Microelectronic Engineering 141 (2015) 160–167

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

# Effects of alcohol diluents on nanopore structure of electrochemically etched silicon membrane

Norhafizah Burham [a,b,*], Azrul Azlan Hamzah [a], Burhanuddin Yeop Majlis [a]

[a] Institute of Microengineering and Nanoelectronics (IMEN), Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
[b] Faculty of Electrical Engineering, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia

ARTICLE INFO

Article history:
Received 31 October 2014
Received in revised form 5 February 2015
Accepted 16 March 2015
Available online 20 March 2015

Keywords:
Silicon membrane
Alcohol
Hydrofluoric acid (HF)
Electrochemical etch
Nanoporous

ABSTRACT

An efficient method to control the nanoporous structure of a silicon membrane is presented. Nanoporous silicon membrane plays an important role in separating nano-sized particles in biological applications. The nano-sized filter can be fabricated by controlling the various fabrication parameters like hydrofluoric acid (HF) concentration, type of doping and current density. This paper explores the effect of alcohol to the pore formation through the electrochemical etching process. The fabrication process starts with the thinning of a silicon substrate to produce the membrane and rapidly performing an electrochemical etch to produce the pores. The variation in alcohol used is studied to verify the pore structure and distribution on silicon substrate. There are three types of alcohol used in this experiment, namely ethanol, methanol and propanol. These alcohols are mixed with hydrofluoric acid (HF), forming an electrolyte aqueous solution for the electrochemical etch. Due to alcohol diluents effect, it is observed that circle and star shaped pore structures are produced using the electrochemical etching process. This variation in shape can be used in filtering biological particles for an artificial kidney in the future.



## 1. Introduction

Nanoporous silicon membrane is becoming popular especially in biological filtration. This nanoporous membrane can be integrated with other components to assemble a device for separating gas or particle [1–3], biosensor [4], or for optical [5,6], tissue engineering [7], and radiotherapy applications [8]. Nanoporous structures with pore size of 100 nm have been fabricated using different materials like silicon [9–11], aluminum oxide and titanium oxide. Silicon gives the most advantages in terms of physical and chemical stability compared to the other materials [12]. In addition, nanoporous silicon is good in separating particles for a biological application due to its bio-compatibility and anti-biofouling properties with the surface modification using polyethylene glycol (PEG). This nanoporous silicon membrane were used in filtering biological particle like vitamin, amino acid, very small plasma protein, virus and small bacteria with the size less than 100 nm [13].

Electrochemical etching process is performed to prepare the nanoporous silicon using a solution of hydrofluoric acid with electrical current supplied. The electrochemical etching method is not a complicated process, but it is very challenging to control the pore structure since it depends on several factors. The key factors that affect the silicon nanoporous structures are the concentration of hydrofluoric acid, type of dopant, current density, etching time, resistivity of silicon, illumination, electrolyte stirring and wavelength [14–16]. Typically, electrochemical etching is performed by applying a constant current between two electrodes immersed in an electrochemical cell which contains an electrolyte aqueous solution of hydrofluoric acid and ethanol [17,18]. This electrochemical etching process is very economical, reliable and easy to accomplish compared to the other method which used a laser interference lithography to produce smaller pores [3].

This paper presents another factor that affects the pore size diameter which is the electrolyte solution used. The basic electrolyte solution is hydrofluoric acid. The hydrofluoric acid will be mixed with other solutions like alcohol [19], deionized water (DI water) [20], hydrogen peroxide ($H_2O_2$) [21–23], and acetonitrile in forming pores. In this experimental setup, the effect of mixing various alcohols in an electrolyte solution is studied to verify the pore formation of porous silicon. The process starts with wet etching using Potassium Hydroxide (KOH) to thin the silicon substrate to get the silicon thickness to less than 1 μm. Then electrochemical etch is carried out to form the pores. Finally, the analysis of various alcohols' effects to the pore structure is made in evaluating the

* Corresponding author at: Institute of Microengineering and Nanoelectronics (IMEN), Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia.
E-mail addresses: azlanhamzah@ukm.edu.my, fiezah@msn.com (N. Burham).

http://dx.doi.org/10.1016/j.mee.2015.03.019
0167-9317/

fabrication of a nanofiltration system for filtering nano-sized particles in the future.

## 2. Fabrication process

The fabrication process is divided into two parts which is thinning silicon for membrane and electrochemical etch to produce the pores. Silicon membrane fabrication is discussed in the first part of fabrication process. Then, electrochemical etch to form the pores on silicon membrane is discussed in the second part.

### *2.1. Silicon membrane fabrication*

The membranes were fabricated on ⟨100⟩ 400 μm thick doubled-sided polished (DSP) silicon. The substrates were precoated on both sides with 200 nm thick of silicon nitride. The substrates were patterned with a square dimension of 2 mm × 2 mm using AZ 4620 positive photoresist on 3 cm × 2.6 cm square sample. After being exposed under UV light for 80 s, the samples were developed using AZ 400 K developer. The substrates were dipped into the developer, and then rinsed with de-ionized water (DI). This process is repeated until no photoresist is left on the exposed surface area. In the process, developing the samples takes around 4 min. The exposed layer nitride was then removed by 4 h of etching in a buffer oxide etch (BOE) solution. Next, the samples were dipped into a 45% KOH + 10% IPA solution with constant temperature of 75 °C for 9 h to thin the bulk silicon until it reached approximately 300 nm thickness as depicted in Fig. 1.

The silicon membrane needs to be handled carefully because the thin membrane is easy to break during the electrochemical etching experiment stage. Before the membrane is immersed in electrochemical bath, the membrane need to be immersed in BOE solution again for 4 h to remove nitride remain on the silicon surface [24]. If the silicon membrane is not in hydrophobic condition, silicon membrane will dip in 10% HF to remove all stain on silicon membrane. Any impurity will affect the pore formation throughout the process.

Fig. 2(a) shows the top view of silicon membrane after KOH process. The sample was dipped in 45% Potassium Hydroxide (KOH) with a constant temperature of 75 °C. By repeating and controlling the process, the silicon membrane is thinned down to less than 1 μm thick. The 300 nm thickness membrane was validated using a Scanning Electron Micrograph (SEM) as shown in Fig. 2(b).

The membrane thickness less than 1 μm is fabricated to mimic the filtration system in human body especially kidney filtration system. The thick membrane will issues clogging on silicon membrane surface and affect the filtration rate during filtering biological particle. The silicon membrane size 2 mm × 2 mm with ≈300 nm thick can withstand the pressure up to 7.3 kPa [25]. The pressure used in kidney filtration system is from 15 mmHg (2 kPa) up to 55 mmHg (7.3 kPa) [13]. Simulation is performed to execute and estimate membrane deflection and stress on silicon membrane. The membrane is simulated using Comsol 4.3 shows the maximum deflections at the middle membrane is 0.7135 μm with the maximum stress $8.0467 \times 10^7$ $Nm^2$. So, 300 nm thick can withstand the pressure applied and allow the biological particle to penetrate silicon membrane (see Fig. 3).

### *2.2. Electrochemical etching setup*

Electrochemical etching was performed to form pores on the silicon membrane surface using hydrofluoric acid (HF) solution [18,26–28]. The experiment setup was shown in Fig. 4 by supplying a constant current between two electrodes immersed in a Teflon cell containing an aqueous solution of HF and alcohol which is methanol, ethanol or propanol. Most researchers used ethanol and HF as the electrolyte aqueous for electrochemical etch. This is because ethanol acts as the surfactant in reducing the hydrogen

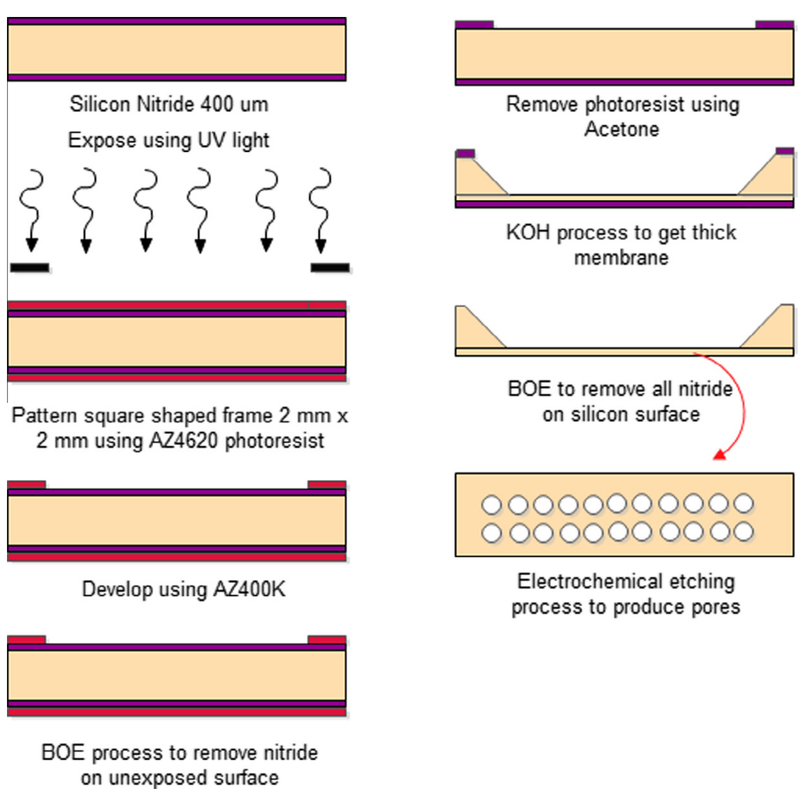


**Fig. 1.** Silicon membrane fabrication process.