Effect of current density on silicon surface in electrochemical etching

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A simple and reliable fabrication technique for producing nanoporous filters is presented. The nanoporous filter plays an important role in biomedical microelectromechanical systems applications, especially in filtering out waste and solute from inside human blood. Nanosized components in the biological fluid are filtered using silicon membranes that are controlled by nanosized pores. The technique explored was the electrochemical etching (ECE) process of silicon. This approach starts with thinning the bulk silicon until only several micrometres thick using the KOH process and then carry out ECE to produce pores. The yield of the process was a 3 μm thick nanoporous silicon membrane with pore sizes of less than 100 nm. This physical characteristic enables the membrane to filter all the waste and solute particles of less than 100 nm. Owing to this simple and reliable method, the development of nanoporous silicon membrane can be used in nanofiltration applications especially in an artificial kidney.

1. Introduction: Porous silicon is a versatile component that can be integrated with other components such as a micropump, microchannel, and microfluidic to make a complete device. This device can be used in biomedical microelectromechanical systems and lab-on-chip applications for separating micro and nanoparticles. In electrochemical etching (ECE), the pores can be produced by dipping the silicon wafer in HF and ethanol solution with electric currents supplied.

Recently the creation of the smallest pore structures has been studied to suit the application. Many methods have been proposed to understand the variety of sizes and the geometry of silicon pores [1–9]. The smallest pore structure has been developed by a self-adjusting method. There are certain parameters that can be controlled during an electrochemical etch, which are current density [10–12], HF concentration [13, 14], time, silicon orientation [15], doping level [9, 16, 17], lighting and electrolyte mixture [18]. This Letter focuses on the effect of current density on the pore formation and cross-section of the porous silicon layer.

The result is inspected using a field emission scanning electron microscope (FESEM) to verify the pore formation and cross-section of the porous silicon layer. A FESEM has the capability to visualise the porous silicon structure in the nanometre range with higher magnification. The FESEM results also verify the pore formation of porous silicon, whether uniform or non-uniform and the pore diameters. The cross-sectional layer illustrates the influence of current density on the etching mechanism on the silicon substrate. Finally, this method can be correlated to the electric field mechanism in producing porous silicon which is significant in order to control the pore structures.

2. Experimental: Single-side polished p-type silicon wafers (doped with boron) were prepared with a resistivity of 0–100 Ωcm, 800 μm thickness and ⟨100⟩ oriented. The silicon wafers were cleaned with the standard cleaning procedure by dipping into acetone, methanol and 10% HF for 5 min each to remove the stain and native oxide on the silicon surface. The silicon sample then undergoes thinning using 45% potassium hydroxide (KOH) at 75°C to obtain the silicon membrane with a thickness of 3 μm.

Next, the samples were dipped into the mixture of HF and ethanol for the ECE process with different current densities as shown in Fig. 1. The experimental setup for ECE is shown in Fig. 2. The current density value has been categorised by three levels, which are low, medium and high current. This variation in current density characterises the effect of current density on the silicon substrate. Finally, the samples were examined

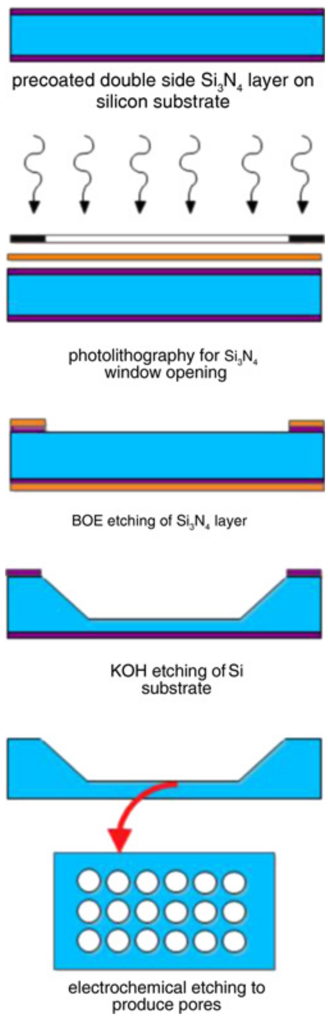

Figure 1 *Fabrication of silicon membrane*

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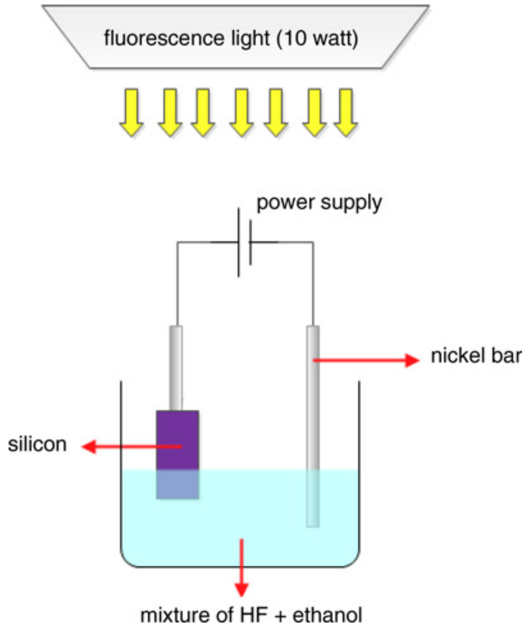

Figure 2 *ECE setup*

using the FESEM to precisely verify the pore formation and cross-section etching formation of silicon for different current densities.

3. Result and discussion: The initial lithography process to pattern the frame on silicon nitride is shown in Fig. 3*a*. The KOH etching step to fabricate a thin silicon wafer produced a 2 mm × 2 mm square membrane, as depicted in Fig. 3*b*. Since the KOH etching step is a relatively highly controllable and repeatable process, the the etch stop was determined by the total etch time in the KOH etch bath. It was observed that 19 h of KOH process to fabricate thin 800 µm silicon wafers resulted in approximately 3 µm membranes. The etching rate was approximately 0.67 µm/min under the aforementioned etching condition. Then, the silicon membrane was dipped in a buffered oxide etch for 4 h to remove the nitride layer on the silicon. The nitride layer must be removed to ensure there is no impurity on the silicon substrate during the electrochemical etch. The silicon membrane sample in Fig. 3*c* is ready for the ECE process.

In the first set of experiments to gauge the effect of current density on the porous membrane structure, it was observed that the membrane etch rate increases proportionally with current density. A 5 mA/cm^2 current yields an etch rate of 12.6 nm/h, whereas a 30 mA/cm^2 current yields an etch rate of 1.3 µm/h. In terms of correlation between the current density and membrane etch rate, it was observed that the etch rate increases linearly with the applied current, as depicted by the graph in Fig. 4. Photo

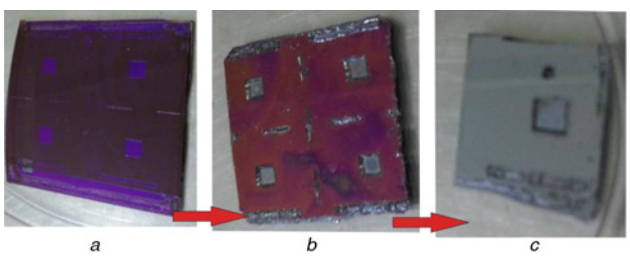

Figure 3 *Silicon membrane frame 2 mm × 2 mm*
a Silicon membrane frame after lithography
b Silicon membrane after the KOH process
c One frame silicon membrane for the ECE process

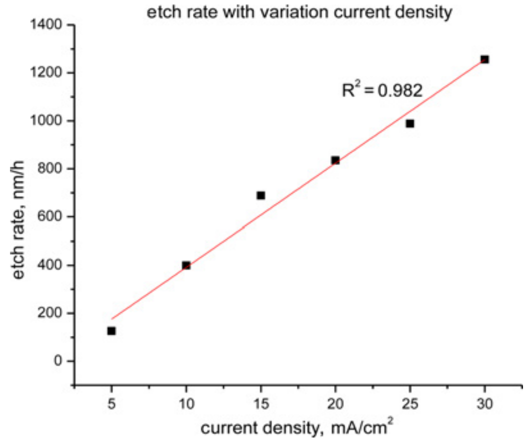

Figure 4 *Correlation between the membrane etch rate and current density in ethanoic HF electrolyte solution*

illumination, HF concentration, distance between the anode and the cathode, and the stirring time were fixed, in order to gauge the sole effect of current density on etch rate. For the purpose of control, a thin 3 µm porous silicon structure that follows ethanoic HF and 30 mA/cm^2 current density was chosen as the ideal parameter because of the ease of process control.

This is based on the study by Hamzah *et al.* [19] which states that the etch rate increases proportionally with applied current. The etch rates observed are in the order of µm/h for a current density varying from 5 to 20 mA/cm^2 for 5% HF electrolyte solution. For ethanoic

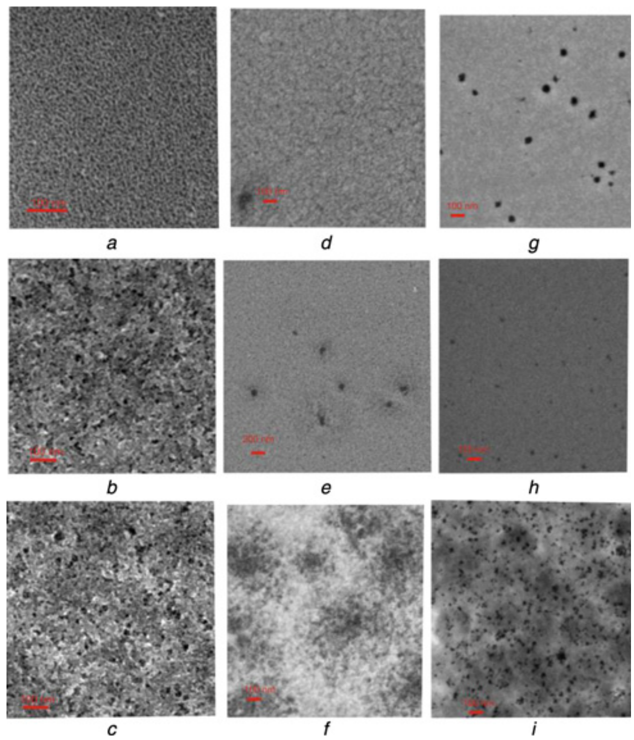

Figure 5 *Surface morphology for variation current density*
a $J = 5$ mA/cm^2
b $J = 10$ mA/cm^2
c $J = 15$ mA/cm^2
d $J = 60$ mA/cm^2
e $J = 70$ mA/cm^2
f $J = 80$ mA/cm^2
g $J = 300$ mA/cm^2
h $J = 400$ mA/cm^2
i $J = 500$ mA/cm^2

HF, the same trend graph was observed; that is, the etch rate increases proportionally to current density. However, the ethanoic HF etch rate became slow due to the fact that ethanol acts as a surfactant in reducing the hydrogen bubble throughout the process [20, 21].

Regarding the second set of experiments, the purpose was to gauge the effect of current density on the surface morphology of the silicon membrane. In this experimental setup, the categories declared are the low current density (5–30 mA/cm^2), the medium current density (60–100 mA/cm^2) and the high current density which is set at 200 mA/cm^2 upwards.

The electrochemical formation of silicon membrane is observed within this current level. According to Fig. 5, the pore structure changes when the current density is increased. Random pore distribution is observed for low and medium current densities. However, a sharp pore structure is observed under a high current density. For the purpose of producing the silicon membrane, a density of 600 mA/cm^2 was chosen as the ideal parameter because of the sharp porous structure and good pore distribution.

The pore size diameter can be measured using the FESEM results. The pore size diameter for various current densities is measured by calculating the mean of 20 samples in different areas. The mean of pore sizes has been plotted in Fig. 6 for different current density levels. The pore size diameter is observed to vary by less than 30 nm for the applied current density. It was observed that the current density has less effect on the pore diameter. From previous studies, the pore size diameter was affected more by the HF concentration [14] and doping level [22, 23].

For the third set of experiments, the aim was to determine the effect of current density on the cross-section of the porous layer. The experimental setup for ECE was maintained from the previous experiment. It was observed that low and medium current densities produce spongy porous silicon layers. However, high current density changes the porous silicon layer from spongy to columnar as shown in Fig. 7. For an artificial kidney application the columnar porous silicon layer is more suitable to ensure that particles are able to pass through the membrane.

The variation in current density affects the dissolution process during ECE. This dissolution process occurred by transferring the ion in the electrolyte solution. Typically, the mechanism of pore formation starts with the migration of electrons and holes when the electric field is applied to attract charge carriers. The chemistry that occurs on the silicon surface involves competition between Si–O, Si–F and Si–H bond formations [24].

The pores are produced through the holes in the silicon substrate by aligning themselves in response to the direction of the current line because of the high current density applied [25, 26]. The high current density induced a strong electric field that in turn exerted a polarising effect onto the silicon substrate. The holes

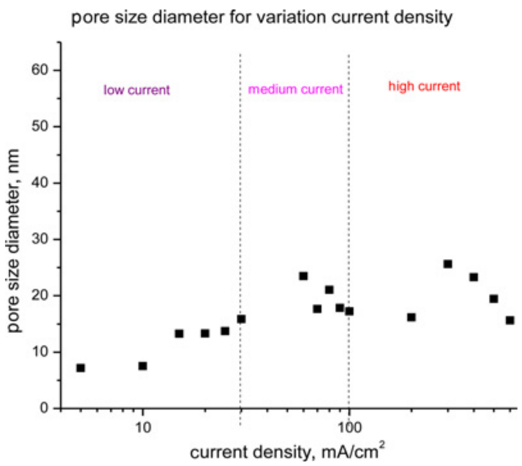

Figure 6 *Pore size diameter for variation current density*

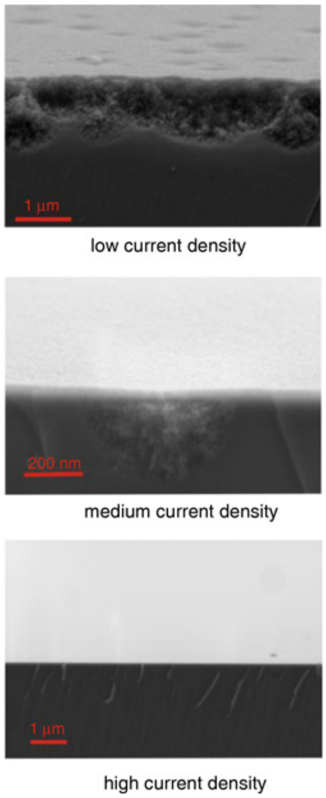

Figure 7 *SEM images of cross-sections for the porous silicon substrate at various current densities*

have a tendency to accumulate at defective sites on the surface as a result of electron excitation when either the silicon or the dopant atom moved into the lattice or non-lattice sites of silicon crystallites.

This condition encouraged the F$^-$ ions in the electrolyte to move to the silicon substrate and subsequent reactions led to dissolution. These holes prefer to accumulate at the pore tip border in the bulk silicon because of the low potential energy as compared with the wall area [8, 27]. As a result, greater silicon dissolution was favoured to form pores with a columnar structure in the ⟨100⟩ orientation.

4. Conclusion: Porous silicon membranes have been successfully fabricated via an initial KOH etching process followed by an ECE step. Through ECE, the effect of current density on the etch rate, pore size diameter and cross-section of the porous layer was observed by maintaining the time, ethanoic HF, and photoluminance factors constant. The correlation between etch rate and current density was observed where the etch rate increases proportionally to the current density. Besides that, the effect of current density is observed by increasing the current density to affect the pore size diameter. The pore structure looks sharper with high density compared with low and medium current density currents. At the end of this experiment, the transformation of a spongy porous layer to a columnar porous layer because of the increase in current density was also observed in the cross-section of porous silicon. Finally, the effect of current density was observed under various conditions for the fabrication of a simple and low-cost silicon membrane. This silicon membrane can be integrated with a microelectromechanical systems lab-on-a-chip system to produce artificial kidneys in the future.

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