# FABRICATION OF POROUS SILICON FOR MEMS DEVICES APPLICATION

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## Abstract

The porous layers can be used as sacrificial layers due to the high reactivity of the material which leads to a new class of micromachined MEMS devices. The porous silicon (PS) has been fabricated on p-type silicon wafers by anodization, photolithographic metal assisted etching and metal assisted chemical etching techniques. The surface and cross-sectional inspections of the silicon wafers were performed with a Scanning Electron Microscope (SEM) and the porosity of wafers is determined Fourier Transform Infrared Spectroscopy (FTIR). It is found that the porous formation in silicon can control with adjustable metal concentration and time by metal assisted etching method. According to the characterization results the metal assisted chemical etching method gives better porous morphological structure which is suitable for MEMS and sensor applications.

**Keywords:** porous silicon, MEMS, microsensor

## 1. Introduction

With the development of micro systems, there is an increasing demand for integrable porous materi als. In addition to those conventional applications, such as filtration, wicking, and insulating, many new micro devices, including micro reactors, sensors, actuators, and optical components, can benefit from porous materials [Natalya Tokranova, 2003]. Conventional porous materials, such as ceramics and polymers, however, cannot meet the challenges posed by micro systems, due to their incompatibility with standard micro-fabrication processes.

Porous Si and its modifications are allowed to fabricate a number of sensors for MEMS [Wolfgang Benecke]:

- gas-sensetive sensors of impedance (conductivity, capacity) or so-called “electrophysical sensors”;

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- optical and optoelectronic sensors (for example, luminescent photovoltaic, photoresistivity ones);
- sensors of mechanical strains (change of volt- ampere characteristics of p-n junctions on porous silicon);
- sensors for determination of changing the intensity of magnetic field in which the change of magnetic permeability is used.

In general, the sponge-like structure of PS is formed by an electrochemical etching process of a silicon substrate in hydrofluoric acid (HF) based electrolytes. The mechanism of pore generation depends on the availability of positive charge in the substrate. Positive charge carriers react at the silicon surface with fluorine ions. Thereby, a parasitic oxidation is an important aspect to release silicon atoms with HF from the substrate to create pores. The free standing porous skeleton retains the same chemical properties as the bulk silicon and the crystalline structure of the silicon is not changed. The new resulting surface is enlarged and very reactive compared to the original silicon surface. Various pore dimensions can be formed and tuned by the fabrication parameters [Jin Zheng, 2006].

The different types of porous silicon formed due to variations formed in the etching/ deposition conditions can be classified (IUPAC classification) into three categories viz.:

| | Pore size range |
|---|---|
| 1. Micro porous silicon | < 2 nm |
| 2. Meso porous Silicon and | 2 - 50 nm |
| 3. Macro porous silicon. | > 50 nm |

In this paper, porous silicon (PS) has been fabricated on p-type silicon wafers by anodization with different HF ratio and different current density, lithographic metal assisted chemical etching, and Ag assisted chemical etching.

### 1.1 Porous Formation Mechanisms in Anodization

In order to produce and optimize porous silicon materials for each application, it is important to understand the fundamentals of porous silicon formation. The most common method of forming porous silicon is electrochemical dissolution of silicon in a hydrofluoric acid (HF) based electrolyte. In the dissolution process, a silicon wafer serves as the anode, while any HF resistant conducting material, such as Pt, is used as the cathode. For this reason, the dissolution process is often called anodization.

Details of the chemical reactions of pore formation are not fully understood yet. Several theories suggest that two types of dissolution processes may be involved. The first one is direct dissolution, where the presence of holes weakens Si–Si backbonds and Si–H surface bonds, allowing them to be attacked by negative F− ions in the HF solution. A compound (SiF4) is then formed at the surface and breaks away from the substrate. In this reaction path, 1,2,3, or 4 holes may be involved. In the other dissolution process, the anodically biased silicon surface is first oxidized. The silicon dioxide is then dissolved by HF. This reaction path requires four holes. Since in the overall reaction the valence, the number of consumed holes for each dissolved silicon atom, is around 2.7, it is believed that the two dissolution processes must coexist. The actual occurrence percentage of each process is self adjusting, decided by the anodization conditions. Since the direct dissolution path etches silicon anisotropically while the oxidation path is more isotropic, any shift of the balance between two processes may cause change in morphologies of the resulting porous silicon [Bisis, et. al., 2000].

### 1.2 Pore Formation Mechanism in Metal-Assisted Chemical Etching

As far as the mechanisms and reactions involved in the formation of PS structures produced by metal-assisted etching is concerned, it is well-known that chemical and electrochemical reactions occur near the interface between the noble metal and the silicon substrate when the system is immersed in an etchant composed of HF and $H_2O_2$. So far, several reaction models have been proposed to describe the electrochemical reactions taking place during the formation of porous silicon by metal-assisted etching [Chunlin He, et. al., 2016]. In this system, the noble metal works as a cathode,

where hydrogen peroxide is reduced at the metal surface following these electrochemical reactions while the silicon works as the anode:

$$H_2O_2 + 2H+ \rightarrow 2H_2O + 2H^+$$

$$2H^+ \rightarrow H_2\uparrow + 2H^+$$

In summary, metal-assisted etching of porous silicon can be divided into four stages Figure 1.

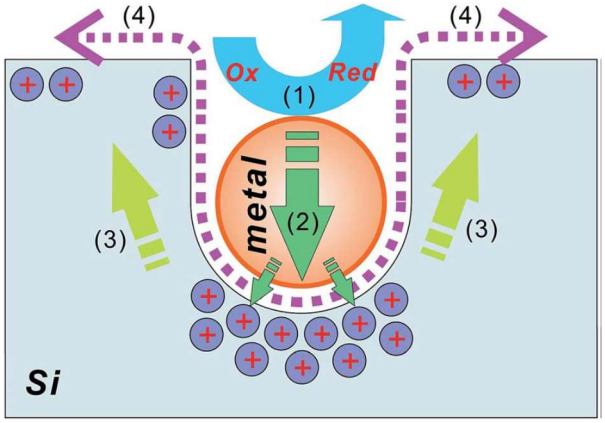


**Figure 1.** Illustration of the metal-assisted chemical etching process:

(1) Reduction of an oxidative agent (such as $H_2O_2$) catalyzed by a noble metal particle;

(2) Injection of the holes generated during the reduction reaction, into the silicon substrate, with the highest hole concentration underneath the metal particle;

(3) Migration of holes to silicon sidewalls and surfaces; and

(4) Removal of oxidized silicon via HF.

## 2. Experimental

### 2.1 Porous Silicon Preparation by Anodization Method

There are two types of anodization cells which is single tank and double tank cells that are commonly used to produce porous silicon. In the single-tank cell, a metallic contact is made to the backside of the wafer. An O-ring is used to seal around the edge of the wafer so that only the front side of

the sample is exposed to the electrolyte. Due to its simple configuration, single-tank cell is the most commonly used arrangement.

All of the etching cells are made of HF resistant materials, such as Teflon and polypropylene. Since HF is a very dangerous and aggressive chemical, safety has been given highest priority in the designs of all etching cells. Figure 2 shows anodization in a single-tank Teflon holder with Pt electrode for etching small samples. The schematic diagram for assembling and using this fixture is shown in Figure 3. The cover piece and the bottom piece of the holder are bolted together during the etching process to hold a silicon sample in place.

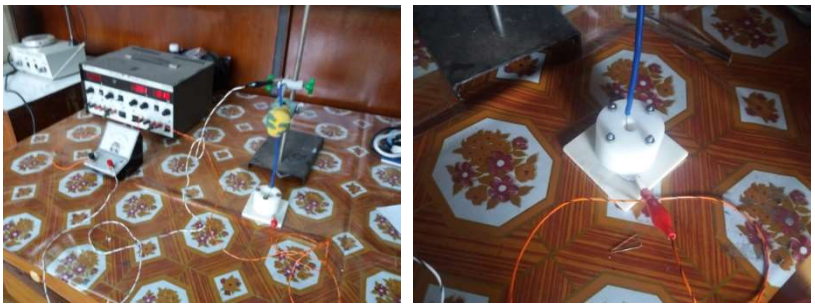

**Figure 2.** Anodization set up by single-tank Teflon holder with Pt electrode for etching small samples

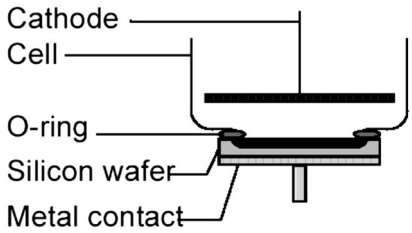


**Figure 3**. Schematic diagram for assembling of anodization

### 2.2 Porous Silicon Preparation by Metal Assisted Chemical Etching Method

Si wafers were etched into a single tank cell with a different concentration and amount of $AgNO_3$ solution by adding in a solution of 1:1:2 (V:V:V) 40%HF:30%$H_2O_2$:$H_2O$. The remaining Ag is removed from the textured Si surface by etching in aqueous solution of 30% $HNO_3$ at room temperature for 20 min.

On the other technique, the silicon wafers were washed with ethanol and acetone under ultrasonic wave, then a silver particle thin layer was electroless deposited by immersing the silicon wafers in a 5 mM $AgNO_3$ salt solution for 5 min at room temperature, after the Ag-covered Si wafers were slightly rinsed in deionized water, they were immersed in a solution of 1:1:2 (V:V:V) 40%HF:30%$H_2O_2$:$H_2O$ in ultrasonic bath for 30min. Finally, the etched Si wafers were rinsed thoroughly with deionized water, ethanol and acetone, respectively, and dried.

### 2.3 Selected Porous Silicon Preparation by Photolithography Method

PS structures with precisely controlled and exquisitely defined morphology and geometric features can be produced when the surface of the silicon wafer is patterned by lithographic techniques prior to the etching step. In particular, some lithographic methods have demonstrated outstanding results when combined with metal-assisted etching in this work.

## 3. Results and Discussion

### 3.1 Characterization of Porous Silicon Prepared by Anodization

Table 1 shows comparison of porous formation with different current density and electrolyte solution ratio and same etching time by anodization method. The size of porous increased with HF ratio according to the SEM images.

Scanning electron microscope (SEM) has been used to analysis surface morphology and cross sectional view of the PS layers produced with different formation parameters. It is found that porous formation in silicon as shown in Figure 4 by anodization. Although porous formation is uniform in electrolyte

HF: ethanol = 2:1 ratio, it is not uniform in HF: ethanol = 1:1 ratio at current density 10mA/cm$^2$ and porous formation is low.

Another porous formation is shown in Figure 5 at same ratio (HF: ethanol: water = 1:2:3) with different current density 10mA/cm$^2$ and 25mA/cm$^2$. The porous formation using 25mA/cm$^2$ is better than 10mA/cm$^2$ according to the SEM images.

Figure 6 shows the porous silicon formation with different electrolyte ratio and current density. It is also found that the porous formation depends on electrolyte ratio and current density. Thus porous silicon making by anodization is difficult to control porous formation and to find optimum point.

**Table 1**. Comparison of porous formation with different electrolyte ratio and current density by anodization method

| **Method** | **Electrolyte Solution** | **Current Density (mA/cm$^2$)** | **Etching Time (min)** | **Porous Formation** | **Average Pore Size(μm)** |
|---|---|---|---|---|---|
| A1 | HF:ethanol (1:1) | 10 | 10 | Non-uniform | 1 |
| A2 | HF:ethanol (2:1) | 10 | 10 | Uniform | 3 |
| A3 | HF:ethanol:$H_2O$ (1:2:3) | 10 | 10 | Uniform | Unobservable |
| A4 | HF:ethanol:$H_2O$ (1:2:3) | 20 | 10 | Uniform | 5 |
| A5 | HF:ethanol:$H_2O$ (1:1:3) | 10 | 10 | Non uniform | 4 |
| A6 | HF:ethanol:$H_2O$ (1:1:3) | 20 | 10 | Uniform | Unobservable |

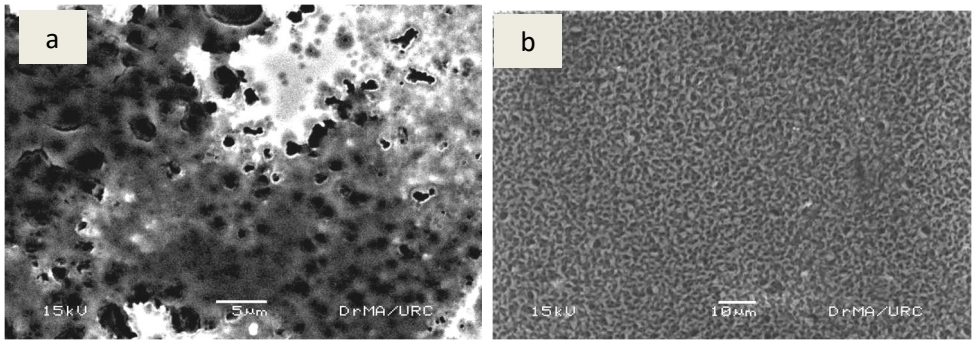


**Figure 4.** SEM photographs of porous formation using (a) A1 and (b) A2 method

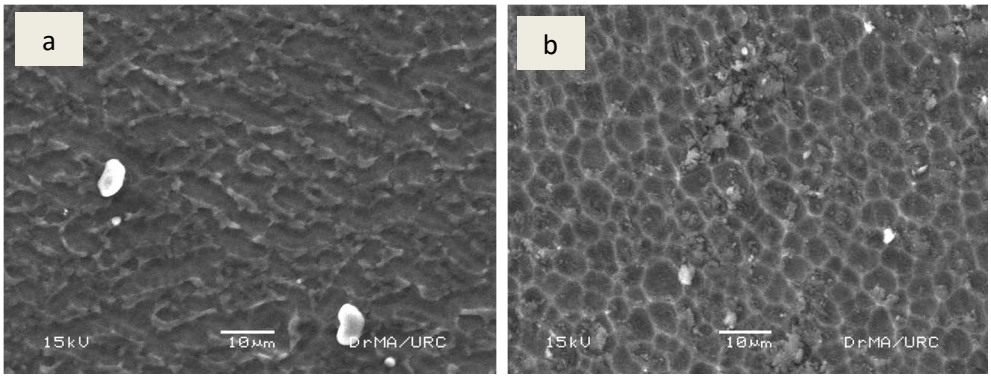


**Figure 5.** SEM photographs of porous formation using (a) A3 and (b) A4 method

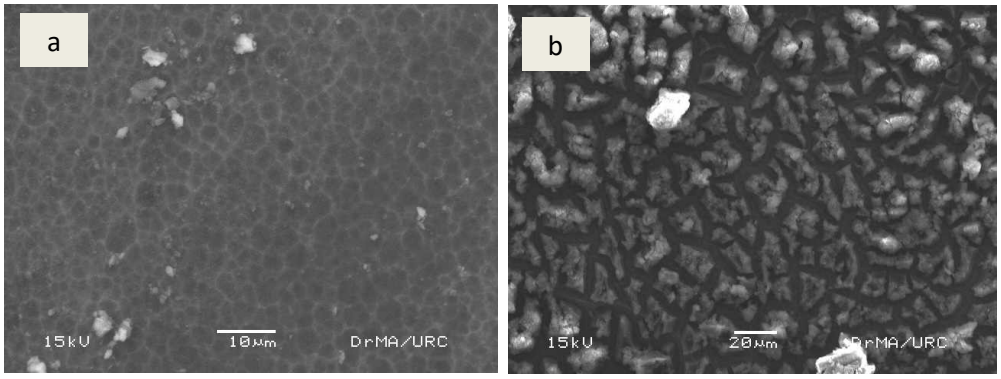


**Figure 6.** SEM photographs of porous formation using (a) A5 and (b) A6 method

### 3.2 Characterization of Porous Silicon prepared by Metal Assisted Chemical Etching

Another technique to make porous silicon is metal assisted chemical etching. In this research, silver is used as novel metal for metal assisted etching. Table 2 shows the comparison of porous formation with different chemical ratio and etching time by metal assisted chemical etching.

It is found that the porous formation is very uniform in 4.7mM of $AgNO_3$ concentration solution with hydrofluoric acid, hydrogen peroxide and water (1:1:2) volume ratio according to SEM images (Figure 7 – 9). It is also found that the pore size depend on the etching times. The average pore sizes are 2 μm for 1 hour, 3 μm for 2 hours and 4 μm for 3 hours etching time as shown in Table 3. Figure 15 shows the porous thickness or pore length using C1 method after 3 hours etching time. Therefore, this etching method was used to fabricate micro sensor in this work.

From the Figure 12, it is found that nano porous formation in low $AgNO_3$ ratio but porous formation is low. In strong $AgNO_3$ ratio, the porous formation is uniform but it is found that silicon is strong etched by this ratio (Figure 13). Thus, it is found that porous formation can control by changing of $AgNO_3$ concentration and amount.

The next method is silver-layer deposition before etching (SDBE). The silicon substrate deposited by electroless plating. Figure 14 is the SEM surface morphology of PS wafer produced by SDBE method in which 5 mM $AgNO_3$ salt solution used for 15 min at room temperature for plating. It is found that the density and thickness of the Ag nanoparticle layer increase with prolonged immersion time (plating time), however, the size of the Ag particles remains almost the same. Fine, uniform and single dispersed Ag nanoparticles benefits to prepare homogenous meso porous structure on the Si surface. It estimates porous size is less than 0.5 μm. Thus, it is difficult to measure accuracy pore size with current facility.

**Table 2.** Comparison of porous formation with different chemical ratio and etching time by metal assisted chemical etching

| **Method** | **HF:$H_2O_2$:$H_2O$** | **$AgNO_3$** | **Etching (hour)** | **Porous Formation** | **Average Pore size (μm)** |
|---|---|---|---|---|---|
| C1 | 1:1:2 | 0.2 mL (4.7mM) | 1 | Uniform | 2 |
| C2 | 1:1:2 | 0.3 mL (4.7mM) | 1 | Uniform | 3 |
| C3 | 1:1:2 | 0.6mL (4.7mM) | 1 | Uniform | Unobservable |
| C4 | 1:1:5 | 0.2 mL (2.3mM) | 5 | Uniform | 1 |
| C5 | 1:1:5 | 0.1 mL (2.3mM) | 5 | Uniform | Unobservable |
| C6 | 5:5:0 | 1mL (5mM) | 15min | Uniform | 0.5 |
| C7 | 1:1:0 | 1mL (0.2M) | 15min | Uniform | Unobservable |

**Table 3.** Comparison of pore formation for different etching time using C1 method

| **Method** | **HF:$H_2O_2$:$H_2O$:$AgNO_3$ (40%V:30%V:V: 4.7mM of V)** | **Etching time (hour)** | **Average Pore Size (μm)** |
|---|---|---|---|
| C1 | 5:5:10:1 | 1 | 2 |
| C1 | 5:5:10:1 | 2 | 3 |
| C1 | 5:5:10:1 | 3 | 4 |

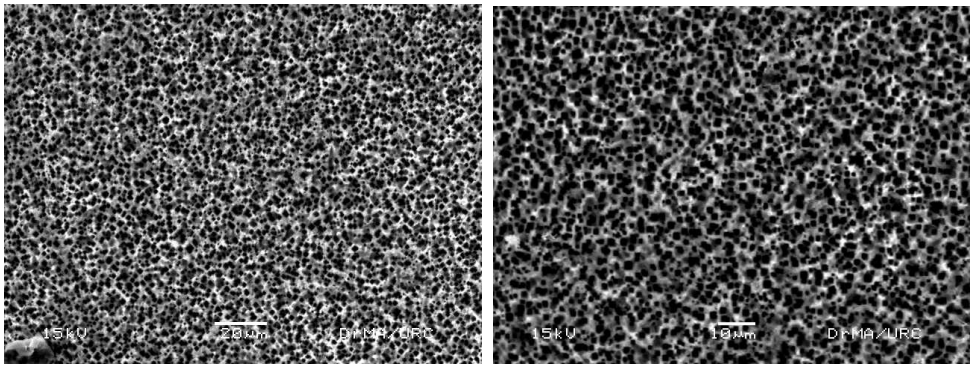


**Figure 7.** SEM photographs of porous formation using C1 method

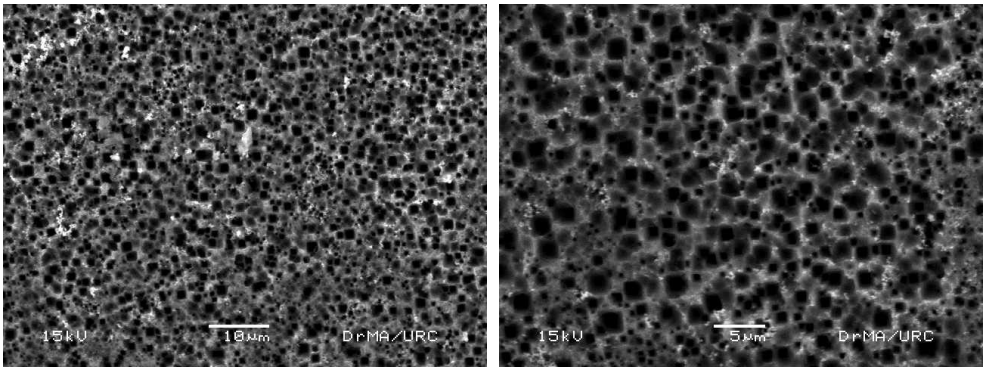


**Figure 8.** SEM photographs of porous formation using C2 method

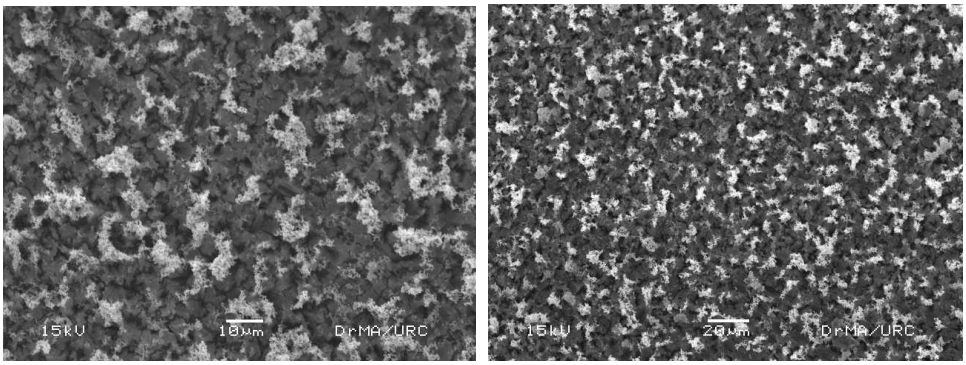


**Figure 9.** SEM photographs of porous formation using C3 method

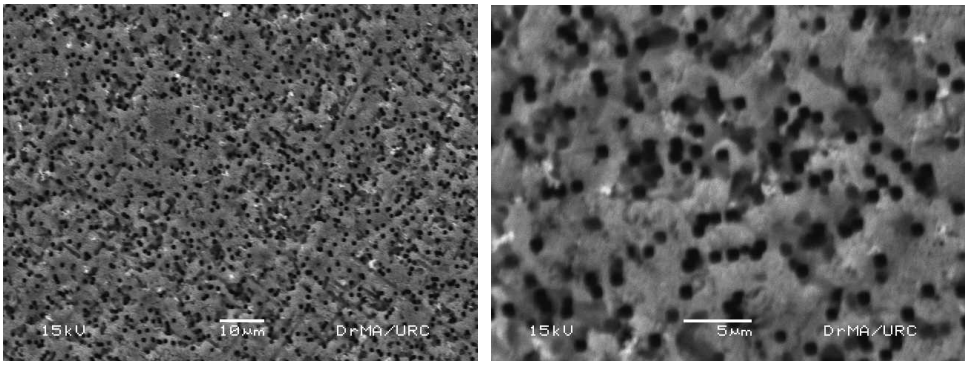


**Figure 10.** SEM photographs of porous formation using C4 method

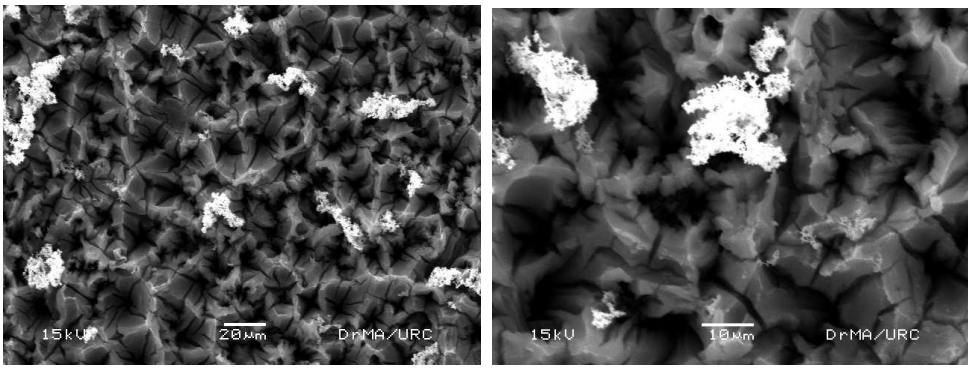


**Figure 11.** SEM photographs of porous formation using C5 method

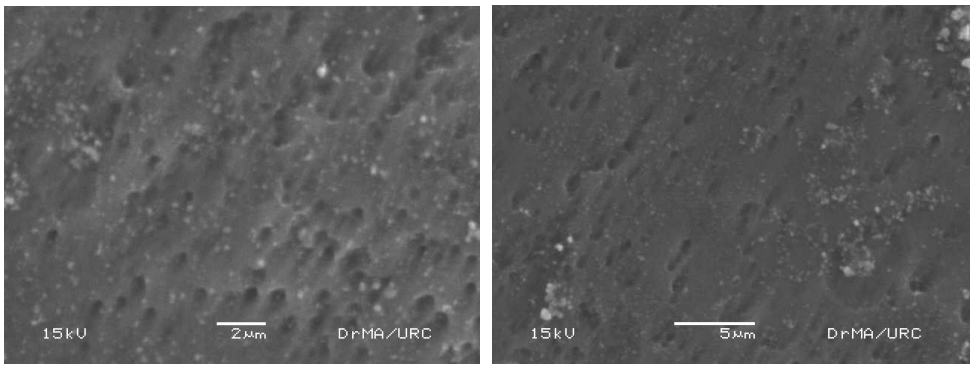


**Figure 12.** SEM photographs of porous formation using C6 method

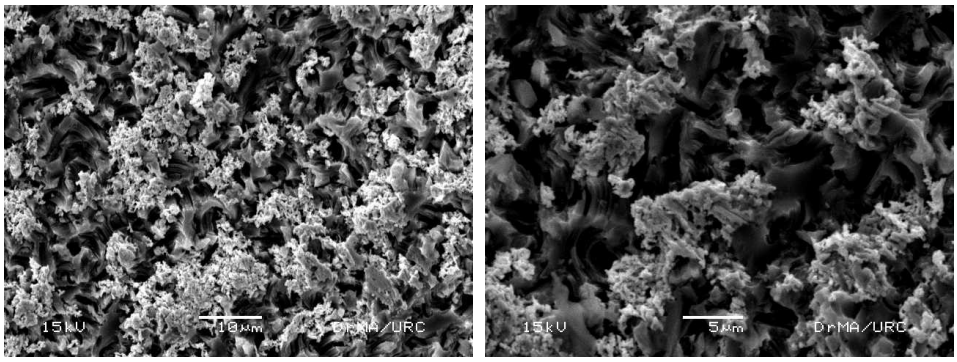


**Figure 13.** SEM photographs of porous formation using C7 method

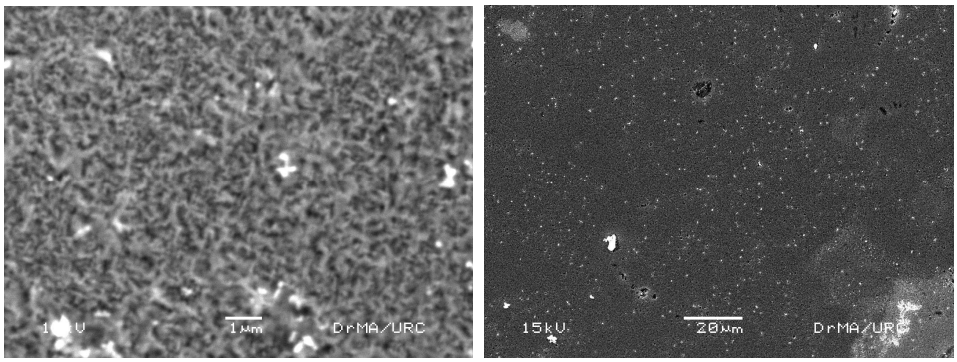


**Figure 14.** SEM images of porous formation using SDBE method

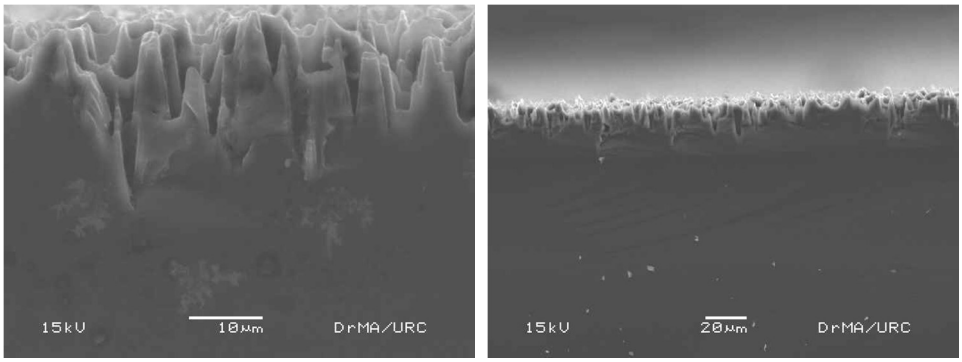


**Figure 15.** SEM images of porous thickness or pore length using C1 method after 3 hours etching time

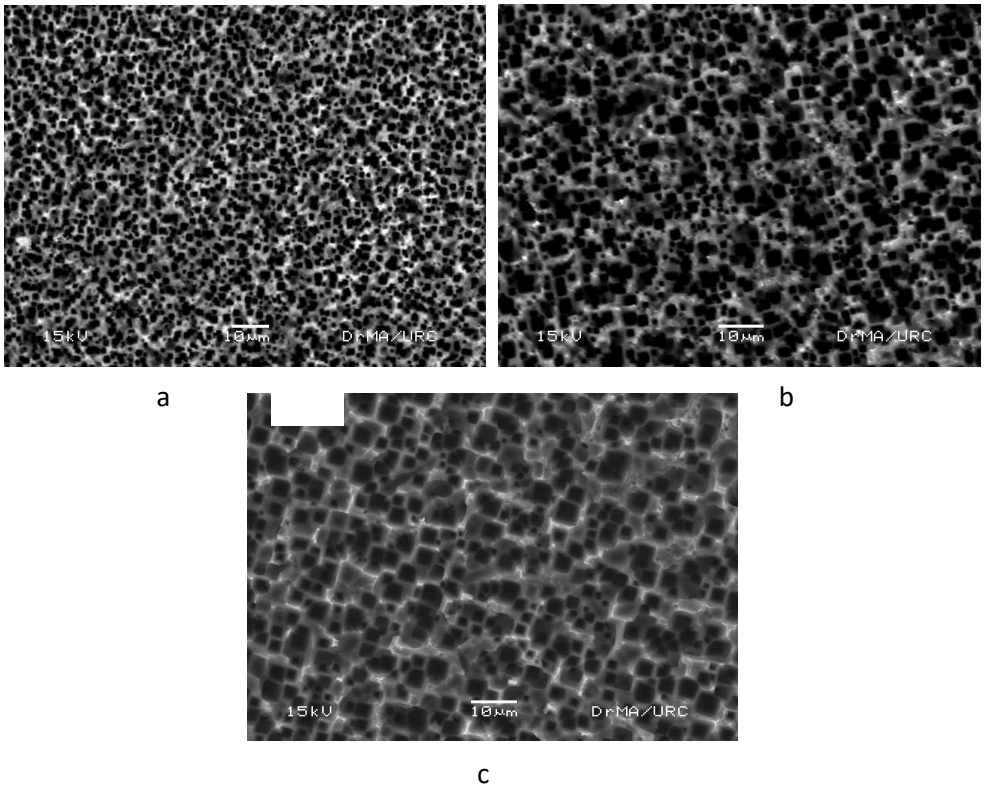


**Figure 16**. SEM photographs of porous size formation using C1 method for (a) 1 hour (b) 2 hours (c) 3 hours

### 3.3 Characterization of Porous Silicon prepared by Hybrid Method

The lithographic approach makes it possible to produce porous silicon on specific area with controlled geometry, morphology and size. The mask design is limited to get sub micron size and the mask is used with 40 µm resolution. Therefore, lithographic approach can select that porous area. The porous formation with Ag assisted chemical etching using lithographic approach is shown in Figure 17. A rounded porous size area is about 250µm$^2$. This method can make a nano porous formation in the specific area.

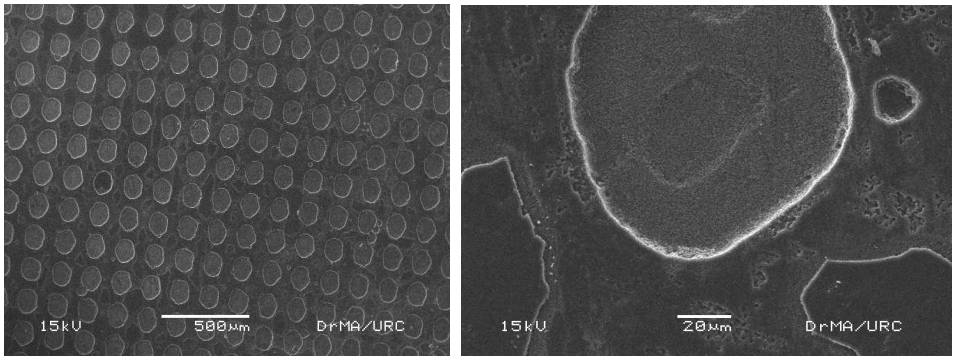


**Figure 17.** SEM photographs of porous formation using lithographic metal assisted chemical etching

### 3.4 Characterization of Porous Silicon by XRD

One important property of porous silicon is that its skeleton maintains the structure of silicon crystalline after anodization by X-ray topography studies. The X-ray beam is diffracted at specific angular positions with respect to the incident beam depending on the phases of the sample. When crystal size is reduced toward nanometric scale, then a broadening of diffraction peaks is observed and the width of the peak is directly correlated to the size of the nanocrystalline domains [Lorusso A., et. al. 2009]. The broadening peak of the PS can be compared with bulk silicon as shown in Figure 18.

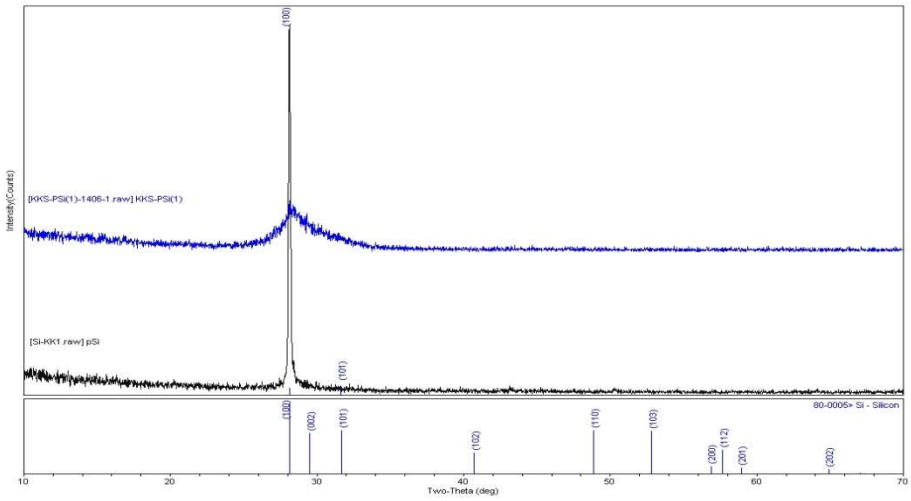


**Figure 18.** XRD characterizations of bulk silicon and porous silicon

### 3.5 Characterization of Porous Silicon by FTIR

Surface chemical composition of PS is best probed with Fourier Transform Infrared (FTIR) spectrophotometer. The FTIR spectra of the p-type porous silicon are shown in Figure 19. In the transmittance spectrum, peak at 624.96 $cm^{-1}$ represents Si-H bending ($Si_3SiH$), peak at 852.56 $cm^{-1}$ shows Si-$H_2$ wagging mode and peak at 910.23 $cm^{-1}$ illustrates Si-$H_2$ scissor mode [Bisis et.al.2000]. The peak at around 1074.30 $cm^{-1}$ is due to Si–O–Si stretching modes [Yue Zhao et. al. 2005], which are depended on the oxidation degree of porous silicon. Furthermore, 2096.69 $cm^{-1}$ and 2922.25 $cm^{-1}$ are, respectively, related to Si–H stretch ($Si_3$-SiH) and C-H stretch ($CH_2$) [Andrea Edit PAP, 2005 and Dimova D., 2000]. Chemical bonds and their IR resonance positions detected in PS are shown in Table 4. Si-H bonds play an important role in regulating optical electrical and gas sensing properties of porous silicon.

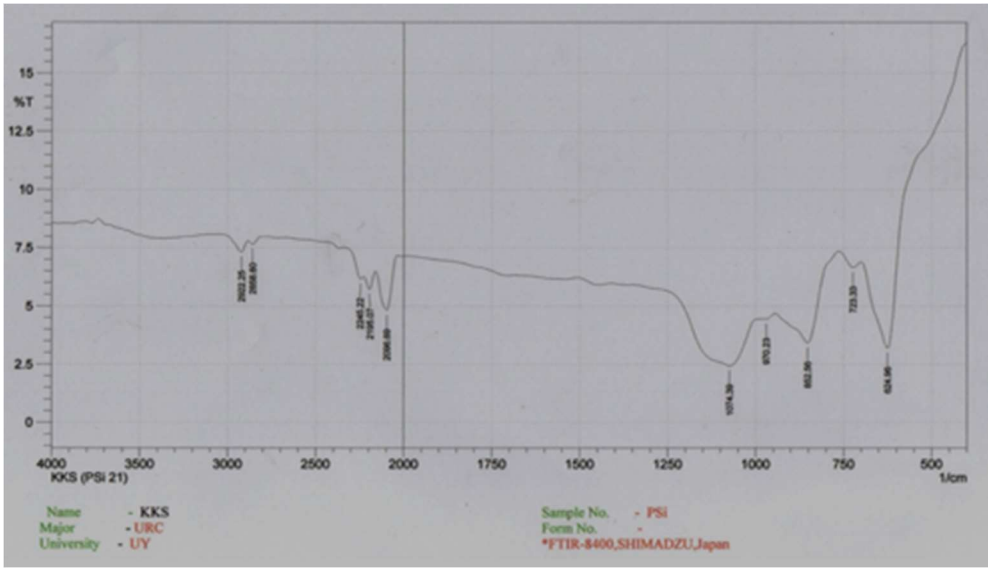


**Figure 19**. FTIR transmittance spectrum of a PS layer

**Table 4.** Peaks of PS sample observed FTIR spectrum

| **Peak position ($cm^{-1}$)** | **Attribution** |
|---|---|
| 624.96 | Si-H bending |
| 852.56 | Si-$H_2$ wagging |
| 910.23 | Si-$H_2$ scissor |
| 1074.30 | Si–O–Si stretching |
| 2096.69 | Si–H stretch ($Si_3$-SiH) |
| 2922.25 | C-H stretch ($CH_2$) |

## Conclusion

Porous silicon has been fabricated in p-type silicon by anodization, metal assisted chemical etching and lithographic metal assisted etching. Although porous formation by anodization technique is more than another technique, it is difficult to make uniform porous silicon. It is found that the porous formation in silicon can control with adjustable metal concentration and time by metal assisted chemical etching method. Lithographic approach method can select uniformly porous area with metal assisted etching but the minimum porous selected area is 250 $\mu m^2$. According to the characterization results the metal assisted chemical etching method gives better porous morphological structure which is suitable for MEMS and sensor applications.

## References

1. Andrea Edit PAP, (2005), "Investigation of Pristine and Oxidized Porous Silicon", University of Oulu.

2. Bisis, Ossicini S. and Pavesi L., (2000), "Porous silicon: a quantum sponge structure for silicon based optoelectronics", Surface science reports 264.

3. Chunlin He, Xuefei Yang, Guofeng Ma, Jianming Wang, Zhaofu Du, Dongliang Zhao, Qingkui Cai, (2016), "Fabrication of Anti-reflecting Silicon Surfaces for Solar Cells Using Ag Assisted Chemical Etching", Liaoning Provincial Key Laboratory of Advanced Materials, Shenyang University, Shenyang University, 110044, China.

4. Jin Zheng, Wallner, (2006), "Porous silicon technology for integrated Microsystems", Dissertation, Michigan Technological University.

5. Lorusso A., Nassisi V., Congedo G., Lovergine N., Prete P., (2009), "Pulsed plasma ion source to create Si nanocrystals in $SiO_2$ substrates", Applied Surface Science.

6. Natalya Tokranova, Xiaojun Feng, Steve Olson, Tang Tang, Bai Xu, James Castracane, (2003), "Fabrication of MEMS Devices with Macroporous Silicon Membrane Embedded with Modulated 3D Structures for Optimal Cell Sorting", School of Nanosciences and Nano Engineering, University at Albany (SUNY), 251 Fuller Rd, Albany, New York

7. Wolfgang Benecke and Alexandra Splinter, "MEMS Applications of Porous Silicon", Institute for Microsensors, -actuators and -systems (IMSAS**),** University of Bremen _ Dept. 1 Physics/Electrical Engineering, Kufsteiner Str. _ D-28359 Bremen GERMANY

8. Yue Zhao, Deren Yang, Dongsheng Li, Minghua Jiang, (2005),"Annealing and amorphous silicon passivation of porous silicon with blue light emission", Applied Surface Science 252, 1065–1069.

9. Zhipeng Huang, Nadine Geyer, Peter Werner, Johannes de Boor, and Ulrich Gösele in memory of Prof. Ulrich Gösele, 2013, "Metal-Assisted Chemical Etching of Silicon: A Review", Max Planck Institute of Microstructure Physics Weinberg 2, D-06120 Halle, Germany, Functional Molecular Materials Centre Scientific Research Academy, Jiangsu University, China.