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# Porous Silicon Surface Stability Studies by Thermal Treatment of Forming Gas

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**Abstract:** Porous silicon sample was electrochemically etched and then treated with forming gas. While investigating with scanning electron microscope (SEM), micro-Raman, Photoluminescence (PL) and Fourier Transform Infrared (FTIR) spectroscopy, it is found that the sample was stable for six months. The Raman and PL results show almost overlapping peak and intensity after six months which depicts six months surface stability of sample. Electrical capacitive sensing technique was also used to check the ageing effect of the sensor device. Ethanol vapor sensing was periodically checked in the range of 25-100 ppm for six months, and no degradation is observed in its sensing performance. *Copyright © 2015 IFSA Publishing, S. L.*

**Keywords:** Porous silicon, Electrochemical etching method, Forming gas, Sensing and stability.

## 1. Introduction

Porous silicon (PS) is a promising material which has attracted numerous attentions, because of its specific large surface area and it is compatible with integrated silicon-based IC technology. PS have a huge technological impact such as microelectronics [1], sensors [2], biochemistry [3] and optoelectronics [4]. From several years, researchers have reported porous silicon formation by various techniques, notably chemical etching [5], electrochemical- and photo-induced electrochemical anodization [6], and Plasma etching[7] etc. The major drawback in all the cases is the surface degradation while exposed to ambient atmosphere. Because of this drawback, the possibility of PS for further use as a device lacks. It has been already reported that the porous silicon is oxidized when store in ambient air and hence the electronic properties of porous silicon get changed [8-9].

Several treatments to stabilize the porous silicon structure have been reported [10-16] from last few years. The thermal oxidation and thermal carbonization, in particular, are very efficient technique reported by many researchers for the surface stability of PS [10-14].

In this work, the authors report, the PS was treated with forming gas (Composition: 10 % $H_2$ and 90 % Ar gas) and examined by transmission FTIR studies, SEM results, Raman and PL measurements. The results show that if a PS sample is intentionally thermally treated with forming gas, then its surface remains stable for one year. These results are also verified by testing the sensor cycle performances of ethanol vapors over a period of one year by using capacitive techniques.

## 2. Experimental

Porous silicon samples were manufactured by electrochemical etching (Fig. 1) of boron-doped p-type Si (100) wafers with a resistivity of 1-10 Ω.cm in an HF and ethanol mixture (1:1 by volume). The

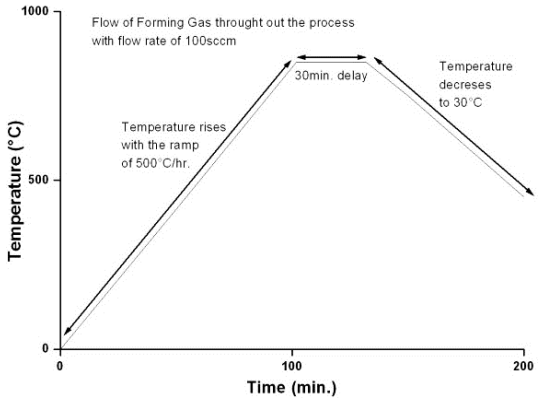
etching current density and time were fixed as 25 mA/cm$^2$ and 25 min., respectively.

Then the sample was kept in a conventional tube furnace (Fig. 2) for treating it with forming gas (Composition: 10 % $H_2$ and 90 % Ar gas). The thermal annealing pressure was kept at 15 mBar with heating rate of 500°C/hr. During this process, the forming gas flow rate was kept at 100 sccm. As the temperature raised upto 850°C, the sample was kept for 30 min. in the presence of forming gas. Experimental protocol of this process is shown in Fig. 3(a) and the schematic diagram of this process is shown in Fig. 3(b).

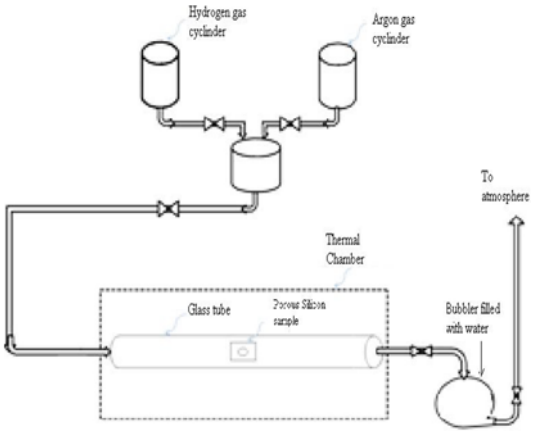
**Fig. 1.** Electrochemical etching cell.


**Fig. 2.** CVD chamber setup.

Fourier Transform Infrared spectroscopy (FTIR) measurements were done with BRUKER vertex 70 V instrument. FTIR spectroscopy was characterized by diffuse reflectance mode to remove the influence of the substrate. For Raman measurement we used micro-Raman spectrophotometer (LabRAMHR800, JY) fitted with Peltier cooled CCD detector and an Olympus BX-41confocal microscope. The excitation of the samples was performed with an air-cooled argon laser (Spectra Physics) tuned at 488 nm. The spot size was 1.19 μm at sample surface under optimal conditions. Measurements were carried out in the back scattering geometry using a 50X LWD microscope objective. The laser power was kept low on the sample surface to avoid excessive heating.




(a)




(b)

**Fig. 3.** (a) Experimental Protocol, (b) Schematic diagram.

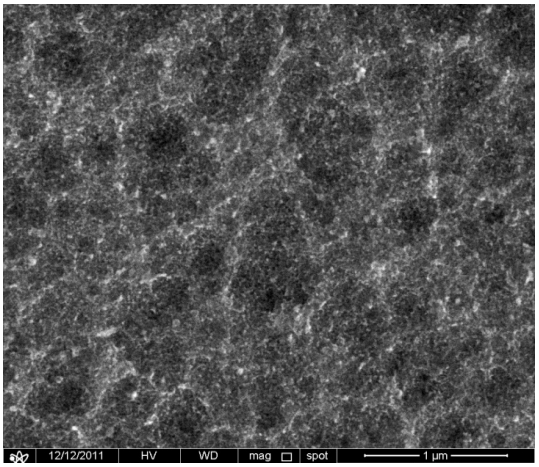
## 3. Results and Discussion

### 3.1. SEM Analysis

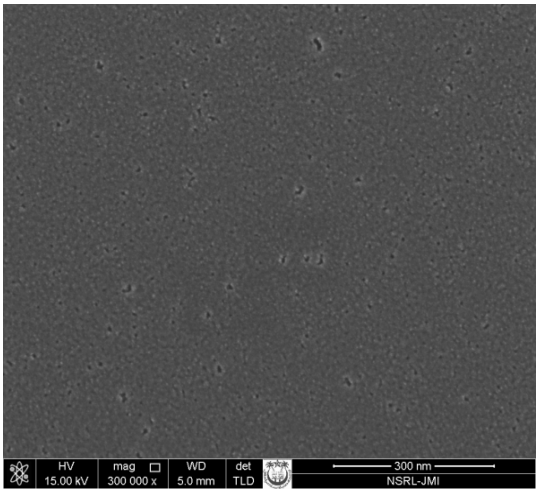
For surface structural analysis, Field Emission Scanning Electron Microscope (FEI, Nova Nano SEM 450) was used. The SEM image of PS (Fig. 4(a)) indicates the presence of well-dispersed nanopore of diameter distribution in the range 40-60 nm. Fig. 4(b) shows SEM image of sample after thermally treated with forming gas and it is observed that an oxide layer has been developed on sample.

### 3.2. RAMAN Analysis

The Raman measurements were taken up by LabRAM HR800 JY. The Raman Peak of Sample just after treated with forming gas was found at 514 cm$^{-1}$ (Fig. 5).




(a)




(b)

**Fig. 4.** SEM image of Sample: a) before thermally treated, and b) After thermally treated with forming gas.

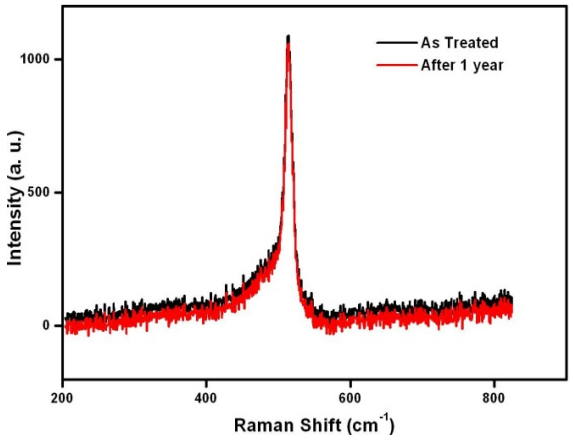



**Fig. 5.** Raman Spectra of Sample which was thermally treated with forming gas.

The Raman peak positions and spectral asymmetry profiles confirm (a) faster etching rate, (b) increase in porosity of porous silicon (PS), and (c) decrease in silicon crystallite size [17]. After one year, the Raman Peak positions remain unchanged for sample.

### 3.3. Photoluminescence (PL) Analysis

Surface stability of PS samples was checked by PL studies over a period of one year. With aging the surface of porous silicon samples degrades while creating surface functional complex either with oxygen, or hydrogen or both. These complexes basically create surface states in the electronic band structure of porous silicon and photoluminescence emission takes place via these states. These states act like non-radiative recombination centre for e-h pairs; as a result there is a loss in emission intensity causing the decrease in PL intensity [6, 18]. Due to this treatment, PL peaks was observed at 1.81 eV. After one year of shelf life, it was observed that PL of sample (Fig. 6) shows almost overlapping spectra which shows good stability of PS surface.

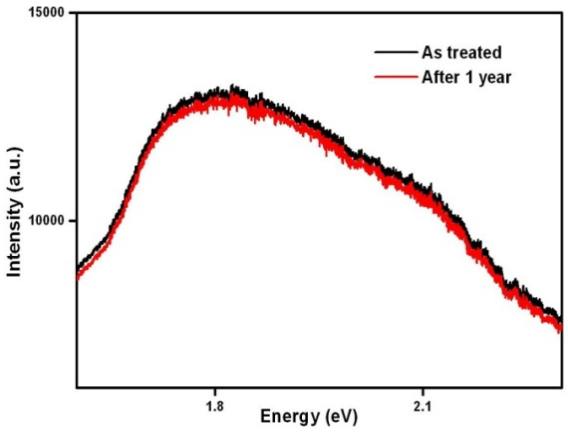



**Fig. 6.** PL Spectra of Sample which was thermally treated with forming gas.

### 3.4. FTIR Analysis

FTIR studies have been performed in the range of 500 to 4000 $cm^{-1}$ for the identification of the functional group attached on the surface of sample after thermally treated with forming gas. Fig. 7 shows FTIR spectrum of thermally treated sample. The peak at 3491 $cm^{-1}$ are attributed to γ(Si-OH) stretching modes. At lower wave numbers, the γ(-$O_y$Si-$H_x$) and γ(Si-$H_2$) absorbencies at 2749 and 2170 & 1636 $cm^{-1}$ are present. As well as the Si-O-Si modes at 1258 $cm^{-1}$ and $O_3$Si-H modes at 845 $cm^{-1}$ are present. Also, various deformation modes overlapping the silicon crystal modes which are observed 510 $cm^{-1}$ are present. The FTIR spectra show that the Si-O bonds formed due to the oxidation of sample. The samples were periodically checked for one year and it was found that all the specific modes mentioned above retain their characteristic peak position and intensity and this confirms the achievement of surface stability

(Fig. 7).The significance of FTIR peaks and their corresponding presence in sample are mentioned in Table 1.

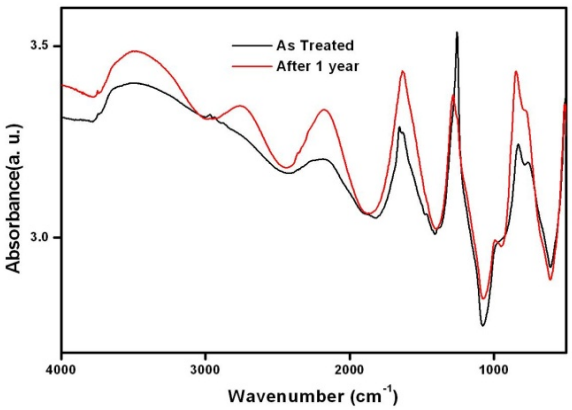



**Fig. 7.** FTIR Spectra of Sample which was thermally treated with forming gas.

**Table 1.** FTIR modes with their significance. (Note: signifies the presence of FTIR modes in samples, while X signifies the absence of FTIR modes in samples.)

| Frequency ($cm^{-1}$) | Significance (Modes) | Sample | |
|---|---|---|---|
| | | As treated with forming gas | After 1 etar |
| 845 | $O_3Si-H$ [19] | ✓ | ✓ |
| 1258 | Si-O-Si [20] | ✓ | ✓ |
| 1636 | $\gamma(Si-H_2)$ [19] | ✓ | ✓ |
| 2170 | $\gamma(Si-H_2)$ [19, 21] | ✓ | ✓ |
| 2749 | $\gamma(-O_ySi-H_x)$ [19] | ✓ | ✓ |
| 3491 | γ(Si-OH) [19,22] | ✓ | ✓ |

### 3.5. Sensing Analysis

The sensing studies by PS based capacitive sensor were done for ethanol vapor in the range 25-100 ppm. Fig. 8 shows the sensitivity (%) vs. quantity (μL) of sample with ethanol concentration, and it is observed that it exhibits best sensing performance as well as surface stability for a longer duration of time. The sensitivity measurement of sample was plotted in Fig. 8 where it characterizes the magnitude of a response to a particular analyte. The sensitivity in this work has been calculated as the incremental change in the output of the sensor to its incremental change in the measured input. Sensitivity is calculated with the following formulae [23]:

$$Sensitivity(\%) = \frac{(C_{initial} - C_{final})}{C_{initial}} \times 100, \qquad (1)$$

where $C_{initial}$ is the initial capacitance before exposing to the analyte, in our case ethanol vapors, $C_{final}$ is capacitance when the sample was fully exposed by ethanol vapors.

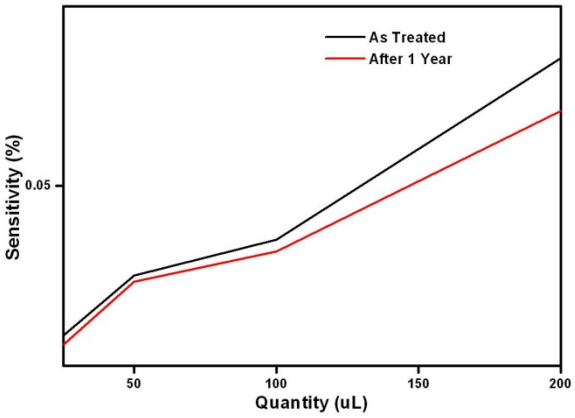



**Fig. 8.** Quantity (μL) vs. Sensitivity (%) Plot.

## 4. Conclusions

We have presented a technique to achieve the surface stability of PS by thermally treated the PS surface with forming gas. The surface morphology studies were carried out by SEM, Raman, PL and FTIR studies. These results show that there is no degradation of surface for one year after treating the sample with this technique. Ethanol sensing of treated sample was also done and the results confirm that the sample was sensitive for longer duration of time (one year).

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