Wet isotropic chemical etching of Pyrex glass with masking layers Cr/Au

Ž. Lazić, M. M. Smiljanić, M. Rašljić, I. Mladenović, K. Radulović, M. Sarajlić, D. Vasiljević-Radović

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Abstract – In this paper we developed various techniques of wet isotropic chemical etching of Pyrex glass in an aqueous solution of 49% HF. The techniques are based on the processes of sputtering and photolithography. The various thin films of Cr/Au were sputtered. Layers of Cr/Au and photoresist serve as a masking material during etching of Pyrex glass in aqueous HF.

Keywords - wet etching, Pyrex glass, masking layer, Cr, Au.

I. INTRODUCTION

One of the most commonly used materials, besides silicon, in fabrication of various sensors and actuators besides is Pyrex glass. Pyrex glass is used as a structural material of MEMS sensors and actuators, because it forms almost unseparable compound with silicon during anodic bonding. The thermal coefficient of expansion of Pyrex glass has close value to the value of a thermal expansion coefficient of silicon, it is transparent in a wide wavelength range, has good chemical stability and biocompatibility [1], it is an excellent electrical insulator. Because of these characteristics Pyrex glass has an increasing use in development of biochips, RF-MEMS devices as well as in fabrication of sensors and actuators.

Mechanical treatment (drilling), dry and wet chemical etching [2] are the most common processes which are currently used for micromachining of glass. Isotropic wet chemical etching in aqueous HF is relatively simple and inexpensive process. Wet chemical etching in aqueous HF is proved to be the best technological process because it has the highest etch rate of glass, and at the end of processing retain the best quality of surfaces and edges of three-dimensional Pyrex glass structures. Various masking materials are used in the wet chemical etching of Pyrex glass: photoresist, layer of Cr/Au, multiple layers of Cr/Au, layer of LPCVD polycrystalline silicon, sputter amorphous silicon [1]. In this paper we developed a technique where layers of Cr/Au and photoresist are used as a masking material during etching of Pyrex glass in aqueous HF.

II. EXPERIMENT

Experiments with glass etching were performed on 1″× 2″ Pyrex glass, thickness of 1.7 mm. We used a test mask which had a number of standard test structures, Fig. 1. In the corners of the mask were four squares which had been designed for measuring the depth of etching on the comparator. Dimensions of mask are 18.5 mm × 18.5 mm.

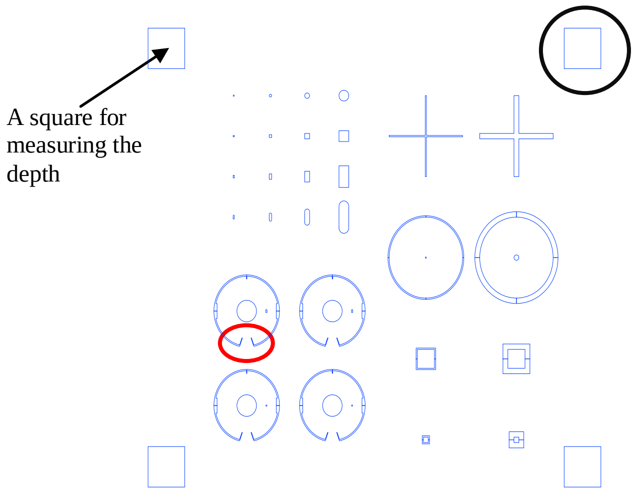

Fig. 1. Test mask with test structures for etching of a Pyrex glass.

In the experiment, on the glass were sputtered layers of Cr/Au, and after sputtering photoresists, Microchemicals$^{®}$ AZ1505 and AZ1518, were applied. Samples were etched in an aqueous solution of 49% HF at room temperature with a masking layer of Cr/Au and photoresist. Gold is inert in the solution for etching. Layer of chromium was used as a sublayer which increases the adhesion of gold to the glass. Photoresists also has the role of masks, but in a very short period of etching time. Hard baking the photoresists at the

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Žarko Lazić – Institute of Chemistry, Technology and Metallurgy-Center for microelectronic technology and single crystals, Njegoševa 12, 11000 Beograd, Srbija (e-mail: zlazic@nanosys.ihtm.bg.ac.rs).

Milče M. Smiljanić – Institute of Chemistry, Technology and MetallurgyCenter for microelectronic technology and single crystals, Njegoševa 12, 11000 Beograd, Srbija(e-mail: smilce@nanosys.ihtm.bg.ac.rs).

Milena Rašljić – Institute of Chemistry, Technology and Metallurgy-Center for microelectronic technology and single crystals, Njegoševa 12, 11000 Beograd, Srbija (e-mail: milena@nanosys.ihtm.bg.ac.rs).

Ivana Mladenović – Institute of Chemistry, Technology and Metallurgy-Center for microelectronic technology and single crystals, Njegoševa 12, 11000 Beograd, Srbija (e-mail: ivana@nanosys.ihtm.bg.ac.rs).

Katarina Radulović – Institute of Chemistry, Technology and Metallurgy-Center for microelectronic technology and single crystals, Njegoševa 12, 11000 Beograd, Srbija (e-mail: kacar@nanosys.ihtm.bg.ac.rs).

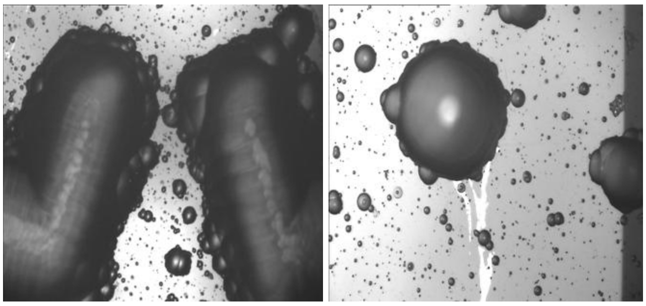
Milija Sarajlić – Institute of Chemistry, Technology and Metallurgy-Center for microelectronic technology and single crystals,Njegoševa 12, 11000 Beograd, Srbija (e-mail: milijas@nanosys.ihtm.bg.ac.rs).

Dana Vasiljević Radović – Institute of Chemistry, Technology and Metallurgy-Center for microelectronic technology and single crystals, Njegoševa 12, 11000 Beograd, Srbija (e-mail: dana@nanosys.ihtm.bg.ac.rs).

appropriate temperatures the good hydrophobicity was obtained. Better hydrophobicity prevented the diffusion of an aqueous solution of HF through cracks in the masking layer of Au, which was on the other side hydrophilic [3].

III. RESULTS

The first samples were etched with one masking layer of Cr/Au, thickness of 10/200 nm. Gold was sputtered in Perkin Elmer 2400, for 5 min with pause of 10 min in four cycles of 5/10 min (sputtered around 50 nm in one cycle). Photolithography process was made with standard procedure: (~~s~~oftbake) 5 min at 100°C after applying photoresist AZ1505 (nominal thickness 0.5 µm) on a spinner and (hardbake) for 30 min at 100°C after development of the photoresist. Then Pyrex glass was etched in concentrated HF (49%). Measured etch rate was about ≈ 7 µm / min. As shown on Fig. 2, a large number of defects are uniformly distributed over the substrate: larger defects have dimensions between 50 - 150 µm, and smaller one about 10 µm.



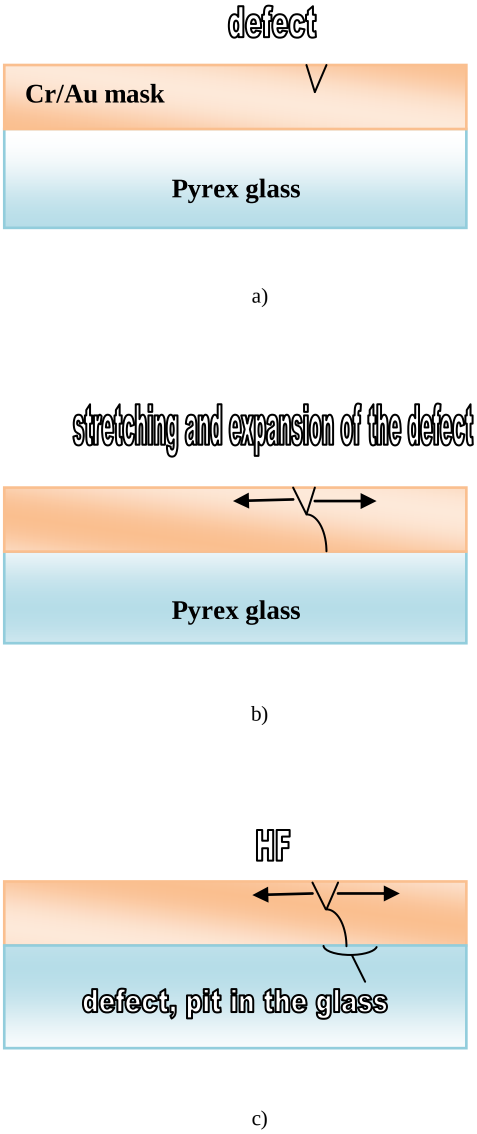
a) b)

Fig. 2. a) The depth of etching is 150 µm. Mask Cr/ Au (10/200 nm), standard photolithography process with photoresist AZ1505/0.5 µm (softbake 5 min 100 ° C, hardbake 30min 100°C). Red marked detail in Fig. 1; b) enlarged defect diameter ≈ 150 µm.

Larger defects were probably the result of dust particles or bubbles of air or N2 in the photoresist. Air bubbles were formed during the refilling photoresist from the original bottle to work bottle or when photoresist was taken with pipette for applying on substrate. The bubbles were formed by thermal decomposition of nitrogen compounds in photoactive photoresist (DNQ-DiazoNaphtho-Quinone-sulphonate) [4]. On the places where these defects occurred, during the etching of gold, under the photoresist, were formed holes in gold and chromium. Through these defects HF quickly diffuses and starts etching glass. Smaller defects are probably the result of defects in gold, as well as from micro-cracks that formed during cooling of sputtered layer of gold due to the presence of embedded mechanical stress. It takes some time for HF to go through the defects and therefore their dimensions were significantly smaller (~ 10 µm).

The mechanism of the formation of these smaller defects is shown in Fig. 3. [5]. In order to reduce the number of these defects, gold was sputtered in several layers, and between each layer was made a break at least 30 min, in order to cool the layer [4]. Due to the built-in mechanical stress in gold, which is always present, and positive (tensile stresses) in each layer there will be always some defects, but because of the low probability that they coincide in two or more layers, the total number will be lower.

More experiments were carried out with different thicknesses of layers of Cr and Au, and the double and inserted photolithography process. Double photolithography process (applying two layers of photoresist) on a single layer of Cr/Au or two layers of Cr/Au (which were sputtered one after the other) were needed to reduce the influence of impurities in photoresist that affect ~~on~~ the quality of the etched surface of the Pyrex glass. As in the case of two layers of Cr/Au, it was assumed that there was little probability that position of defects from impurities match when using two layers of photoresist.

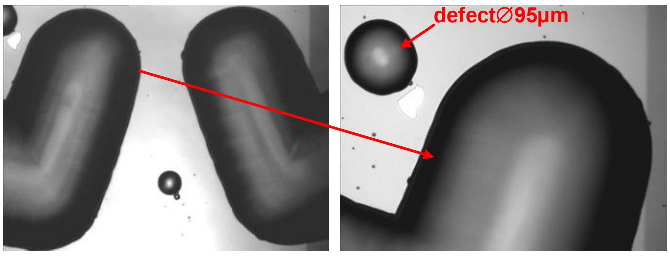


a)

b)

c)

Fig. 3. The mechanism of defects formations (pit) in the glass: a) defects in gold; b) due to the built-in stress in a layer of gold, at the place of the defect micro-cracks are formed; c) HF diffuse through the gap and form a defect in the glass.



a) b)

Fig. 4. a) The depth of etching is 150 µm. Mask Cr/ Au / Cr /Au (60/750/60/650 nm), double hardbaked photolithography process. The first photolithography process was done with crosslinking (softbake 5 min 100 ° C, hardbake 30 minutes 145 ° C); the second photolithography process was standard process (softbake 5 min 100 ° C, hardbake 30 min 100 ° C); b) enlarged detail of a). A defect in the glass is ∅ 95 µm.

Photoresists AZ1518 and AZ1505, can be treated to a temperature of about 160°C for different purposes. The softening point of these photoresist is above 100°C - 110°C. In that point a phtoresist starts to "flow" (the top of patterns edge of the photoresist tends to round) [4]. This does not affect the contact photoresist-substrate, and the width of the pattern. For temperatures above 140°C complete crosslink of photoresist is achieved.

It was noted that crosslinked photoresist (hardbaked on the temperature above 145°C) was hard to be removed after the etching, Fig. 4. For this reason, we did an experiment with hardbake of the first photoresist at 120°C for 30 min to avoid its crosslinking. The substrate was with a double layer of Cr/Au/Cr/Au (60/750/60/650 nm). In the next photolithography process, a second layer of photoresist AZ1505 (standard hardbake on 100°C for 30 min) was applied over the patterns from the first photolithography process. Patterns were not dissolved in a solvent of other photoresist. It was noticed that after etching edges of the patterns were a bit uneven and appearance of somewhat larger number of small defects. Considering the thickness of the gold (1.4 µm) it could be expected, Fig. 5. Edges in the previous version, Fig. 4. were better because of the better adhesion of crosslinked photoresist.

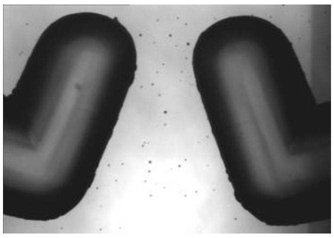
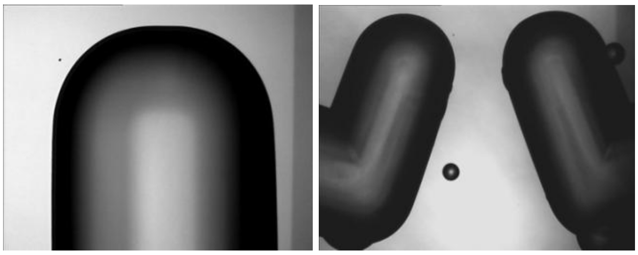


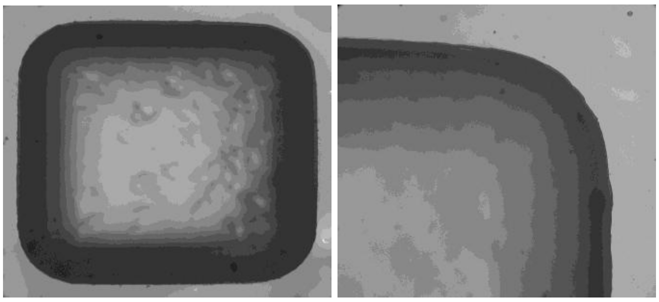
Fig. 5 The depth of etching is 130 µm. Mask Cr /Au /Cr /Au (60/750/60/650 nm), double baked photolithography process. First process was done without crosslinking (softbake 5 min 100°C, hardbake 30 min 120 ° C); the second photolithography process was standard process (softbake 5 min 100°C, hardbake 30 min 100 ° C).



a) b)

Fig. 6 a) The depth of etching is 125 µm. Mask Cr/Au/Cr/Au (60/650/60/800 nm) with inserted photolithography process The first photolithography process was standard process (softbake 5 min 100 ° C, hardbake 30 min 100 ° C); the second photolithography process was also standard process (softbake 5 min 100 ° C, hardbake 30 min 100 ° C). b) enlarged detail of a).

The inserted photolithography process was done after applying AZ1505 on the first layer of Cr/Au. The second photoresist AZ1505 was applied after the second masking layer of Cr/Au was sputtered. This technique reduces the probability of defects appearance in gold, which were formed in the first photolithography process, to coincide with defects that were formed in the second photolithography process. It was shown that this technique gives the best edges and the surfaces of three-dimensional structures of Pyrex glass, Fig. 6. This technique is complicated because of masking layer preparation and it takes too much time than the previous two techniques. It was necessary to take out samples from the sputter equipment to perform the first photolithography process.



a) b)

Fig. 7 a) The depth of etching is 320 µm. Mask Cr /Au (50/1000 nm) with two layers of photoresist. After development photoresist was treated at temperature of 130°C for 30 min .b) enlarged detail of a)

Another technique of the process was performed with a single masking layer of Cr/Au (50/1000 nm), but we used photoresist AZ1518 (nominal thickness 1.8 µm). Photolithography process was done with two layers of photoresist AZ1518. The first layer of photoresist is treated at a temperature of 100°C, for 15 min. Immediately, after softbake the second layer of photoresist was spinned and treated at the same temperature, but for 30 min. The aim of applying double photoresist is to reduce the number of defects, as discussed in previous experiments. The resulting thickness of double photoresist was 3.6 microns. A pattern on substrate was developed, but the treatment of the two-layer photoresist after development was different than for the standard process. In this experiment, the photoresist was treated at a temperature of 130°C. At this temperature photoresist partially crosslink and has a good hydrophobicity which prevents a large number of defects [3]. After etching the sample, in 49 % aqueous solution of HF (for 50 min), the sample was etched to a depth of 320 microns, Fig. 7. The same mask was used as for the previous experiments, Fig. 1. and a pattern which is shown on Fig. 7. is on Fig. 1. marked by black circle. Result of this experiment was good quality edges and smoother surfaces under the masking layer. But, on the bottom of the etched structure we can see a new effect, which can be explained as deposition of insoluble salts during the etching of Pyrex glass in aqueous HF [6].

IV. CONCLUSION

A technique with a sputtered layer of Cr/Au thickness of 50/1000 nm and with two layers of photoresist AZ1518 treated on a temperature of 130°C gives the best edges and the surfaces of three-dimensional structures of Pyrex glass, for the larger etching depth. However, for the shallow etching best edges and surfaces under the masking layer gives the technique with inserted photolithography process between two layers of Cr/Au. This technique has complicated preparation of masking layers compared to other techniques. Depending on requirements for the quality of the edges and surfaces of three-dimensional structures of Pyrex glass and the time required for masking layer preparation we will use one of these two techniques.

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REFERENCES

[1] C. Iliescu, B. Chen, J. Miao, ″On the wet etching of Pyrex glass″, Sensors and Actuators A 143 (2008) 154–161.

[2] M. Bu, T. Melvin, G.J. Ensell, J. S. Wilkinson, A. G. R Evans, ″A new masking technology for deep glass etching and its microfluidic application″ Sensors and Actuators A 115 (2004) 476-482.

[3] JY Jin, S Yoo, JS Bae, YK Kim, ″Deep wet etching of borosilicate glass and fused silica with dehydrated AZ4330 and Cr/Au mask″, J. Micromech. Microeng. 24 (2014).

[4] Microchemicals GmbH, ″Photolithography: Theory and Application of Photoresists, Etchants and Solvents″ (2012)

[5] C. Iliescu, J. Miao, F. E. H. Tay, ″Stress control in masking layers for deep wet micromachining of Pyrex glass″, Sensors and Actuators A 117 (2005) 286–292.

[6] C. Iliescu, J. Jing, F. E. H. Tay, J. Miao, T. Sun, ″ haracterization of masking layers for deep wet etching of glass in an improved HF/HCL solution″, Surface and oatings ehnology 198 (2005) 314 – 318