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Abstract

The first step in the fabrication of microstructures using deep x-ray lithography (DXRL) is the irradiation of a x-ray sensitive resist like polymethylmethacrylate (PMMA) by hard x-rays. At the Advanced Photon Source, a dedicated beamline allows the proper exposure of very thick (several mm) resists. To fabricate electroformed metal microstructures with heights of several mm, a PMMA sheet is glued onto a metallic plating base. An important requirement is that the PMMA layer must adhere well to the plating base. The adhesion is greatly reduced by the penetration of even a small fraction of hard x-rays through the mask absorber into the substrate. In this work we will show a novel technique to improve the adhesion of PMMA onto high-Z substrates for DXRL. Results of the improved adhesion are shown for different exposure/substrate conditions.

Introduction

In the LIGA process [1], used for the fabrication of electroformed microstructures, the first step is deep x-ray lithography (DXRL). DXRL consists of exposing a thick resist, which has been coated onto a substrate, to x-rays through a x-ray mask. At the Advanced Photon Source (APS), the deep x-ray exposure is performed at beamline 2BM [2] using thick (> 1 mm) polymethylmethacrylate (PMMA) resists. After the exposure the resist is

developed and used as a template for electroforming various metals. Finally the resist is stripped off, leaving the desired metallic structures, Figure 1.

One of the most important requirements of this technique is good adhesion of the PMMA layer to the plating base[3], [4], [5]. As described by Pantenburg et al. [6], the adhesion can be greatly reduced by electrons and fluorescence photons that are created during the irradiation beneath the mask absorber. X-ray absorption by the metallic plating base results in substrate-generated photoelectrons being absorbed in the resist near the substrate. The exposure of the resist by these additional photoelectrons from the substrate makes the PMMA near the interface soluble in the developer and thus contributes to loss of adhesion.

High energy photons are desirable for DXRL due to their greater penetration and therefore their ability to uniformly expose very thick resist layers (up to several mm). In Figure 2, the transmitted x-ray intensity versus energy during PMMA exposures for DXRL at the APS is shown. Loss of adhesion may become especially pronounced when using these very high energy photons, because of the increased range of the substrate-generated photoelectrons and their higher intensity.

A 1-mm PMMA sheet was patterned by exposure at the APS with a 0.15° Pt-mirror and a 1-mm C-filter followed by GG development [7], [8]. This sample was prepared by gluing PMMA on a Si wafer coated with Cr/Au using a standard gluing process [9]. The resulting structures (Figure 3) show a significant loss of adhesion.

A common solution to the problem of poor adhesion is to increase the gold absorber thickness of the mask or to replace the plating base with a lower density metal. An increase in the gold absorber thickness is not always possible or desirable mainly because of the high stress of the electroplated gold and difficulties to plate uniformly over 100 μm or more. Also the choice of substrate/plating base is often determined by constraints other than the desire for low x-ray absorption.

Our approach does not seek to reduce the secondary electron emission from the plating base but rather to improve adhesion by moving the resist away from the substrate where the photoelectrons are generated. This is achieved using an inert low-Z organic material as a buffer layer with a thickness of the order of the penetration length of the photoelectrons, in our case $\sim 3\text{ }\mu\text{m}$. The thickness of this layer is set to be just greater than the range of energy dissipation of substrate-generated photoelectrons.

In order to move the resist away from the region where the electrons are generated, the standard LIGA process has been consequently modified as shown in Figure 4. In the substrate preparation, we spin-coat a buffer layer. A polyimide film such as the Dupont Pyralin® resin PI2545, has been used as a buffer layer as it meets the requirements; other radiation-resistant polymers may also be used. The adhesion between the polyimide layer and the PMMA can be further enhanced by roughening the polyimide with a short RIE/plasma etching step.

The photoelectrons generated in the substrate will be absorbed in this buffer layer and dissipated without damaging the resist. After developing the resist, the buffer layer is removed by anisotropic etching using oxygen RIE with negligible harm to the resist layer. Thereafter, the patterned resist layer can be plated as usual and the resist stripped with solvent. After the stripping, additional RIE is required to remove the remaining buffer layer.

Optimization of the buffer layer has also been investigated. This is necessary because it is very important to achieve negligible damage to the resist layer during the anisotropic etching step. Different buffer layers have been tested with the objective of minimizing the oxygen plasma power/time. Polyimide gives the best results in terms of adhesion, but to remove it requires more than 2 h at 100 W of oxygen plasma, which damages the PMMA structures. The use of materials that are easy to remove (like AZ resist) has disadvantages primarily due to the fact that the stress of a thick AZ resist is high, and it

is damaged by the secondary electron emission from the plating base. The best solution has been a suitable combination of these two materials, i.e., we first spin a thin layer of polyimide, $\sim 0.5\text{-}1\text{ }\mu\text{m}$, directly on the substrate, and then to reach the required thickness we spin a second layer of AZ1828 resist. In this way, by keeping the AZ far from the interface, we greatly reduce its radiation damage and we keep the polyimide thin enough to be removed easily.

Results and Discussion

The use of an optimized buffer layer has improved the adhesion under different DXRL exposure/substrate conditions. In particular, we have used a resolution mask, consisting of a $300\text{-}\mu\text{m}$ Si membrane and $\sim 70\text{-}\mu\text{m}$ thick Au absorbers, to expose different substrates; with the same beamline configuration, substrates were prepared having 15, 30, and 45 nm Au as a plating base and 1-mm glued or $150\text{-}\mu\text{m}$ spin-coated PMMA. All substrates were prepared with the optimized buffer layer. No differences were observed among the different Au plating base substrates of various thicknesses. In Figure 5, the smallest ($2\text{ }\mu\text{m}$) attached structures are shown for a resolution mask exposure onto a $\sim 1\text{-mm}$ PMMA glued substrate. The aspect ratio in this case is ~ 475 . In Figure 6, $100\text{ }\mu\text{m}$ still attached structures are shown for a resolution mask exposure onto a $\sim 2.5\text{-mm}$ PMMA glued substrate. The aspect ratio in this case is ~ 25 .

The buffer layer has also improved the adhesion of structures exposed with poor contrast masks. Graphite masks [10] were replicated in 1-mm PMMA at the APS using a Pt-mirror (higher energy) and a mask with a gold absorber of $15\text{ }\mu\text{m}$. For substrates prepared without the buffer layer, the adhesion loss observed can be explained by the excess dose in the adhesion layer, which results from fluorescence and secondary electron emission. This secondary emission is generated by the high-Z plating base absorbing high energy x-rays that penetrate the gold absorber. Shown in Figure 7 are 1-mm PMMA

structures replicated using the buffer layer exposed under the same conditions of [10]. None of the features exhibit adhesion loss.

Copper is a desirable substrate for some of our devices [11] and is an example of where a high-Z substrate must be used to achieve the requirements for the final part. While the buffer layer works as previously described for gold substrates, copper has another problem: this developer attacks copper, further degrading the adhesion and finish quality on the final part. However, the use of the GG developer is essential to maintaining good development contrast. Thus an additional benefit of the buffer layer is that it enables the use of “GG” developer with copper substrate/plating bases.

Conclusion

The loss of adhesion of PMMA resists on high-Z substrates is a significant problem for DXRL using higher energy x-rays. The use of an optimized buffer layer consisting of spun polymer films has been shown to significantly reduce the problem. Another benefit of the buffer layer is that it enables the use of "GG" developer by protecting sensitive substrates such as copper.

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Figure Captions

Figure 1 - "Standard" LIGA. After the exposure (a) the resist is developed (b) and used as a template for electroforming various metals (c). Finally the resist is stripped off, leaving the desired metallic structures (d).

Figure 2 - Transmitted x-ray intensity versus energy during PMMA exposures at the APS.

Figure 3 - A SEM of a 1-mm PMMA sheet prepared by gluing PMMA on a substrate using the standard process [9]

Figure 4 - "Modified" LIGA. After the exposure (a) and development of the resist (b), the buffer layer is removed by anisotropic etching using oxygen RIE (c). Thereafter, the patterned resist layer can be plated (d) and the resist stripped with solvent (e). After the stripping, additional RIE removes the remaining buffer layer (f).

Figure 5 - Resolution mask exposed with a 0.15° Cr mirror, 1-mm C filter onto 1-mm PMMA glued onto a 45-nm Au plating base substrate.

Figure 6 - Resolution mask exposed with a 0.15° Pt mirror, 1-mm C filter onto 2.5-mm PMMA glued onto a 30-nm Au plating base substrate.

Figure 7 - Graphite masks replicated in 1-mm PMMA using the buffer layer.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

(a)

(b)

(c)

Figure 7

Figure 8