# Fabrication of Microstructures Using Aluminum Anodization Techniques

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## ABSTRACT

A promising technique for the fabrication of high-aspect-ratio microstructures, presented by Tan et. al. at MEMS-95, takes advantage of the highly ordered pore structure of anodic metal oxides. In this work, we have extended and simplified this method. This process is capable of producing high-aspect-ratio microstructures oriented normal to a nonplanar substrate.

Unlike the original process in which the aluminum substrate was anodized to the desired depth, masked and subsequently etched, the modified process involves performing the masking lithography prior to anodization. Patterned areas of an aluminum substrate are masked with a 0.6 $\mu$m layer of sputtered silicon dioxide. The $SiO_2$ layer prevents anodization in masked areas while the oxide grows in unmasked areas.

In this paper, we present preliminary results using this local anodization process on aluminum substrates and discuss the use of the process for fabricating structures on nonplanar substrates.

## 1. INTRODUCTION

High-aspect-ratio microstructures can be produced using a variety of techniques, including the reactive ion etching process [1], LIGA [2] and spatial forming processes [3]. The resulting structures are usually produced on planar substrates. Most technologies for MEMS fabrication on nonplanar substrates result in microstructures aligned to the axis of mask illumination. There are many applications where this constraint is too limiting. For example, biomedical devices operating in the vascular system need to be cylindrically symmetric to conform to the shape of blood vessels. Standard lithographic pattern transfer techniques, even on nonplanar substrates, cannot produce microstructures with this shape.

We have developed a local anodization process which is useful for fabricating high-aspect-ratio microstructures on nonplanar substrates. The technique is an extension of the anodic oxide method developed by Tan [4]. Anodic alumina has also been used to fabricate microfilters [5] and one-dimensional microhole arrays [6].

## 2. MASKED ANODIZATION PROCESS

The anodization of aluminum results in the generation of a hexagonal structure of porous aluminum oxide. The pores are in a regular array, 40 to 600 nm apart. Because they are formed by the electrochemical dissolution of the oxide during the anodization process, they are always oriented normal to the metal surface. There is also a very slow lateral etching process which occurs inside the pores. This phenomenon can be used to enlarge the pores, independently of their spacing.

A method for fabricating high-aspect-ratio microstructures from anodic oxides [4] is illustrated in Figure 1. Here, the idea is to laterally etch the alumina after patterning with a layer of chromium. The anodic oxide etches laterally due to efficient mass transport of the etchant, resulting in near-vertical sidewalls. A disadvantage of this method is that mask adhesion to the alumina can be difficult to achieve, which results in lifting and poor sidewall quality.

Our alternate process is shown in Figure 2. The aluminum substrate is covered with a thin film of $SiO_2$ which is lithographically patterned prior to the anodization process.

Because aluminum is considerably more reactive than alumina, mask adhesion is vastly improved. The $SiO_2$ acts to prevent anodization, but the field regions are exposed to the electrolyte and are anodized normally. For moderately thick alumina films, mask encroachment is minimal, resulting in near-vertical interfaces. After stripping of the alumina and masking $SiO_2$, the aluminum microstructures are formed.

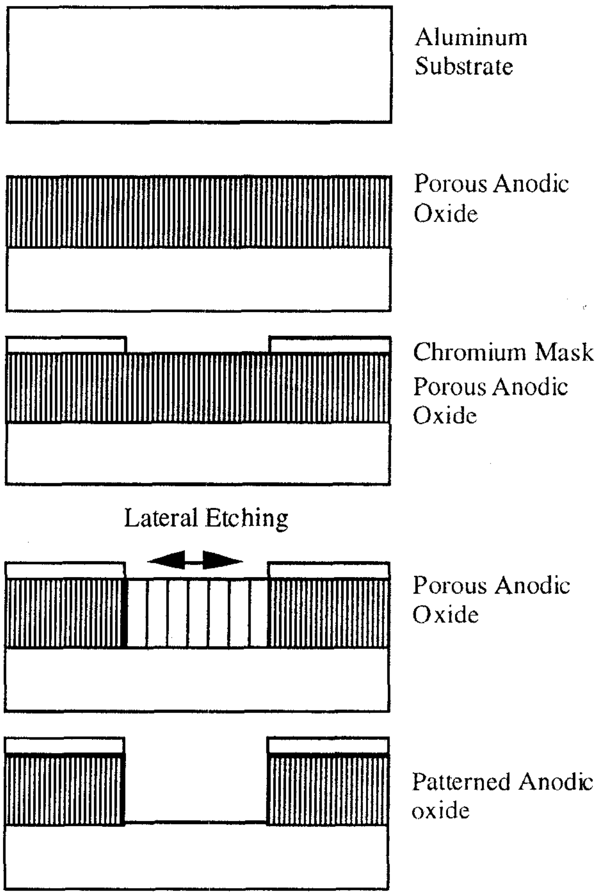

Figure 1: High-aspect-ratio microstructure process developed by Tan et. al. [4]. An aluminum substrate is anodized, masked and etched to produce alumina patterns.

In our experiments, we used 99.99% aluminum substrates, 1 mm thick, obtained from ALFA-AESAR. The substrates were degreased in boiling trichloroethane, acetone and 2-propanol. The samples were then chemically polished in an Aupol-V bath [7] (340 ml 85 wt. % $H_3PO_4$, 90 ml 98% $H_2SO_4$, 20 ml 100% $HNO_3$) and then electropolished in a Battelle type of bath [7] (130 ml deionized $H_2O$, 40g $CrO_3$, 260 ml 85% $H_3PO_4$, 40 ml 98% $H_2SO_4$). The resulting substrates were mirror-like and had a rms roughness on the order of 40 nm.

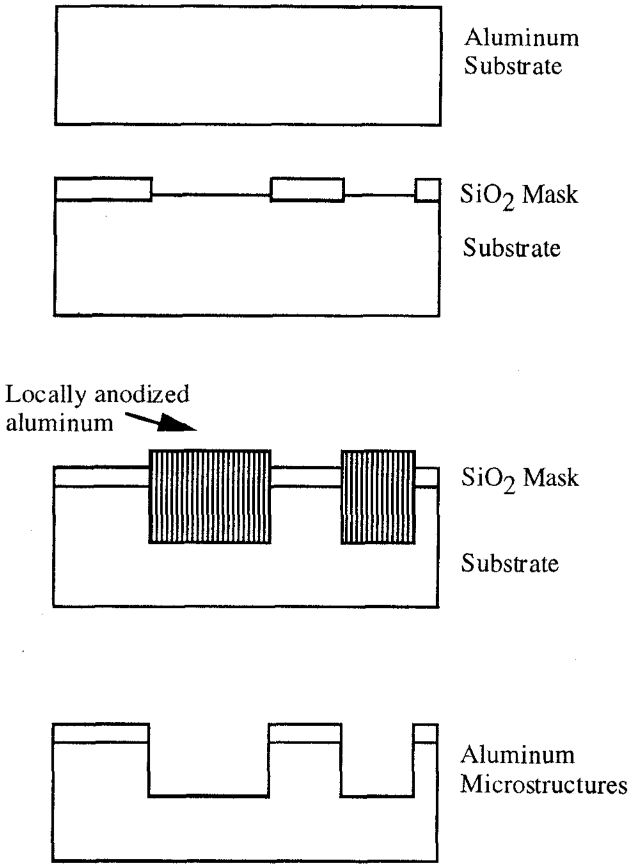

Figure 2: In the present process, an aluminum substrate is masked, anodized and etched to produce aluminum patterns.

A 600 nm layer of $SiO_2$ was sputter coated on each of the substrates and patterned using positive AZ P4110 photoresist. Silicon dioxide was chosen as the masking material due to its adhesion to aluminum and unreactivity with sulfuric acid (the electrolyte). The resist was exposed for 1.5 minutes at 8 $W/cm^2$. The substrates were then developed and carefully etched in buffered hydrofluoric acid to pattern the silicon dioxide mask.

The patterned substrate was then anodized in 10% sulfuric acid for 45 minutes at a temperature of 8 $^{o}C$ and a voltage of 22 volts. These conditions resulted in an alumina layer of 33.4 $\mu m$. The anodic oxide was stripped in 5% sulfuric acid for 55 minutes.

## 4. RESULTS AND DISCUSSION

Figure 3 is an example of one of the structures produced just after anodization of the substrate. The $SiO_2$ mask adheres well to the aluminum, except in a narrow region immediately adjacent to the edge where some lifting and cracking is apparent. This is due to the volumetric expansion which occurs during anodization; we observe approximately 3 μm of anodic oxide for every 2 μm of consumed aluminum.

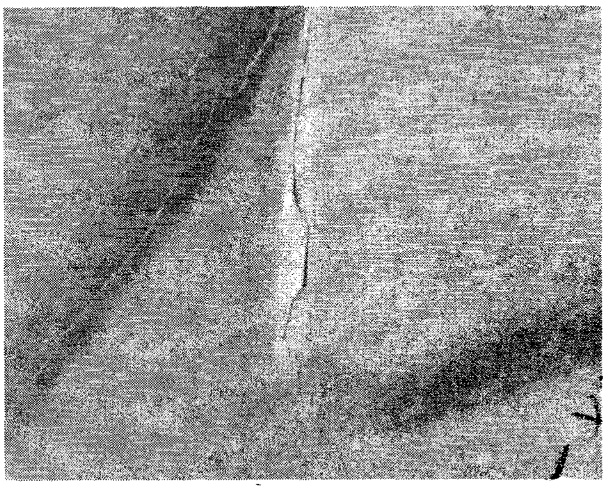

Figure 3: Top-down view of the substrate after anodization but before anodic oxide stripping.

Figure 4: Aluminum microstructure after stripping of anodic oxide. Note the quality of the bottom surface.

After stripping the anodic oxide, the microstructure appears as shown in Figure 4. In this figure, the masking oxide has not yet been stripped; it appears visible as a thin overhang around the periphery of the aluminum microstructure. The sidewall quality, and the smoothness of the bottom aluminum surface are both very good (Figure 5).

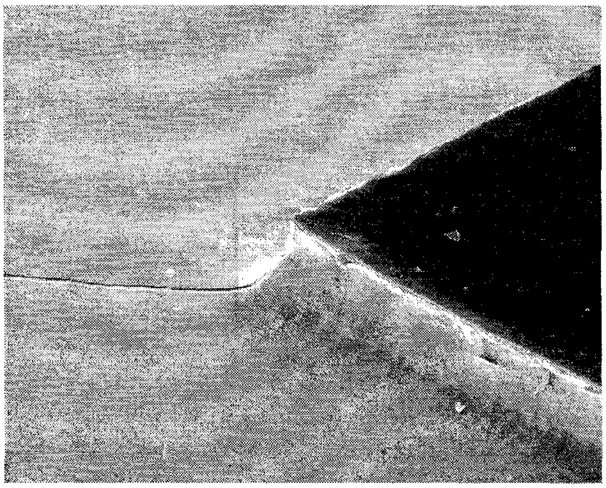

Figure 5: Close-up view of tip in figure 4 showing the side-walls that are smooth and vertical.

The structures produced above are perpendicular to the substrate - in the direction of the electric field lines during anodization. Micrographs of structures patterned along the sides of milled grooves [9] confirm that this process produces uniformly high microstructures oriented normal to the nonplanar surface.

One aspect of the process is the volume expansion associated with the growth of the anodic oxide. For films greater than approximately 30 μm, stress concentrations in the anodic oxide are sufficiently high to cause cracking. This effect is visible in Figure 5, where a stress fracture has resulted in a slight furrow in the aluminum surface after the anodic oxide is stripped.

## 6. CONCLUSIONS

A local anodization technique to fabricate high-aspect-ratio microstructures on metal substrates has been developed. Biomedical applications of this process currently under development include the design and fabrication of a cylindrical stent for intravascular drug and gene delivery [8] and fabrication of molds and templates for manufacturing microminiature polymer fasteners for joining tissues.

## 7. ACKNOWLEDGMENTS

One of the authors (A.N.) was supported by a graduate fellowship in bioengineering at the University of Pittsburgh Medical Center. Special thanks to Dr. Tom Nufer of the CMU Materials Science and Engineering Department.

# REFERENCES

[1] H. Jensen, M.D. Boer, B. Otter and M. Elwenspoek, "The Black Silicon Method IV: The Fabrication of Three Dimensional Structures in Silicon With High Aspect Ratios For Scanning Probe Microscopy and Other Applications", Proc. MEMS 95, pp. 88-93, 1995.

[2] E. Becker, "Fabrication of microstructures with high aspect ratios and great structural heights by synchrotron radiation lithography, galvanoforming, and plastic moulding (LIGA process)", Microelectronic Eng., pp. 35-36, 1986.

[3] C. Taylor, "Spatial Forming: a Three Dimensional Printing Process", Proc. MEMS 95, pp. 203-208, 1995.

[4] S. Tan, M. Reed, H. Han and R. Boudreau, "High Aspect Ratio Microstructures on Porous Aluminum Oxide", Proc. MEMS 95, pp. 267-272, 1995.

[5] H. Masuda, "Preparation of Microporous Metal Membranes by Two-step replication of the Microstructure of Anodic Alumina", Thin Solid Films, pp. 1-3, 1993.

[6] H. Masuda, "Fabrication of a One-dimensional Microhole Array by Anodic Oxidation of Aluminum", Appl. Phys. Letters, pp. 3155-3157, 1993.

[7] P. Dettner, "Electrolytic and Chemical Polishing of Metals", Ordentich Publishers, Tel Aviv, 1987.

[8] J. R. Kneller, C. C. Wu, S. Watkins, A. Nadeem, M. Reed, L. Weiss, M. D. Feldman, "Microfabricated Device for Arterial Wall and Atherosclerotic Plaque Penetration", Proceedings of the IEEE Engineering in Medicine and Biology Conference, Chicago, 1997.

[9] A. Nadeem, M. Mescher, K. Rebello, L. E. Weiss, C. Wu, M. Feldman and M. L. Reed, submitted to Applied Physics Letters, 1997.