Wet and dry etching techniques for the release of sub-micrometre perforated membranes

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Abstract. For the production of microsieves we studied the release of perforated silicon nitride membranes from a silicon substrate. During the release by KOH etching the pressure build-up due to hydrogen gas formation can be quite large and cause rupture of the membrane. We explored the use of anisotropic etching with an SF_6/O_2 plasma to replace KOH etching. For sub-micrometre pores excellent results were obtained.

1. Introduction

Microsieves are a promising innovation in filtration technology. Silicon micromachining allows for the fabrication of microsieves with well defined pores of arbitrary shape, size and distribution [1, 2]. Figure 1 shows an example of a sieve with 0.5 μm pores.

The base material of a microsieve is a $\langle 100 \rangle$ oriented silicon wafer. This wafer is coated with a silicon-rich nitride layer (intrinsic stress 10^8 Pa [3]) by means of LPCVD (low-pressure chemical vapour deposition). This layer is perforated using photolithography and reactive-ion etching with a CHF_3/O_2 plasma. Finally, the silicon underneath the perforated layer is partially removed by anisotropic KOH etching to form a support.

This last step is crucial for the production of microsieves. If the silicon is etched from the back side with a KOH
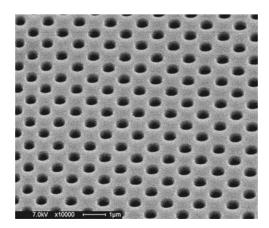

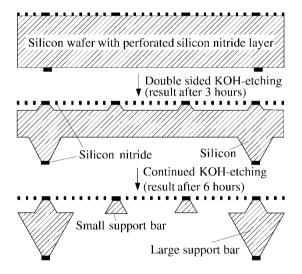**Figure 1.** Surface of a 0.8 μm thin microsieve with a 0.5 μm pore diameter.

Figure 2. Release of the perforated membrane by anisotropic KOH etching from both sides of the wafer.

solution, a substantial part of the membrane will not be released, due to the oblique {111} crystal planes in the $\langle 100 \rangle$ wafer. A much better result is obtained when the etching takes place from the backside as well as through the pores on the front side. An additional advantage of this method is the possibility to etch extra support bars underneath the membrane (see figure 2).

The hydrogen bubbles that arise from KOH etching (25%, 70 °C) cause a pressure build-up underneath the membrane. This pressure may cause rupture of the membrane. We investigated under what conditions KOH etching through the pores is still applicable and we explored the possibilities of dry etching to release the membrane.

2. Wet etching through the pores

During KOH etching hydrogen gas is formed. To push the liquid out of the pores, the gas has to overcome the capillary forces. The required pressure p_b for this is given by [4]

$$p_b = \frac{4\gamma \cos\theta}{d} \qquad (1)$$

where γ is the surface tension of the KOH solution, θ the liquid–solid contact angle and d the diameter of the pores. After the hydrogen gas has pushed the liquid out of a pore it will form a bubble on top of this pore. When the contact angle of the bubble with the pore wall becomes $0°$, the gas pressure reaches a maximum value. For our KOH solution with an estimated value for γ of 0.075 N m^{-1} [5], equation (1) then reduces to

$$p_b = \frac{0.30}{d}. \qquad (2)$$

The bubble-point pressure increases for smaller pores. If the pore size is below a certain value, the gas can break the membrane. The maximum pressure p_{max} that an unperforated membrane can stand can be calculated [6]:

$$p_{max} = 0.58\frac{h\sigma_{yield}^{3/2}}{lE^{1/2}} \qquad (3)$$

where h is the thickness of the membrane, σ_{yield} is the yield stress, l is the distance between the silicon support bars and E is Young's modulus. Insertion of some typical values for an unperforated low-stress silicon nitride membrane into (3) ($h = 1.0$ μm, $l = 200$ μm, $\sigma_{yield} = 4.0 \times 10^9$ MPa and $E = 2.9 \times 10^{11}$ Pa) leads to a calculated maximum pressure of 14 bar. Our experience is that during etching the membranes break for pores below about 1 μm, which should give a bubble-point pressure of only 3 bar according to (2). The observed difference has several causes. A significant weakening is caused by the perforations [6, 7]. Furthermore, the irregular release of the membrane during etching causes membranes to break far below the maximum allowable pressure for a released membrane. Just before the membrane is entirely released, it will be attached to the silicon by only a few points (besides the sidewalls). Around these points huge stress concentrations will occur, which can cause the membrane to break. This is in agreement with the observation that the ruptures usually occur during the release process.

Equation (3) shows that a decrease in size of the membrane field leads to a stronger membrane. In this way, membranes with pores below 1 μm may be released without damage. However, in addition to the fact that the effective filtration area decreases, another problem arises. For pores around 1 μm we observe that the etch rate of the silicon underneath the membrane decreases and varies strongly over the wafer surface. Several channels are so shallow that the total sieve resistance increases. We do not know the exact mechanism behind this effect. Possibly the small pores in combination with the large hydrogen pressure hinder the supply of fresh KOH into the channel. The KOH underneath the membrane continuously creates hydrogen gas, which causes an increasing pressure. This pressurized gas pushes most of the KOH through the pores out of the channel, which
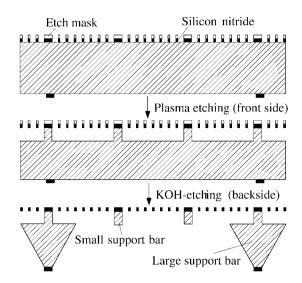

Figure 3. Process scheme for the release of perforated membranes by plasma etching.

reduces the etch rate and thus the rate of pressure build-up. Only after the gas exceeds the bubble-point pressure it can escape and fresh KOH can enter the channel. Obviously this cycle takes much longer for smaller pores and is therefore more sensitive to small variations in pore size. We also observe that for small pores the channels reach a certain maximum depth, after which the etching almost stops. This effect is possibly caused by the fact that the pressure build-up in a deeper channel takes more hydrogen and thus more time. If, during this time, all the KOH has been pressed out of the channel, the etch process will stop.

3. Dry etching through the pores

In order to overcome the problems of wet etching, we investigated the possibility of releasing the membrane with the use of dry etching through the pores. The basic idea is given in figure 3. A patterned etch mask (photoresist or chromium) is used to perforate the silicon nitride layer by CHF$_3$/O$_2$ etching. The mask is not removed from the nitride layer, as it will serve again as a mask for the silicon dry etching. The use of an isotropic etch gas is not satisfactory as the small support bars would be etched away. Therefore an anisotropic-etch recipe is required, with just enough undercut to remove all the silicon between the pores. Plasma etching gives such an anisotropy as the ions can be accelerated into a vertical direction by an electric field. We chose a SF$_6$/O$_2$ mixture, as SF$_6$ etches silicon isotropically while O$_2$ gives an anisotropic profile by passivating the silicon sidewalls of the trenches. Unfortunately the silicon nitride showed a poor etch resistance to the plasma. It is attacked from the inside of the pores as shown in figure 4.

In order to obtain higher etch selectivity between the silicon support and the silicon nitride membrane, the etch step was repeated in an apparatus with cryogenic substrate cooling (Plasmalab 100, Oxford Plasma Technology [8]). Using this apparatus we attempted to release a membrane with a pore diameter of 1.5 μm and a pitch (pore-to-pore distance) of 4 μm by etching with a SF$_6$-plasma at different temperatures.
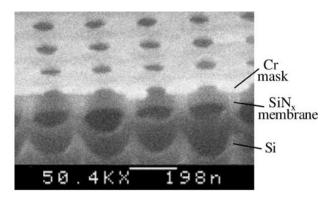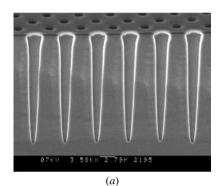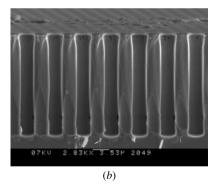
Figure 4. Silicon etching with an SF_6/O_2 plasma at room temperature through a 100 nm thick silicon nitride membrane covered with a chromium mask. Already, after the removal of 1 μm of silicon the membrane shows a significant underetch.
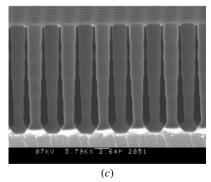

(a)

(b)

(c)

Figure 5. Results after 15 min etching with an SF_6 plasma at different temperatures: (a) $-90\,°C$; (b) $-110\,°C$ and (c) $-130\,°C$.

The SEM micrographs of the results after 15 min etching are given in figure 5. The pictures show a vertical profile for a temperature of $-110\,°C$. For $-90\,°C$, the profile is positively
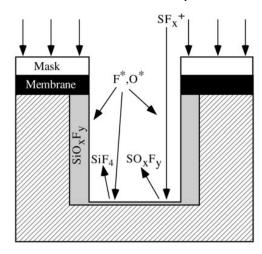

Figure 6. Schematic diagram of the process of etching with an SF_6/O_2 plasma and cryogenic substrate cooling. The erosion of the quartz reaction chamber creates the oxygen.

tapered, for $-130\,°C$ it is negatively tapered. Addition of O_2 is not necessary to obtain anisotropy, as the quartz reaction chamber provides for the O_2 while being eroded by the plasma. Bartha *et al* [9] explain the changing profile by a temperature-dependent sidewall passivation. Figure 6 shows a schematic diagram of the mechanism that provides a vertical profile. The silicon is attacked by radicals (F^* and O^*) and forms volatile SiF_4 molecules and a passivating SO_xF_y layer [10]. On the bottom of the trench this layer is removed through sputtering by accelerated plasma ions. A more extensive description of the phenomenon we observed is given by Jansen *et al* [11].
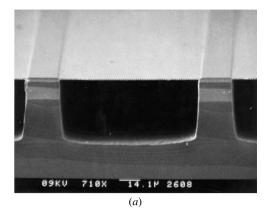
The samples in figure 5 do not show enough lateral etch (undercut) of the silicon to connect the trenches. After a second etch of 30 min the membranes are still attached to the silicon, although the sample in figure 5(c) has almost been released. However, so far our experiments were merely tests to find the right settings of the process parameters. In practice membranes with large holes such as these can still be released by KOH etching.

For sub-micrometre pores—where KOH etching gives problems—the release of the membrane by plasma etching is much easier, as less undercut is required to remove all the silicon between the pores. We applied the $-130\,°C$ recipe on membranes with pore sizes of 400 nm and 70 nm. Figure 7 shows that the results are excellent: the membrane is released entirely and the support bars have an acceptably vertical profile. Even the membrane with the 70 nm pores does not show any etch attack by the plasma.

In contrast with KOH etching, the depth of the channel underneath the membrane does not seem to be influenced by the pore size. The porosity will play a much more important role in the silicon etch rate, as it determines the amount of plasma that can enter the channel.

4. Discussion

Anisotropic plasma etching seems to be a useful tool to replace KOH etching for the release of perforated membranes with small pores. For pores below 1 μm—where wet etching
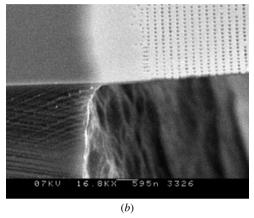
(*a*)

(*b*)

Figure 7. SF_6/O_2 etching for 45 min at $-30\,^\circ C$ through very small pores: (*a*) 400 nm and (*b*) 70 nm.

causes pressure problems—good results are obtained for plasma etching with cryogenic cooling. The reproducibility is good and the membrane is not attacked. However, at this moment plasma etching with cryogenic cooling can only be done in small batches: the apparatus we use is a single-wafer etcher and the whole process takes about one hour. For mass production of microsieves this is still a problem. Therefore it would be worthwhile trying to attack the wet etching problems from a different angle.

An option might be the addition of a surfactant to the etch solution to decrease the surface tension and thus the bubble-point pressure. Also, the etch conditions may be changed in such a way that no gas is formed. If the etch rate is lowered by lowering the temperature and/or the KOH concentration, the hydrogen created may remain in solution. However, one must keep in mind that these changes will effect the anisotropic profile, which may not be in the best interest for the fabrication of microsieves.

Another way to avoid the problems is to etch gas escape holes from the back side of the wafer. This is difficult for $\langle 100 \rangle$ wafers as the etch planes are oblique, which requires large holes on the back side of the wafer. We are currently investigating the fabrication of microsieves on $\langle 110 \rangle$ wafers, as they allow for the etching of vertical escape holes, which

require only a very small space on the back side. The first results are promising and will be presented in a following paper.

5. Conclusions

The release of perforated membranes by KOH etching is difficult for small pores as the pressure build-up by the hydrogen gas may break the membranes. Anisotropic etching with an SF_6/O_2 plasma can solve the problem. During etching cryogenic substrate cooling is necessary to protect the membrane against lateral etching under the mask. For sub-micrometre pores excellent results are obtained. An important finding is that the anisotropy of the etch recipe is maintained, despite the in between hanging perforated membrane.

Acknowledgment

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