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Bias-assisted KOH etching of macroporous silicon membranes

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Abstract
This paper presents an improved technique to fabricate porous membranes from macroporous silicon as a starting material. A crucial step in the fabrication process is the dissolution of silicon from the backside of the porous wafer by aqueous potassium hydroxide to open up the pores. We improved this step by biasing the silicon wafer electrically against the KOH. By monitoring the current–time characteristics a good control of the process is achieved and the yield is improved. Also, the etching can be stopped instantaneously and automatically by short-circuiting Si and KOH. Moreover, the bias-assisted etching allows for the controlled fabrication of silicon dioxide tube arrays when the silicon pore walls are oxidized and inverted pores are released.

1. Introduction

The versatility of macroporous silicon [1, 2] is greatly improved when the pores are opened up and *membranes* are fabricated. These membranes consist of ordered macropore arrays with pore diameters in the range of 500 nm to 5 μm and are used in electroosmotic pumps with highest flow rates [3] as well as photonic crystal gas sensors [4]. They are investigated in lab-on-a-chip particle separation experiments [5] and can form templates for polymer microfiber arrays [6]. The membranes are formed by etching away the backside of a macroporous silicon wafer with aqueous potassium hydroxide until the tips of the macropores are reached. To prevent the KOH from entering the pores and dissolving the membrane, the pore walls are thermally oxidized first with the silicon dioxide forming a thin etch stop layer. This layer can be subsequently removed by hydrofluoric acid to complete the membrane fabrication. Alternatively, short SiO_2 caps can by used as x-ray transmissive windows [7]. Due to the high KOH etch rate of silicon compared to SiO_2, longer micro-tubes or -pillars [8] can also be released. They can form microneedle arrays and have been proposed for use in DNA separation [9].

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2. Experiments and discussion

2.1. Macroporous silicon membranes

Macroporous silicon wafers are fabricated by photoelectrochemical etching [1, 2]. This process is briefly summarized here: lithographically defined KOH etch pits act as nuclei for the pore growth. A triangular pattern with a 3 μm lattice constant is structured on a (1 0 0)-oriented n-type silicon wafer. Macropores are grown into the [1 0 0] direction by etching with 5% hydrofluoric acid (HF) at 10 °C and applying a voltage of 2–2.8 V between a platinum cathode and the silicon wafer. The backside of the n-type silicon wafer is illuminated to generate defect electrons, which diffuse to the pore tips where they induce the dissolution of silicon. The pore diameter is controlled via the illumination intensity, and thus the fabrication of diameter-modulated pores is possible (see figure 1). An approximately 100 nm thick silicon dioxide layer is grown on the wafer by thermal oxidation (2 h at 900 °C in air) to act as an etch stop for the subsequent KOH etching. The oxide is removed by HF in an area on the silicon wafer's backside corresponding to the area of the membrane to be fabricated.

In the conventional pore opening process, the wafer is mounted in a steel etching cell, and the SiO_2-free area is etched anisotropically with 25% KOH at 80 or 90 °C at a rate of 1.3 or 2.8 μm min^{-1}, respectively. If the process is stopped at the

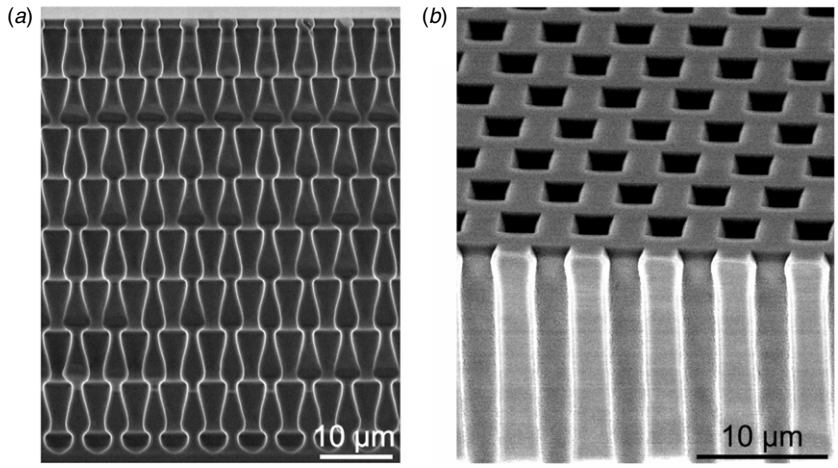

Figure 1. Electron micrographs of cleaved macroporous silicon wafers: (*a*) side view of 60 μm long pores with a modulated diameter. (*b*) Bird's-eye view of straight pores reveals triangular ordering with an interpore distance of 6 μm.

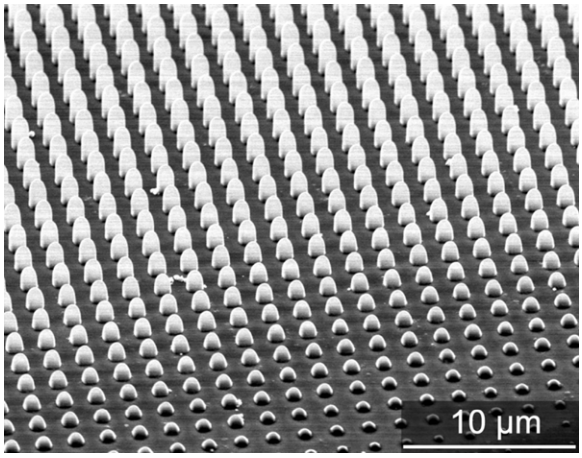

Figure 2. Electron micrograph of an array of silicon dioxide shells protruding from the backside of a macroporous silicon wafer. The pores are ordered in a square lattice with a 4 μm pore distance. The image is taken at the edge of a membrane and reveals the inhomogeneity of the KOH front (notching).

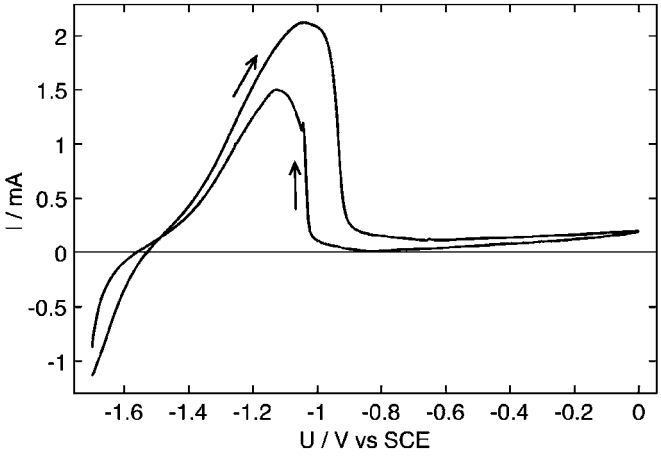

Figure 3. Cylcic voltrammogram of a 0.5 cm^2 n-type Si(1 0 0) wafer in 25% KOH at 70 °C. The potential was scanned from −1.7 V at a rate of 5 mV s^{-1}.

right time, the oxidized pore tips remain protruding out of the silicon surface (see figure 2). Removing the remaining oxide with HF completes the membrane fabrication. Unfortunately, this conventional KOH backside opening suffers from several disadvantages: the etching time cannot be predicted exactly due to the strong dependence of the etch rate on temperature. The end of the etching process is therefore determined by shining light onto the wafer surface and observing the appearance of a coloured diffraction pattern by the ordered SiO_2 shell array. Since the view of the silicon wafer is partially obstructed by emerging hydrogen bubbles, and since at 90 °C the selectivity of etching rates [10] of SiO_2 and Si is reduced to 1:190, only a time window of less than 10 min remains after 140 min of etching (if 400 μm bulk Si are etched) to end the process before the SiO_2 shells crack, KOH enters the pores, and the membrane starts to dissolve. In the fabrication of macroporous silicon membranes, the KOH backside opening is the most time-consuming processing step with the lowest yield. Moreover, light diffraction is detected when only the forefront of a pore tip protrudes, and the KOH etch front does not progress homogeneously over the etched area due to a 'notching' effect [11] (see figure 2). Thus the yield of membranes with homogeneously fully opened pores is considerably reduced.

We improved the backside opening by taking advantage of the fact that KOH and Si form a coupled chemical–electrochemical system [12, 13]. By electrically biasing the KOH and Si against each other we can monitor a current which is proportional to the area of the etch front. When the pore tips are reached, this area is reduced. Therefore we determine the end of etching when a current drop is observed. We can then stop the dissolution immediately by short-circuiting Si and KOH and thereby driving the system into a passivating regime.

The current–potential characteristics [13] of an area of 0.5 cm^2 of an (1 0 0) n-type (5 Ω cm) silicon wafer in a 25% KOH solution is shown in figure 3. As the potential is made positive with respect to the open circuit value of −1.53 V, the system is driven in reversed bias. In the voltage range up to −1 V silicon is etched by water with OH^- ions acting as

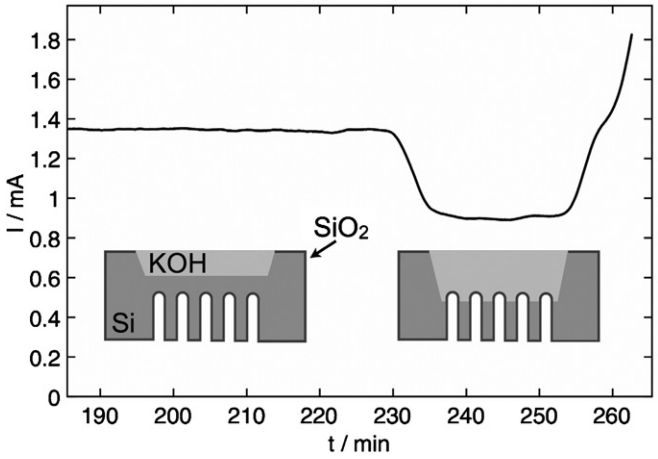

Figure 4. Current–time curve of etching the backside of a 0.5 cm^2 n-type Si(1 0 0) wafer at a bias of −1.2 V in 25% KOH at 70 °C. 300 μm long macropores with a porosity of 36% were grown in the 508 μm thick sample. The pores are oxidized to a 140 nm thick thermally grown SiO_2 layer.

a catalyst. The anodic current is caused by the injection of electrons into the conduction band. At voltages above −1 V passivation occurs due to the formation of a blocking oxide layer. The current decreases, and the dissolution of silicon stops. In the return sweep the oxide layer causes a lower current that sets in below −1 V.

In the −1.5 to −1 V range the current is proportional to the etched area. We utilize this to control the dissolution of silicon by monitoring the current: when the etch front reaches the macropores, the current is reduced by a factor of the sample's porosity. This decrease in current determines the end of the process. Switching the voltage to 0 V then stops the etching instantaneously by passivating the silicon.

In our setup, macroporous silicon wafers are etched in a steel cell with a copper base plate. A wafer of approximately 3 cm^2 is electrically isolated against the metal and an area of 0.5 cm^2 of its backside is exposed to a 25% KOH solution. An electric bias of −1.2 V is applied between the silicon wafer and the KOH solution. This voltage leads to a relatively high etch rate of 0.9 μm min^{-1}, which is—however—not significantly higher than the etch rate in an unbiased sample [14]. The voltage is controlled in four-point probe measurement using a Keithley 2410 Sourcemeter and a saturated calomel electrode as a reference. The KOH is kept at 70 °C.

The current–time characteristics of etching an area of 0.5 cm^2 of a 508 μm thick wafer with 300 μm long triangular ordered straight pores with a diameter of 3.8 μm (corresponding to a porosity of 36%) are shown in figure 4. The current is proportional to the etched area. When the etch front reaches the pores after 230 min, the current decreases by the factor of the sample's porosity. After 270 min, the silicon oxide etch stop shells start to crack and the current increases, since the KOH attacks the area of the inner pore walls. Monitoring the *I–t* curve brings the advantages that the current drop clearly indicates the end of the process, which can then be *automatically* terminated without disassembling the setup by driving the KOH–Si electrochemistry in the passivating regime, i.e. short-circuiting. Additional information is gained from the *I–t* curve: the step height reveals the sample's porosity (the current drop of 35% in figure 4 is congruent with the porosity of 36%). The step width is a measure of the homogeneity of the etch front. The 6 min wide step indicates an inhomogeneity of 5.4 μm across the wafer. However, one has to take into account that the pore's diameter increases to its full width within 1.5 μm at its tip, and that the *I–t* curve is the convolution of the tip shape and the KOH etch front. (The differences in pore lengths are negligibly small due to self-ordering during the photoelectrochemical growth.)

The appearance of a lower plateau in the *I–t* curve allows for the *reliable* fabrication of membranes with homogeneously fully opened pores. This is of importance if the membranes are used for microfluidic applications because the hydraulic resistance depends strongly on the diameter of the pores. Also the reliable fabrication of better x-ray transmissive windows is made possible, which consist of membranes with only 60 nm thick oxide shells protruding from the silicon surface and can be used in environmental scanning electron microscopes due to their transmissibility of both electrons and x-rays [7].

2.2. Silicon dioxide tube arrays

The higher selectivity [10] in etching rates of Si and SiO_2 at lower temperatures (300:1 at 70 °C) allows not only the fabrication of short oxide shells but of arrays of longer SiO_2 microtubes if a thicker oxide is used. A macroporous silicon wafer with diameter-modulated pores was oxidized in air for 4 h at 950 °C to grow an oxide layer of a thickness of approximately 140 nm. After the KOH etch front reaches the pore tips, SiO_2 microtubes of up to 100 μm can be 'excavated' before the SiO_2 is dissolved. (At lower temperatures and considerably lower etching rates the length of the tubes is only limited by the pore length due to increased selectivity.) When microtubes with a modulated diameter are manufactured, the modulation is mirrored in the *I–t* curve (see figure 5); the controlled fabrication of SiO_2 microtube arrays with a defined tube length and a defined number of diameter modulations is possible. In general, these arrays can be useful for a large number of applications due to their high surface-to-volume ratio, their biocompatibility, and the good control over their exact shape. Specifically they could be used as femtolitre containers or as scaffolds for tissue engineering. Even more applications will become accessible if the arrays are used as templates for further structuring, e.g. when the sample is replicated into another material [15].

3. Summary

We have reported on the bias-assisted KOH etching of macroporous silicon membranes. Membranes are fabricated by etching the backside of a macroporous silicon wafer to open up the pores. By electrically biasing the KOH and silicon, a better control of the etching process is achieved; the end of the process step is determined when the etch front reaches the oxidized pore tips and a drop in the monitored current is detected which corresponds to the sample's porosity. The

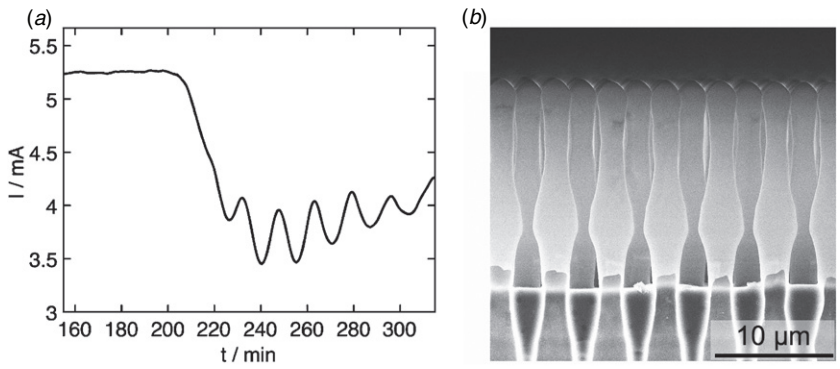

Figure 5. (*a*) Current–time characteristics of etching the backside of a 1.7 cm^2 n-type Si(1 0 0) wafer at −1.2 V in 25% KOH at 70 °C. The 508 μm thick sample contains 350 μm long pores with modulated diameters. (*b*) Side view of an array of silica microtubes with modulated diameters.

etching can then be stopped immediately by changing the bias voltage.

We also demonstrated the controlled fabrication of silicon dioxide microtube arrays or inverted macropores with well-defined length. These are released with the same method by using a thicker SiO_2 etch stop layer at the pore walls or increasing the selectivity of the etch rate of silicon and SiO_2 by lowering the temperature.

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