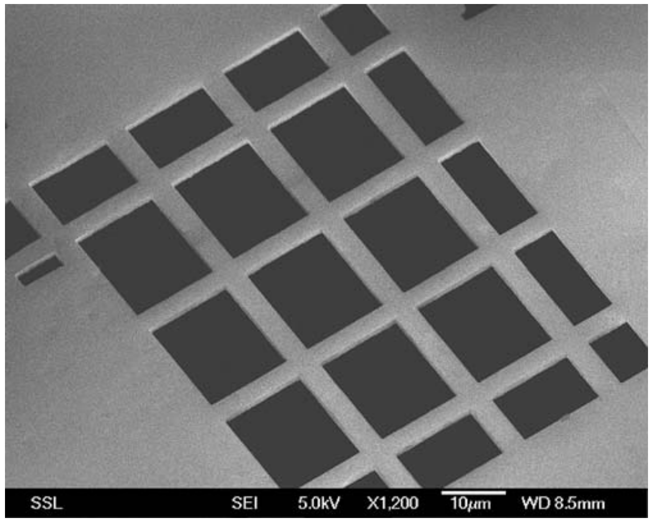

Fig. 4 SEM of 2 μm thick Ni stencil mask produced by p-beam writing in a 3 μm PMMA layer followed by Ni electroplating

reduce the Cu etching time the stencil mask was made with many large open areas to ensure an easy access of the Cu etch solution to the Cu seed layer. Full delamination was observed after 14 h of Cu etching. A low magnification optical micrograph of the 3×3 mm^2 stencil mask is shown in Fig. 5, as can be seen on the left the Ni between the smallest openings of 2×2 μm^2 didn't survive all the processing steps, the 2.5×2.5 μm^2 openings on the top and bottom and the 4×4 μm^2 openings on the right were successfully produced. These investigations indicate that proton beam fabricated free standing PMMA structures with an aspect ratio of more than 10 are on the limit of the structural stability of PMMA, similar results have been obtained by Achenbach for X-ray produced PMMA structures (Achenbach 2004). We found that freestanding SU-8 structures with

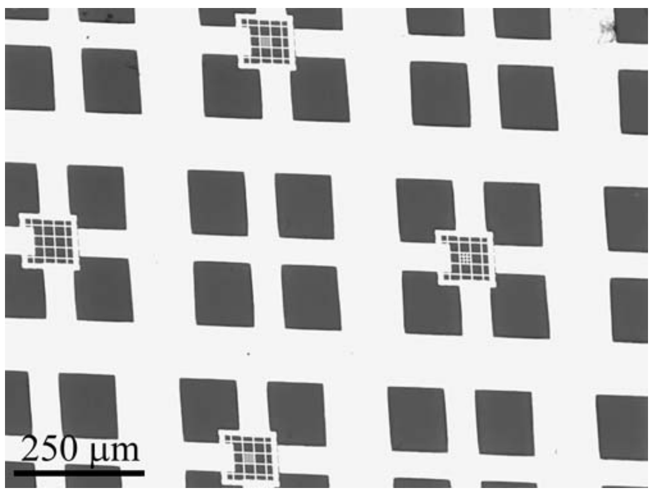

Fig. 5 Optical photograph of a 20 μm thick Ni stencil mask produced by p-beam writing in a 25 μm PMMA layer followed by Ni electroplating

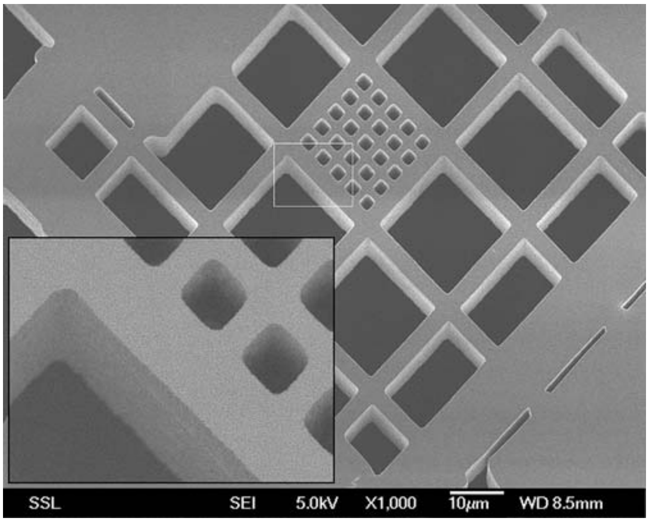

Fig. 6 SEM of the 20 μm thick Ni stencil mask featuring 1 μm details and an aspect ratio of 20. The inset shows the marked area

an aspect ratio of 10 or more also show limited structural stability. The high aspect ratio obtained for SU-8 in Fig. 2 is possible because of the nearby supporting pillars. SEM micrographs, see Fig. 6 are taken of the smallest details in the Ni stencil mask which are about 1 μm, featuring an aspect ratio of 20. Tests to improve the Cu etching process by increasing the temperature to 40°C were not successful: Although the etching time was reduced to 9 h the Ni was also etched by about 0.5 μm resulting in increased side wall roughness.

3 Conclusions

P-beam writing is capable of creating high aspect ratio polymer structures with sub 100 nm features, which can be used as molds to produce X-ray masks, either in the form of stencil masks or supported by a carrier. This initial study shows the fabrication of Ni stencil masks with smooth sidewalls, details down to 1 μm and aspect ratios up to 20. In a later stage we plan to use Au plating to produce more effective X-ray masks. This new lithographic process appears ideally suited to directly write X-ray masks with nano sized features, high aspect ratios, ultimate lateral feature sizes and smooth and vertical sidewalls in a single-step process. Mask production is one of the most difficult and expensive steps in LIGA technology, which is rapidly becoming a standard tool in many industrial production processes. Therefore we expect p-beam writing not only to contribute to progress in nano-technology, but also indicates that the p-beam writing mask production process could become a commercially viable option in LIGA technology.

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