Development of Porous Silicon Microfilters

Jenna Campbell

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Faculty Advisor: Dr. J. L. Gole

Second Reader: Dr. E. Conrad

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Abstract:

This study develops a one-step anodization separation process (OSS) after examining two step and multi step liftoff procedures in which porous silicon (PS) films lift off from their substrates. This lift-off process provides a means to produce silicon filters, a worthy alternative to alumina filters that cannot withstand high temperatures as well as silicon and whose pore diameter has yet to reach into the order of microns. By electrochemical etching of p-type silicon wafers in a hydrofluoric acid-based solution, microporous filters with pore diameters varying from 1 to 2 microns whose depths range from 3 to 70 micrometers are fabricated. Using wafers with a resistivity of 14-22 Ω-cm, mobile filters with consistent structural qualities can be reproduced.

Introduction:

This project involves utilizing known etching techniques in an attempt to develop microporous filters using a single step "liftoff etch." These microporous filters can ultimately be integrated into gas sensors if they exhibit similar properties to porous silicon left on the substrate, or they can be used to filtrate large proteins. The goal of the liftoff etch is to create a solid porous structure and then have the top layer of porous silicon float off from the wafer. The desired product is a thin, mobile layer of microporous silicon. While much effort has been put forth by several research groups, there has not been much progress on the development of these films. Films that have been successfully produced have generally been nanoporous.[1-3] The nanostructures created are not particularly useful. The films are very fragile and extremely hard to handle. Since the diameters of the pores are only on the order of nanometers, their ability

to be used as filters in ultrafiltration is limited compared to filters made up of pores on the order of micrometers.

One Step, Two Step, and Multi Step Liftoff Processes

Two popular lift-off approaches that currently exist are the one step process (OSS) and the two step process (TSS).[2] The one step anodization liftoff procedure is driven by the dissolution of fluorine ions as the pores grow deeper.[1,2,4,5] The dissolution of fluorine ions creates a high porosity layer below a less porous layer. The pores then expand to overlap one another until the PS breaks away from its substrate. The two step liftoff procedure will do the same by enlarging the bases of the pores to the point of separation.[1,3] In order to perform the TSS, a silicon wafer is etched at a constant current density to create long, straight pores, and then a dramatic boost in the current density expands the pores rapidly to create an electropolished layer that then allows the porous silicon to disconnect from the wafer. Some methods also include an annealing process to cleanly remove the PS layer from its substrate.[2]

The physical structure of the etch-generated pores is dependent upon many aspects of the experimental set up, including the chemical composition of the electrolyte and the properties of the wafers.[5-8] Across a single silicon wafer, the nucleation time can vary since the resistivity of the wafer can also fluctuate. Generally, it is difficult and rather expensive to obtain Si wafers that have a very narrow resistivity range (<3 Ω-cm). To create nearly identical pores and to be able to control precisely the formation of these pores, wafers with a narrow resistivity range must be obtained to accurately predict the time it takes for the pores to nucleate.[9] As a result, when applying the two step procedure to release PS from its substrate, the inconsistency of the wafer's resistivity leads to an

imperfect porous structure which causes the porous layer to flake off in small pieces. The immobility of filters made through using TSS approach makes handling the PS problematic and does not produce porous media which are particularly useful. If the electropolishing step, the second step in the TSS, runs too long, the less porous layer can be destroyed or eaten away by the intense current. However, if the second step does not run long enough, the pores will not all expand to overlap and separate from the substrate.

The idea of a multi step process (MSS) has been suggested. The MSS can be implemented by raising the current density in smaller increments to remove the porous layer more slowly. Hopefully, by taking smaller steps, the individual pores will be given more time to expand without having to undergo the harsh conditions of a high current density boost. Ideally, through the OSS, TSS or MSS, the effort considered in this proposal shall be carried out in hopes to fabricate a thick, mobile, microporous filter.

Experimental:

Experimental Set Up

Unless otherwise noted, the results discussed in this article develop from the use of p-type silicon wafers with a resistivity of 14-22 Ω cm (250-300 μm thick; 100 face orientation). To fabricate PS filters, pores are etched into the wafers at a constant current density delivered by an Agilent power supply (model 6634B) at room temperature with an etching region of either 1 cm^2 or 4 cm^2. The silicon wafers are soaked in a dilute hydrofluoric acid (HF) solution for several hours to remove surface oxidation, rinsed with methanol to wash away the remaining HF, and then placed in trichloroethylene for several minutes to remove organics that could be found on the wafer upon arrival. Placed

in an electrochemical cell with a platinum anode, the prepared silicon wafers etch in an electrolytic solution. The electrochemical cells are made of high density polyethylene (HDPE). A computer-controlled power supply utilizes the aluminum cathode and the platinum anode pictured in Figure 1 and 2 to run a constant current through the cell. A magnetic stir bar can also be placed in the electrochemical cells.

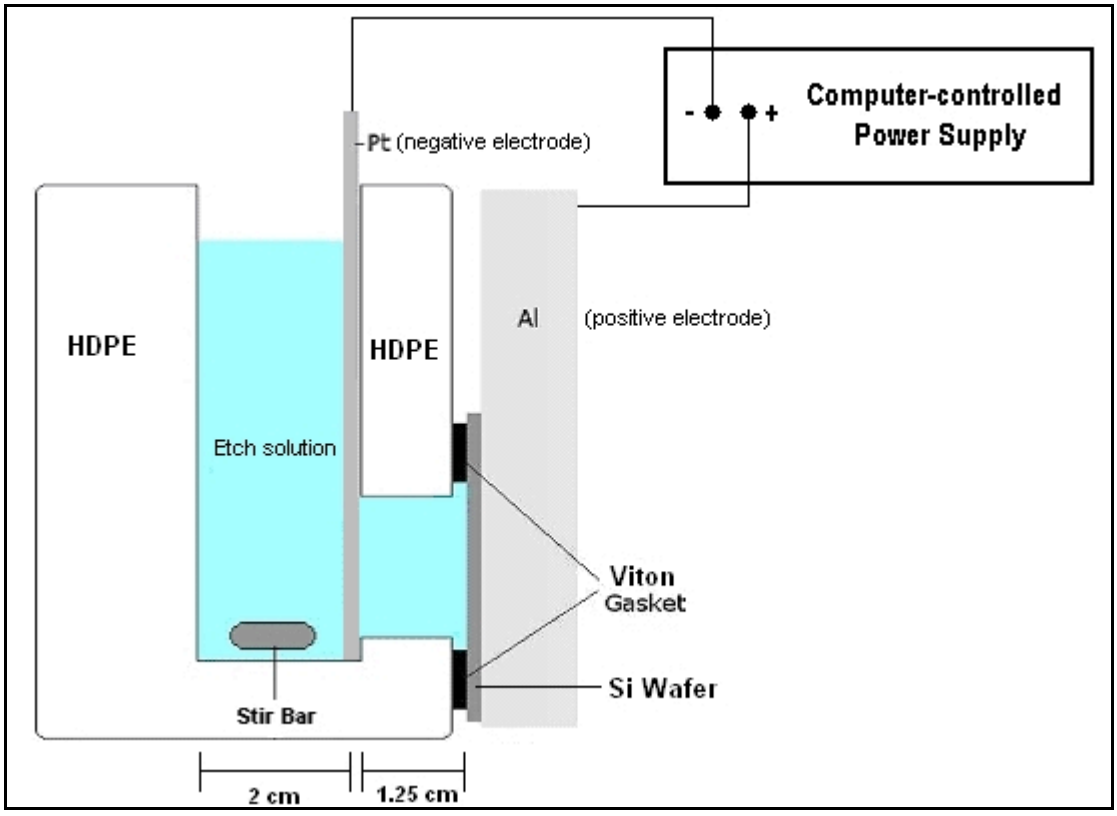

Figure 1: Cross section diagram of the larger etch cell (etches areas of 4 cm^2) with the electrode placed on in the closest position. The Pt electrode can be removed and be placed on the other side of the etch solution. Since the distance between the anode and the cathode directly effect the strength of the electric field inside the cell, the chosen concentration of HF is dependent on this distance.

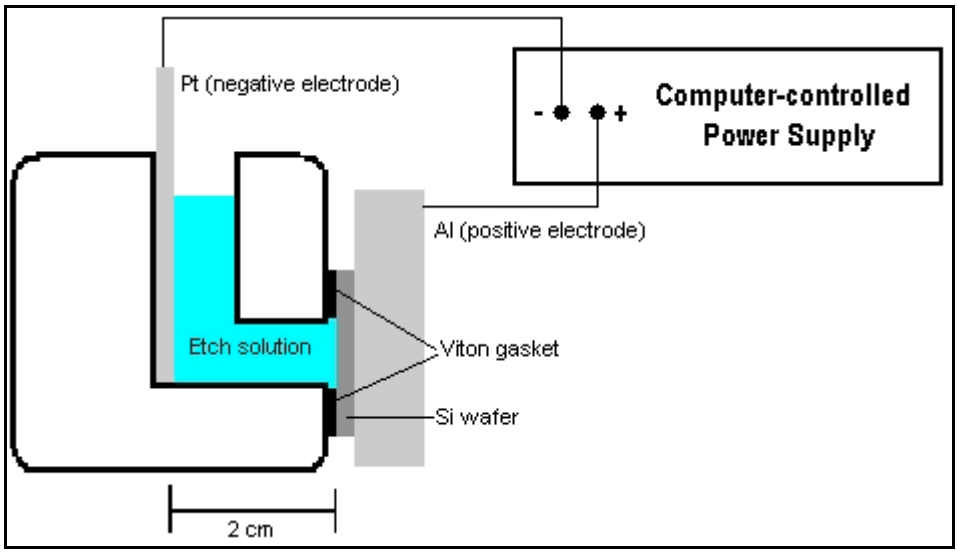

Figure 2: Cross section diagram o the smaller cell (etches areas of 1cm^2)

Two Step Process (TSS)

The two step etch process (TSS) was carried out successfully in both aqueous and organic etching solutions. The aqueous TSS filters are produced using a 49% HF and ethanol solution at a 1:1 or 1:2 ratio by volume concentration. Aqueous TSS filters are fabricated using p-type silicon wafers with a resistivity of 1-20 Ω cm (250-300 μm thick; 100 face orientation).The initial layer of the TSS filter that has a lower porosity is etched at room temperature with a current density ranging between 15 to 60 mA/cm^2 for anywhere between 45 minutes to one hour. These initial etching conditions create the main part of the porous filter. Boosting the current density after the initial step of this etching process will cause the bases of the pores to expand and overlap, thus causing the filter to separate from its substrate. This electropolishing liftoff step is carried out for three to seven minutes at current densities ranging from 280-600 mA/cm^2. All the parameters above can be tuned to create porous structures of different sizes.

The TSS is applied using an organic electrolyte solution to fabricate microporous filters with a depth of <10 μm. The TSS is carried out with the 14-22 Ω cm substrate following the experimental procedure outlined above. The Si is initially etched in the 49% HF/DMF solution for at least 5 minutes with a constant current density of 6 mA/cm^2. This time frame ensures that the pores have a sufficient time to nucleate [4]. With a 49 % HF/DMF solution (~3.2-6.3% volume concentrations of 49% HF) and a relatively low current density, SEM images produce evidence that allowing the silicon to etch for about five minutes is a sufficient amount of time for nucleation to occur and for consistent, well defined pores to form and begin to grow deeper. The initial etching time can be lengthened to increase the depth of the PS. A liftoff current of ~20 mA/cm^2 lasting 7 minutes in the same 49% HF/DMF solution is sufficient to remove the thin filter from its substrate. The PS can be rinsed with methanol immediately after etching to remove HF from the surface

Multi Step Process (MSS)

The MSS filters can also form in both organic and aqueous electrolytes. The aqueous etches are performed on the same wafers with a resistivity ranging from 1-20 Ω cm as described above. The electrolytic solution contains a 1:1 49% HF and ethanol concentration by volume. By observing many cross sectional images of MSS filters, the etch steps can be adjusted to produce a desired result. The aqueous etches produced in this study required anywhere from 3 to 11 steps, including the initial etch. The purpose of the initial etch is to form a strong porous base structure so, depending on the filter's ultimate goal, the "initial etch" can also be broken up into steps including steps that are analogous to the previously mentioned "electropolishing steps." These aqueous MSS

filters begin with an initial etch with current density ranging from 50-60 mA/cm^2. The following steps, which can be either evenly or unevenly spaced, gradually increase the current density to the 270-500 mA/cm^2 range which results in the separation of the PS filters.

Organic MSS filters utilize the 14-22 mA/cm^2 silicon wafers and an electrolytic solution composed of 49% HF and DMF at volumetric ratios ranging from 1:10 and 1:30 respectively. As mentioned previously, the MSS can consist of as many steps as one deems necessary. Since the organic electrolytic solutions generally etch with a considerably lower current density when compared to the aqueous solutions, the ultimate current needed for liftoff in an organic solution is also much lower. Thus, the MSS organic filters require fewer steps, (only three to four). The initial current density for the less porous region is 3 mA/cm^2 with the current density moving up in steps to a magnitude ranging from 10-12 mA/cm^2. The first step lasts for a period between 45 minutes to one hour while each additional step runs for several minutes.

One Step Process (OSS)

A one step anodization process has been developed using 14-22 Ω cm silicon wafers and an organic electrolytic solution composed of 49% HF and DMF. With ~3.2-9.1% volume concentrations of 49% HF, the porosity and depth of the filter can be tuned. The OSS can separate the filter from its substrate after running the anodization process for a period lasting between thirty minutes and one hour. Under these parameters, a silicon fluoride polymer ((Si_xF_y) Figure 3), determined by energy dispersive X-ray spectroscopy (EDS), is frequently formed between the silicon substrate and the lift-off filter in the form of a white foam.[10,11] A microporous silicon filter with a thickness

ranging from ~10 to 40 μm separates from the substrate. These OSS polymer samples along with the images of the filters were analyzed and examined by a Hitachi S-800 FE-SEM.

Removal of the Filters

Although a thin liftoff is not as visibly apparent as a thicker one, a razor blade can be used to remove these filters. Some PS filters may float off into the solution during the etching process; others may be easily removed immediately after the substrate is removed from the cell, but it is best to let the filter and the residual oxyflouride which is sometimes formed under the filter dry completely to obtain the largest liftoffs possible. Once dry, the region corresponding to a PS filter is effectively separated and can be lifted off easily with a razor blade.

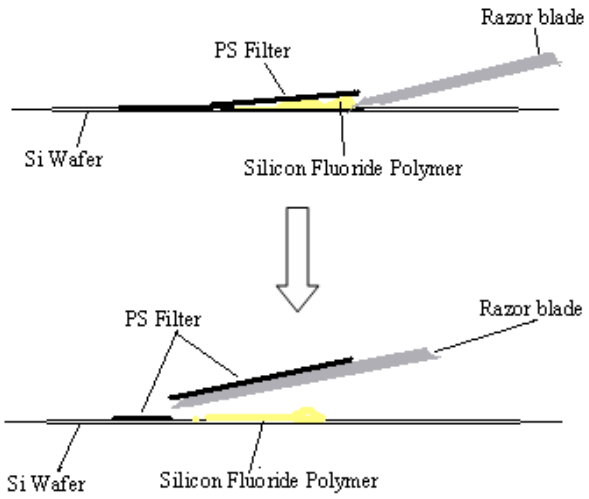

Figure 3: Schematic of the mechanical liftoff of the filter from its silicon substrate and the silicon fluoride polymer that often forms between the filter and the wafer. This method is also effective if the polymer does not form.

Results and Discussion:

Although certain parameters for the TSS, MSS, and OSS etching processes have resulted in successful lift-offs, the one step anodization process has proven to be the most efficient and practical method to produce large, microporous filters. Due to the diamond crystal structure of silicon, the tip, or base, of the pores etches downward in a pyramidal shape in the 100 direction (See Figure 5). This pyramidal tip structure and the sensitive nature of silicon's interaction to slight changes in its etching conditions are two crucial elements to the lift-off of microporous filters.

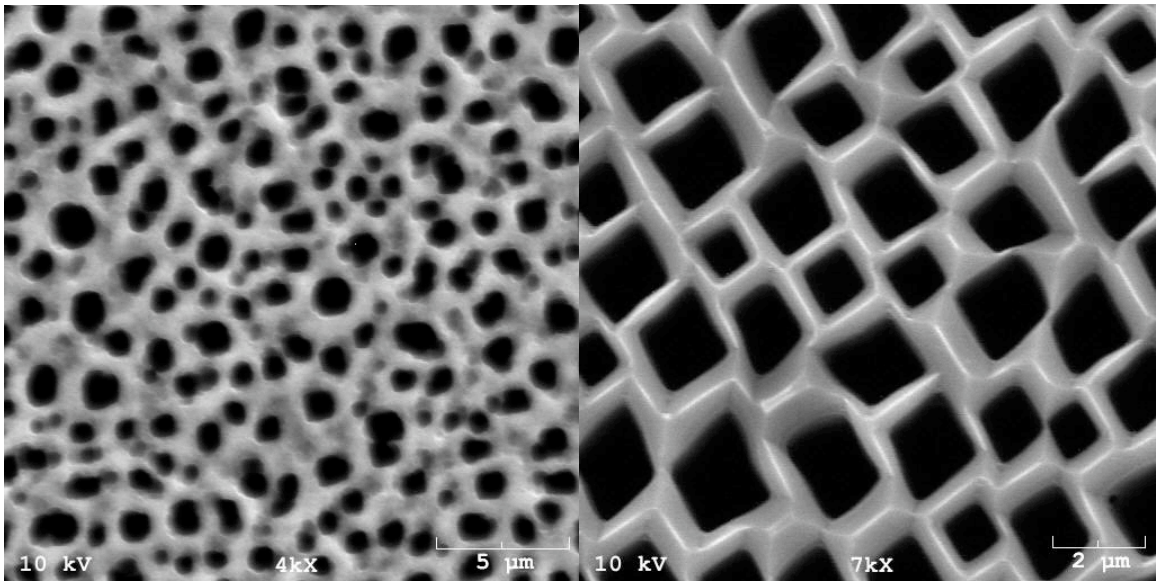

Figure 4: This is an image of the general porous structure of the microporous filters. An overhead view is taken of the filter (left). This is the part of the filter that is in contact with the electrolytic solution during the etch. The backside of the filter (right) illustrates the pore's pyramidal shape.

One Step Anodization Process

The one step anodization liftoff procedure, the most successful method in creating large, microporous filters, is driven by the dissolution of fluorine as the pores grow

deeper[1,2,4].(see Figure 5) Once the pores become deep enough so that the fluorine ions cannot reach the tip of the pore sufficiently, the pores begin to expand as the fluorine based dissolution can proceed laterally. The dissolution of fluorine ions creates a high porosity layer below a less porous layer. The pores then expand to overlap one another until the PS breaks away from its substrate. To ensure a lift-off and to expedite the dissolution of fluorine, we maintain a more stagnant electrolytic solution which allows the fluorine ions becoming sparser in a shorter period of time. Better results were thus obtained with etches done without a stir bar in the electrochemical cell. While successful liftoffs can be produced with a stir bar, those fabricated without a stir bar in the electrochemical cell proved to be larger liftoffs with a more consistent porous structure.

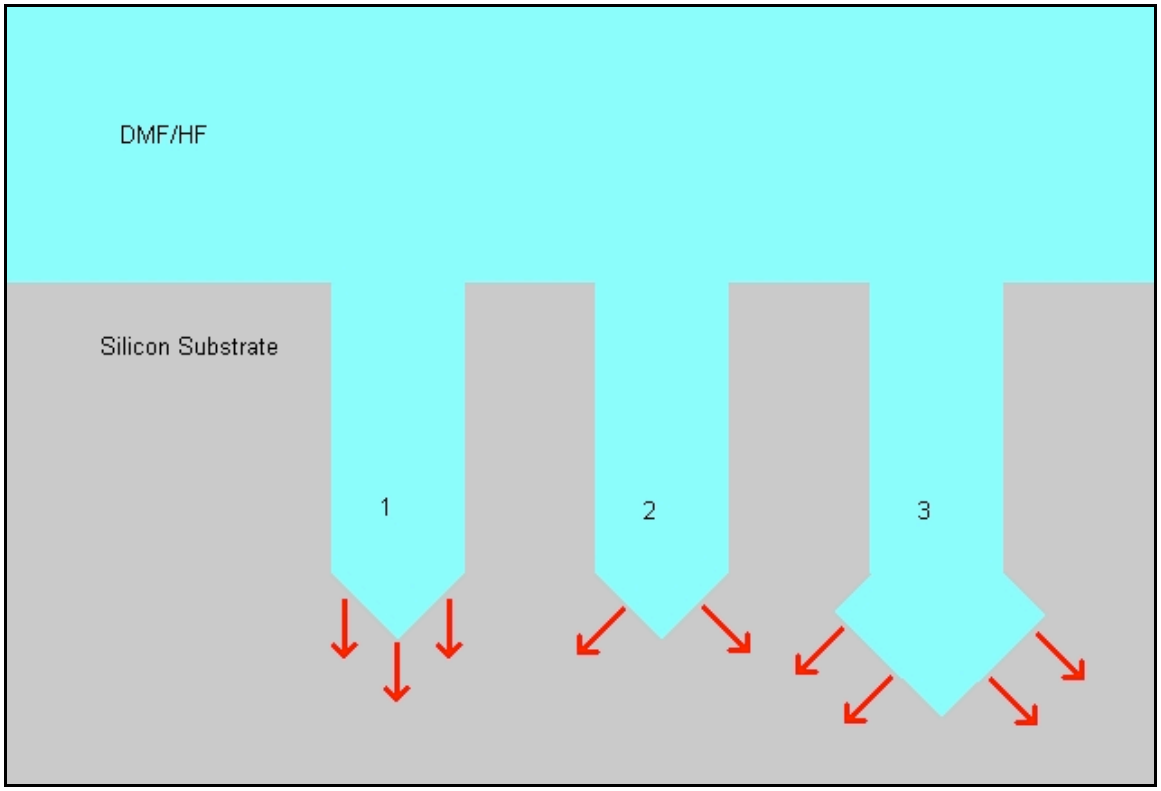

Figure 5: "Schematic representation of the filter separation process. During the initial phase of etching (1), the pore etches straight down in the <100> direction. When the process leading to lift-off begins (2), etching instead proceeds into the pyramidal faces of the pore tip, causing the pore tip to expand (3) until neighboring pores begin to overlap."[12]

Since the OSS is driven by fluorine dissolution as opposed to etching parameters that the MSS and TSS depend on, there are fewer factors that play a large role in the lift-off of the filter. For example, the resistivity of the silicon varies across the wafer. The resistivity greatly affects the results of the etch including the pore size, the speed of the etching of the silicon, and the effect that a change in current density has on the pore structure. Since the OSS does not strongly depend on the wafer's response to a change in current density to widen the pores, the resistivity of the wafer does not affect the OSS liftoffs as much. Instead of increasing the current density and risking the probability that useful portions of the etchant with a lower resistance are destroyed, the time of the etch can be lengthened to encourage the dissolution of the fluorine.

The OSS process is the only lift-off procedure where the silicon oxyfluoride polymer appears during the etch. The polymer develops on the etch in the form of a white foam that can dry after being set out for several hours. The white foam lies in between the separated filter and its substrate. We believe that the silicon oxyfluoride foam does not represent a primary mechanism leading to the liftoff, but that, its existence may assist in separating the PS from the wafer thus creating larger filters that are more easily removable. During some previous attempts to create PS filters, a common problem existed that prevented the filters from lifting off in large pieces. As the silicon etches, hydrogen formed in the pores must escape. This foam could present a means to remove the hydrogen gas that accumulates underneath the separated PS.[1] The silicon polymer seems to form under very particular conditions. Where it comes from and how it forms is still not completely known. The experimental set up consistently results in a filter atop the silicon polymer.

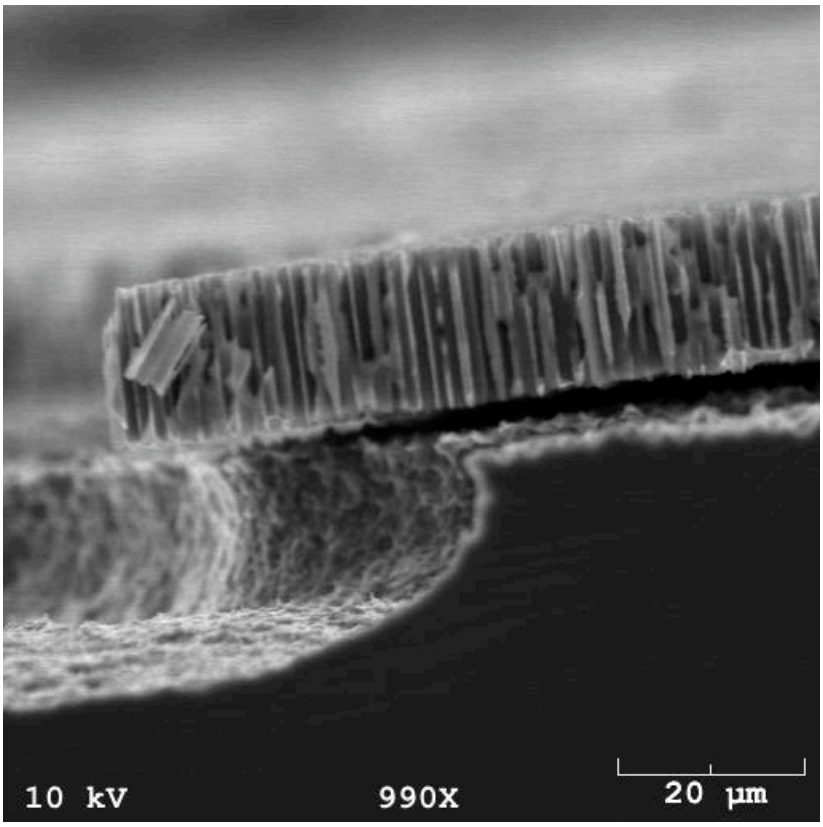

Figure 6: A PS microfilter created by the OSS

Two Step Process

As previously stated, the two step process is driven by a boost in the current density following the etch process to create an electropolished layer beneath the PS. Increasing the current density during the wet etch directly causes the diameter of the pores to grow larger. By boosting the current density dramatically, the bases of the pores expand to overlap (as seen in Figure 7). The resistivity of the wafer plays a major role in the end results of the etch, and affects the results of the filter. Since the resistivity of the silicon varies across the wafer, it is difficult to find a high enough current density that will allow most of the pore tips to grow and overlap without causing the intense current

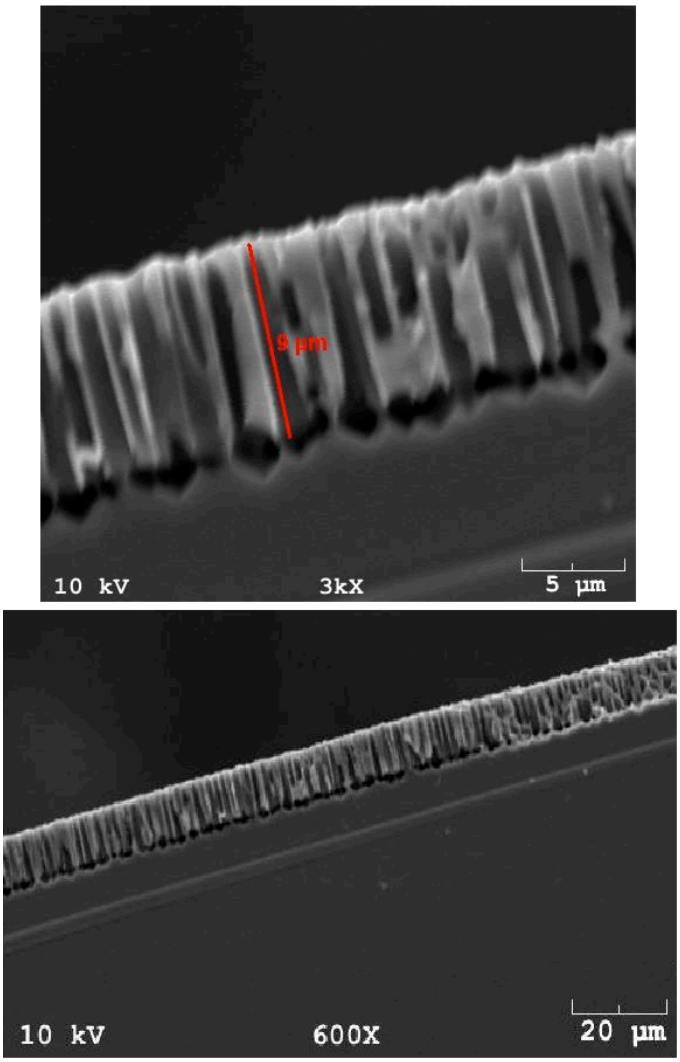

Figure 7: The top SEM micrograph shows the expansion of the bases of the pores that occurs during the electropolishing step. The bottom image shows a larger cross section of the porous silicon. Note that while some pores collide to separate from the silicon substrate, some remain in contact and prevent the filter from lifting off in large pieces

to damage those regions of the silicon with a lower resitivity. Figure 7 clearly illustrates the inability to create a result for which all the pore tips collide. Although certain parameters can lead to the success of a TSS lift-off, these changes generally result in small, immobile filters.

Multi-Step Procedure

The multi-step liftoff procedure and its results are similar to those of the TSS lift-off. The MSS, as with the TSS, enlarges the bases of the pores to the point of separation but does so in smaller steps. As indicated before, it is very difficult to get a majority of the pores to coalesce into one another simultaneously. Although the multi step procedure can release PS from its substrate, the porous layer generally flakes off in very small pieces, which makes handling the PS problematic and does not produce porous media which are particularly useful.

The right half of Figure 8 provides a clear illustration to the problems of the MSS. The image shows the different layers of porous silicon that come off as flakes due to the MSS etch. Three different structures are apparent in this image as are three different layers, or stages, of the PS. The porous structures on the far right of the image are PS microfilters that have separated from the substrate. The second layer that is a little darker from this separated film, and contains square-like pore structures, is located to the left of the filter and then again in small patches along the left side of the image. The areas that this second layer covers have already had a filter develop atop them and are now beginning to etch again. The rectangular shape of these new pores implies that the pores are newly formed. The third covers much of the left hand side of the image. This layer does not have an apparent pore structure because a microfilter has just lifted away from this area. The substrate is slightly damaged as a result of the liftoff and has not been exposed to etching condition long enough to commence etching once again.

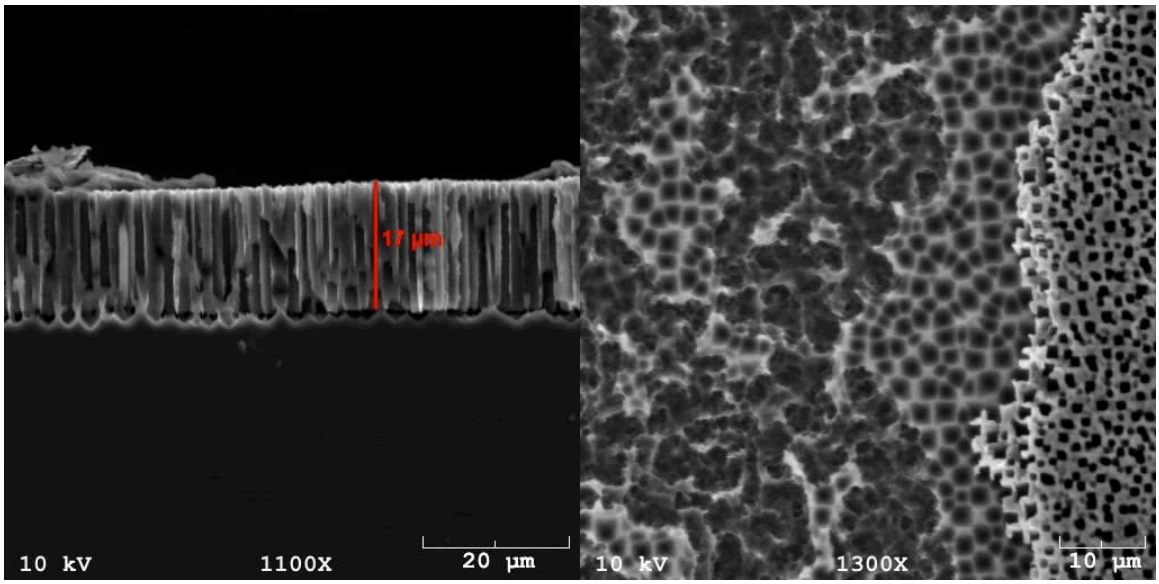

Figure 8: On the left, the bases of the pores can be seen expanding to create a 17µm filter. The overhead image (to the right) shows different layers of porous silicon.

As with the TSS, forming a large, mobile filter from the MSS is very difficult. This again demonstrates that the OSS is the most efficient process for creating PS microfilters.

Acknowledgements:

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