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# A combination of electroless and electrochemical etching methods for enhancing the uniformity of porous silicon substrate for light detection application

N. Naderi, M.R. Hashim*

*Nano-Optoelectronics Research Laboratory, School of Physics, Universiti Sains Malaysia (USM), 11800, Penang, Malaysia*

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ABSTRACT

This paper reports on a combination of electroless and electrochemical etching of a silicon surface for enhancing the uniformity of fabricated porous silicon substrate and improving the sensitivity of photodetectors. Photo-assisted pulsed electrochemical etching of silicon is modified by introducing a novel parameter called delay time ($T_d$), along with cycle time and pause time, of pulsed current, which can affect the morphology of pores. This technique offers the possibility of growing photoluminescent materials with uniform pores and selective wavelength emission. A sample with a $T_d$ of 2 min shows a significant increase in the intensity of the Raman spectrum (10 times stronger than that of the sample without $T_d$ at 518.2 $cm^{-1}$) due to the enhanced surface-assisted multi-phonon processes in porous film. A red-shift of 2.5 $cm^{-1}$ and a peak broadening of 1.4 times are also observed for this porous sample compared with those of crystalline silicon. Porous surface properties and the performance of the optimized PS as photodetectors are discussed.



## 1. Introduction

Porous silicon (PS) has been considered a preferred material for sensor applications over the past few years. Its large effective surface area, photoluminescence (PL) properties at room temperature, and compatibility with silicon-based technologies have been the motivation for the development of this technology [1]. Electrochemical anodization method is an effective technique for the fabrication of uniform pores on the surface of silicon. Several parameters are used to optimize the surface characteristics of a porous layer, such as current density, time of etching, light with several frequencies, shape of current, and electrolyte composition.

PS is mostly formed by the constant current electrochemical anodization of Si in hydrofluoric acid (HF)-based electrolytes [2,3]. This technique is very sensitive to the concentration of HF. The most important concern in this technique is the decreasing rate of etching because of the decrease in HF concentration near the silicon surface as a result of the consumption of acid during anodization. Furthermore, the creation of hydrogen bubbles in pores decreases the speed of etching [4]. The most fundamental solution to this problem is to allow the sample to rest and to pause the current for a while. This technique will enable the sample to eject the $H_2$ bubbles and allow fresh HF to enter the pores and react with silicon substrate, which can increase the etching process at a significant rate [5]. The pulsed-current method, which can be controlled by changing the cycle time ($T$) and pause time ($T_{off}$) of the current during the etching process, has been introduced recently [6].

The novelty of the present research is in the application of delay time ($T_d$) before the cell is connected to the power supply, which can be described as a time when samples experience electroless chemical etching prior to electrochemical anodization. To the best of our knowledge, there has been no report that uses $T_d$ before electrochemical etching to control the formation of PS.

The potential applications of PS include visible and non-visible light detectors [7,8] and gas sensors [9]. In the current report, the PS samples were used to fabricate metal–semiconductor–metal (MSM) photodetectors to investigate the potential applications of the improved PS in optoelectronic devices.

## 2. Experiment

The c-Si samples used in this work were cut from an n-type Si (1 0 0) wafer with a resistivity of 16 mΩ cm. The measurements presented here were performed on square samples (10 mm × 10 mm). To facilitate anodization, a 264 nm-thick aluminum thin film was coated at the backside of the Si sample through the evaporation of pure Al in a vacuum chamber at a pressure of $3.8 \times 10^{-5}$ mbar. This process decreased the surface resistivity to 0.067 mΩ cm after 10 min of annealing in tube furnace at a temperature of 450 °C in a nitrogen gas flow.

The electrochemical solution was a mixture of HF (49%), ethanol (95%), and hydrogen peroxide ($H_2O_2$) with the volume ratio of

* Corresponding author. Tel.: +60 4 6533677; fax: +60 4 6579150.
*E-mail address:* roslan@usm.my (M.R. Hashim).

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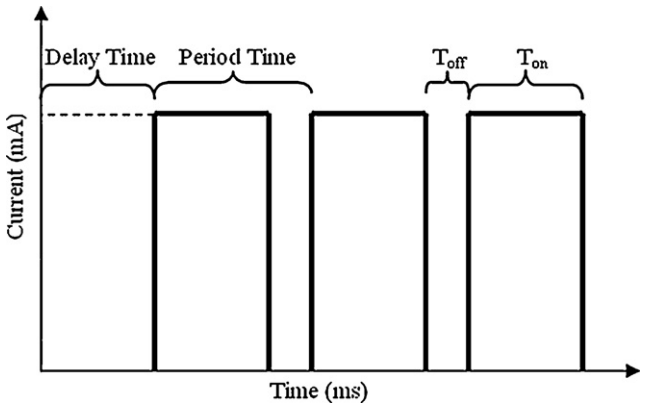


**Fig. 1.** Schematic diagram of the waveform for the pulse current used in the electrochemical etching of silicon.

1:2:2. The same pulsed signal characteristics from our last work [10] were used to feed the anodic etching circuit, as shown in Fig. 1. The $T_d$ was varied by 0, 2, and 4 min for samples A, B, and C, respectively. After 30 min etching, all samples were washed in deionized water and dried in laboratory air at room temperature. The surface of the etched samples appeared yellowish. All samples showed visible light emission under UV light illumination.

A coplanar structure of Ni was evaporated on porous layers to fabricate Schottky contacts and to study the *I–V* characteristics of the MSM photodetectors. After Ni metallization, samples were subjected to annealing at 400 °C for 10 min in a conventional tube furnace in a flowing nitrogen environment.

For SEM measurements, a Jeol (JSM-6469 LV) microscope was used for surface morphology. The FTIR spectra were collected by a PerkinElmer Fourier Transform Infrared Spectrometer. Raman measurements were carried out at room temperature with a Jobin-Yvon (HR 800 UV) spectrometer.

## 3. Results and discussion

The SEM images of samples A, B, and C are shown in Fig. 2. Sample A (with no $T_d$) experienced the formation of non-uniform pores which decreased the pore density of the whole sample. The electron micrograph of sample B shows that applying the $T_d$ = 2 min produced uniform pores, indicating that a $T_d$ of 2 min is long enough to prepare a silicon surface for homogeneous electrochemical etching and hence produces a uniform porous layer. The SEM image of sample C shows that applying extra $T_d$ ($T_d$ = 4 min) produces a smoother porous surface with lower porosity. Using gravimetric measurements [11], the porosity percentages for samples A, B, and C were calculated to be 71%, 83%, and 56%, respectively. Results show that the overall porosity of PS depends on the duration of electroless chemical etching of samples prior to the application of the pulsed current, whereby sample B produced the highest porosity.

During the delay, the crystalline silicon surface was affected by exposure to oxidant and etchant chemicals in the solution in the absence of a current. The electroless etching of silicon in fluoride solution occurred through the local coupling of redox reactions as follows [12]:

$$\text{Oxidation}: \ H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (1)$$

$$\text{Reduction}: \ Si + 4HF \rightarrow SiF_4 + 4H^+ + 4e^- \quad (2)$$

$$SiF_4 + 2HF \rightarrow H_2SiF_6 \quad (3)$$

$$\text{Overall}: \ Si + H_2O + 6HF \rightarrow 2H_2O + H_2SiF_6 + H_2\uparrow \quad (4)$$

The evolution of hydrogen bubbles during chemical etching proved the overall redox equation. During the delay, some points on the Si surface randomly become oxidation or reduction sites. A localization of primary pores in crystalline silicon happens as random points are resolved [13]. During the chemical process, the entire silicon surface has equal etching parameters, for example,

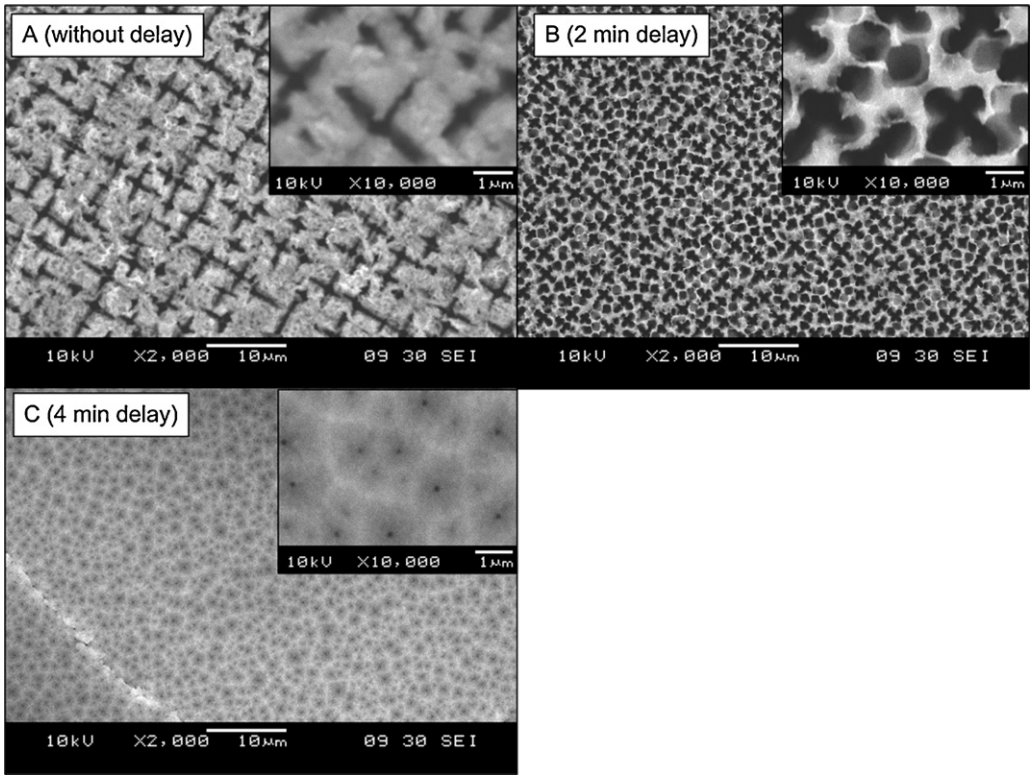


**Fig. 2.** SEM micrographs of porous samples A (no delay), B (2 min $T_d$) and C (4 min $T_d$). The insets are electron micrographs of porous samples with higher magnification.