



## Fabrication of p-Type Nano-porous Silicon Prepared by Electrochemical Etching Technique in HF-Ethanol and HF-Ethanol-H<sub>2</sub>O Solutions

A. Massoudi<sup>a\*</sup>, M.E. Azim-Araghi<sup>b</sup>, M. Keihan Asl<sup>a,b</sup>

<sup>a</sup>Department of Semiconductors, Materials and Energy Research Center, Karaj, Iran

<sup>b</sup>Department of physics, Kharazmi University, Tehran, Iran

### PAPER INFO

#### Paper history:

Received 28 January 2015

Accepted in revised form 16 March 2015

#### Keywords:

Nano-porous Silicon  
Mesopore  
Electrochemical Etch Tuning  
Field emission scanning electron-  
microscopy

### ABSTRACT

Nano-porous silicon were simply prepared from p-type single crystalline silicon wafer by electrochemical etching technique via exerting constant current density in two different HF-Ethanol and HF-Ethanol-H<sub>2</sub>O solutions. The mesoporous silicon layers were characterized by field emission scanning electron microscopy and scanning electron microscopy. The results demonstrate that the width of nano-pores changes from 7 nm to 60 nm by varying current density from 10 mA/Cm<sup>2</sup> to 40 mA/Cm<sup>2</sup>, respectively and the depth of nano-pores also alters by applying different values of etching duration. It is concluded that varying current density leads to different width of pores while varying etching duration results in various depth of pores. Such etch tuning process is applicable for fabricating different nano-sized porous silicon for many modern electronic devices.

## 1. INTRODUCTION

Silicon is a material with many particular molecular properties that can be a worthy candidate for many chemical devices such as sensing systems and anode materials for Li-ion battery [1-3]. Nevertheless, silicon is not considered a suitable material for many devices owing to its low surface area [4-5]. On the other hand, porous silicon (PSi) is currently a very applicable material due to its own unique surface, electrical and optical properties [6]. In general, porous materials are categorized into three classes according to pore sizes: macropore (above 50 nm in size), mesopore (50 – 2 nm) and micropore (below 2 nm) [7]. Recently, the synthesis of mesopore PSi has attracted increasing concerns because of its favorable characteristics for series of fabricating devices ranging from optoelectronics to electrochemical power sources [8-9].

Many fabrication techniques are specified to produce PSi [10]. In particular, electrochemical etch is the main method for fabricating PSi because electrochemical parameters of the process conditions obtaining better control of the physical features of the PSi. The method has benefits of being simple, repeatable and economic

to produce PSi compared to vacuum-based thin film fabrication such as e-beam lithography [11].

Some researchers reported the diverse morphological structures of PSi electrochemically etched under varying the experimental parameters [11]. Kim and Cho reported the changes of the morphology of PSi are in relationship with the Si wafers and electrolyte resistance [12]. Depending on the electrical resistivity of Si wafers compared to that of the electrolyte, the fabrication of mesopores can be triggered at a critical current density [12]. The critical current density is changed when the composition of the electrolytes is varied [12].

In this study we investigated the change of morphological features of PSi samples under a range of electrochemical etching conditions, such as electrolyte composition and concentration, applied current density and etching duration. The morphological properties were scrutinized using field emission scanning electron microscopy (FESEM) and scanning electron microscopy (SEM) and were correlated to the etching parameters.

## 2. METHODS

### 2.1. Preparations

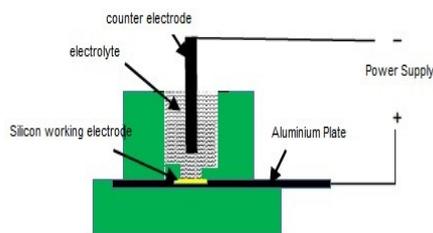
First of all, boron doped p-type single crystalline (100) silicon wafers were prepared by chemical polishing. The wafers were chemically polished by the so-called RCA method [12]. The wafers were subsequently dried by nitrogen

\*Corresponding Author's Email: [massoudi@merc.ac.ir](mailto:massoudi@merc.ac.ir) (A. Massoudi)

blowing. Afterward, the silicon wafers were cut into  $1 \times 1 \text{ cm}^2$  pieces. In addition, a 500 nm aluminum thin film was coated by RF magneto- sputtering of Al-target on the backside of  $1 \times 1 \text{ cm}^2$  pieces for the low resistivity samples and improving the uniformity of the etching current density. The measured resistivity of silicon substrates was ranging from  $0.01 \text{ } \Omega \cdot \text{cm}$  to  $12 \text{ } \Omega \cdot \text{cm}$ .

## 2.2. Electrochemical synthesis

The PSi samples were prepared by electrochemical etching of RCA-cleaned Si substrates. The electrolyte comprised of HF, Ethanol (EtOH) and De-ionized water ( $\text{H}_2\text{O}$ ) by various compositions from 1:4 to 1:1 for two components solutions and different volume ratio of 1:2:2 to 1:1:1 for HF:EtOH: $\text{H}_2\text{O}$ , respectively. Electrochemical etch was carried out at different values of applied current density ranging from  $10 \text{ mA/cm}^2$  to  $50 \text{ mA/cm}^2$ . The etch durations was performed at different times ranging from 5 mins to 30 mins. The electrochemical etching cell consisted of a Teflon walled container depicted in Figure 1. an aluminum back-sputtered silicon substrate as a working electrode sealed with a Viton O-ring and a graphite rod as a counter electrode. The etched samples were dried by sheet tissues after etching.



**Figure 1.** Schematic representation of electrochemical etching cell.

## 2.3. Characterization

To investigate the morphology of PSi, FESEM micrographs were obtained by a TSCAN MIRA3 microscope with high voltage ranging from 10 kV to 15 kV. The SEM images were also obtained by a Cambridge S360 microscope.

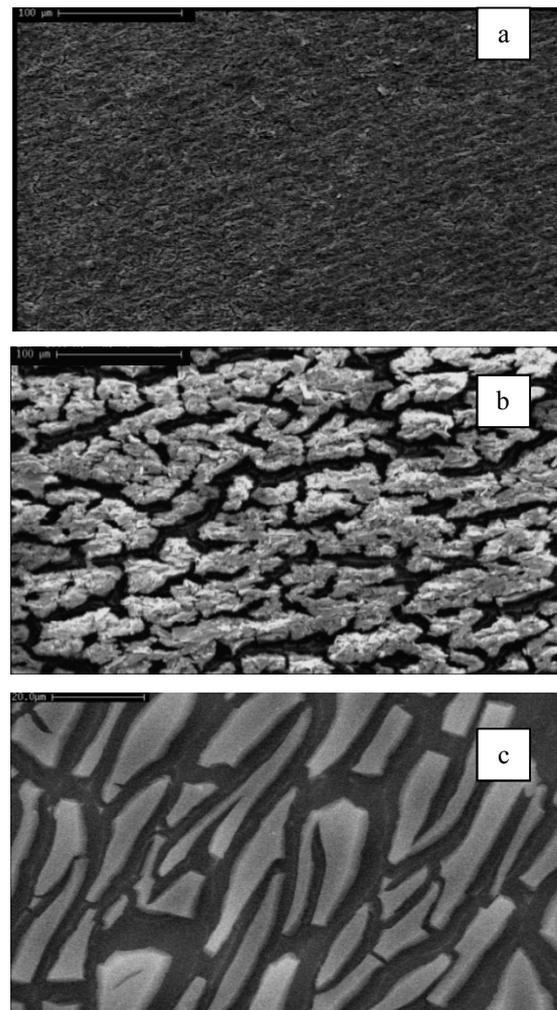
## 3. RESULT AND DISCUSSION

### 3.1. Effect of wafer resistivity

Figures 2-a to 2-c show the SEM images of PSi prepared by electrochemical etch in HF: EtOH solution with different volume ratios of 1:5, 1:4 and 1:3, respectively. The resistance of silicon samples was in the range of  $8 \text{ } \Omega \cdot \text{cm}$  to  $12 \text{ } \Omega \cdot \text{cm}$  leading to macro porosity of silicon. Figure 2-a depicts a uniform flat surface that was not etched completely because of the composition ratio (1:5) and low current density. The low concentration of HF caused a small amount of porous layer that was not

detectable by our SEM microscope. Figure 2-b shows sponge-shaped micrometer pores for the samples which were prepared by a higher HF volume ratio (1:4). If the current density and HF composition ratio increase at the same time, the spongy-like morphology would be destroyed as depicted in Figure 2-c.

If the resistance of silicon pieces decreases to  $0.15\text{-}0.25 \text{ } \Omega \cdot \text{cm}$ , the meso-porosity of silicon will appear in morphology of samples. Figure 3. demonstrates FESEM micrographs of meso-porous Si representing nano-sponge with the average pores size of 30 nm.

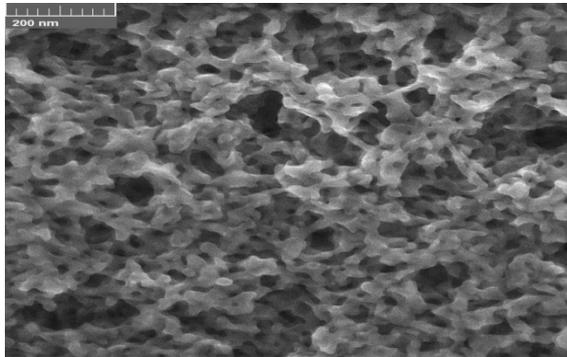


**Figure 2.** SEM images of porous silicon prepared by electrochemical etching of a Si samples with resistivity of  $8\text{-}12 \text{ } \Omega \cdot \text{cm}$  with different etching parameters; a)  $J = 20 \text{ mA/cm}^2$ ,  $t_{\text{etching}} = 10 \text{ min}$ , HF: ETOH (1:5) etchant solution, b)  $J = 10 \text{ mA/cm}^2$ ,  $t_{\text{etching}} = 30 \text{ min}$ , HF: ETOH (1:4) etchant solution, c)  $J = 30 \text{ mA/cm}^2$ ,  $t_{\text{etching}} = 10 \text{ min}$ , HF: ETOH (1:3) etchant solution.

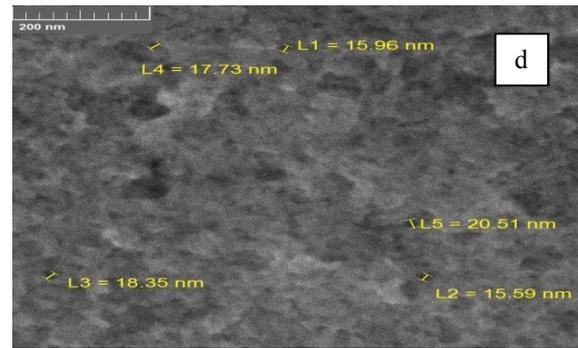
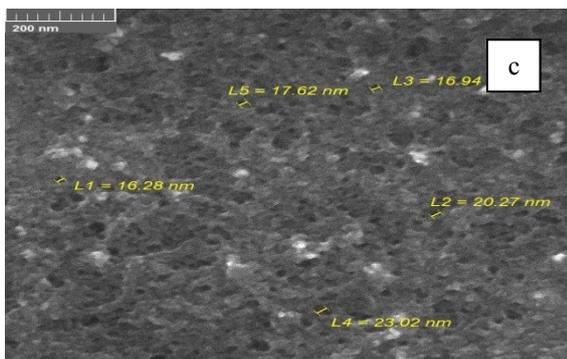
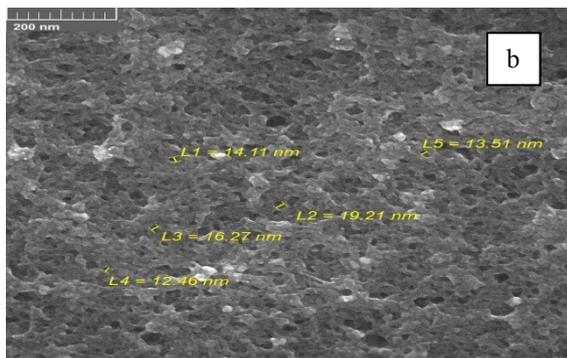
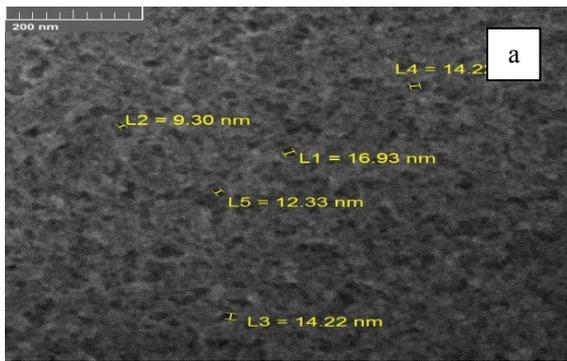
### 3.2. Effect of current density

In electrochemical etching process, current density has an important effect on the width of pores for meso-porous Si samples. Figures 4-a to 4-d show FESEM micrographs of porous silicon samples with different current densities and with

the same chemical ratio of 1:3 for HF/EtOH. Increasing the current density from 10 mA/Cm<sup>2</sup> to 40 mA/Cm<sup>2</sup> leads to increasing pore sizes from 9 nm in Figure 4-a to 23 nm in Figure 4-c, respectively.



**Figure 3.** FESEM images of porous silicon prepared by electrochemical etching of Si wafer with the resistivity of 0.15-0.25 Ω.Cm and with etching parameter of J = 30 mA/Cm<sup>2</sup>, t<sub>etching</sub> = 10 min, HF: ETOH: H<sub>2</sub>O (1:2:2) etchant solution.



**Figure 4.** FESEM images of porous silicon prepared by electrochemical etching of a Si samples with resistivity of 0.15-0.25 Ω.Cm, t<sub>etching</sub> = 10 min, HF: ETOH (1:3) etchant solution a) J = 10 mA/Cm<sup>2</sup>, b) J = 20 mA/Cm<sup>2</sup>, c) J = 30 mA/Cm<sup>2</sup>, d) J = 40 mA/Cm<sup>2</sup>

Remarking that, with the pore size increment, the specific surface area are decreased according to merging of small initial pores to one bigger pore and also crumbling of early pores walls brings about bigger pores formation [13].

On the other hand, the value of current density determines the rate of electrochemical etching reactions occur at the interface layer between silicon and electrolyte. The higher amount of applied current density causes higher width of initial pits which leads to self-assembly of larger pores [13].

Figures 5-a to 5-d also illustrate FESM images for the samples with different current densities of 10 mA/Cm<sup>2</sup> to 40 mA/Cm<sup>2</sup> and with the same volume ratio of 1:2:2 for three chemical components of HF/EtOH/H<sub>2</sub>O respectively.

The results show that by increasing the current density, the pore size increases from 11 nm to 58 nm.

Table 1 and 2 demonstrate the change of pore sizes by varying the current density.

**TABLE 1.** Alternation of pore sizes by varying the applied current density. T<sub>etching</sub> = 10 min, HF: ETOH (1:3) etchant solution. Resistivity of Si wafer=0.15-0.25 Ω.Cm.

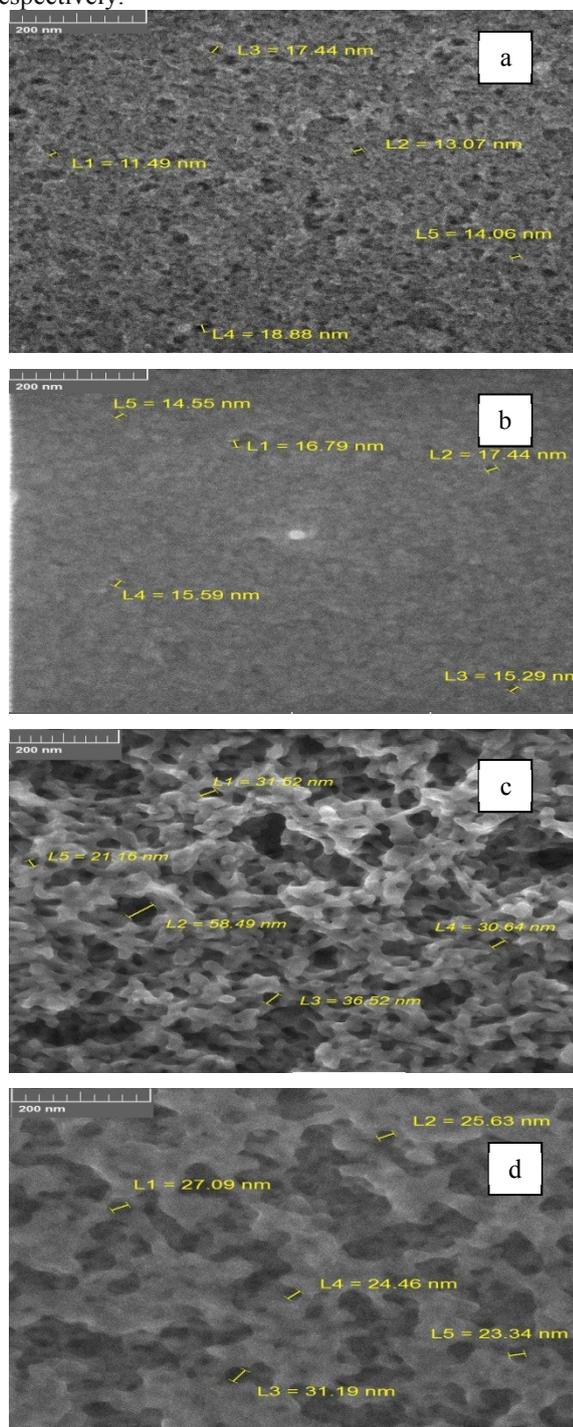
Applied Current Density (mA/Cm <sup>2</sup> )	Averaged Pore Size (nm)
10	11
20	18
30	20
40	22

**TABLE 2.** alternation of pore sizes by varying the applied current density. T<sub>etching</sub> = 10 min, HF: ETOH: H<sub>2</sub>O (1:2:2) etchant solution. Resistivity of Si wafer=0.15-0.25 Ω.Cm.

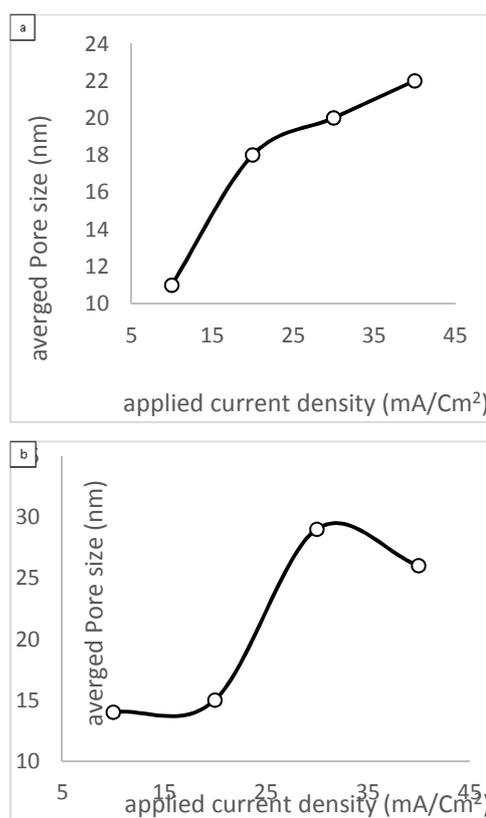
Applied Current Density (mA/Cm <sup>2</sup> )	Averaged Pore Size (nm)
10	14
20	15
30	29
40	26

As tabulated in Table 1 and 2. increasing the current density leads to pores size increment owing to merging

of small pores via corrosion of small pore walls [14]. Figure 6-a and 6-b illustrate ascending of averaged pore sizes with increasing of applied current density in two components and three components solution, respectively.



**Figure 5.** FESEM images of porous silicon prepared by electrochemical etching of a Si samples with resistivity of = 0.15-0.25  $\Omega\cdot\text{cm}$ ,  $t_{\text{etching}} = 10$  min, HF: ETOH: H<sub>2</sub>O (1:2:2) etchant solution, a)  $J = 10$  mA/Cm<sup>2</sup>, b)  $J = 20$  mA/Cm<sup>2</sup>, c)  $J = 30$  mA/Cm<sup>2</sup>, d)  $J = 40$  mA/Cm<sup>2</sup>



**Figure 6.** ascending trend of averaged pores size versus applied current density, a)  $t_{\text{etching}} = 10$  min, HF: ETOH (1:3) etchant solution, b)  $t_{\text{etching}} = 10$  min, HF: ETOH: H<sub>2</sub>O (1:2:2) etchant solution (resistivity of Si wafer=0.15-0.25  $\Omega\cdot\text{cm}$ )

The results demonstrate that rates of pore size increment are about 0.2 nm per mA/Cm<sup>2</sup> of applied current density for two components solution representing a linear trend from 20 mA/Cm<sup>2</sup> to 40 mA/Cm<sup>2</sup>. Table 2 and Figure 6-b illustrate a sigmoid regime for three components solution traced back into the coupling of strong etchant with current density increment [14].

### 3.3. Effect of etching duration

Increasing of etching time give rise to corrode of deeper layer of silicon by an electrolyte had an enough time to reacts with substrate [14]. Figure 3. depicts these circumstances when internal layers of meso-porous silicon observed behind of anterior layers. It seems that increment in etching duration results in depth increasing of pores while increase in applied current density caused to ascending of pores width.

### 3.4. Effect of etchant compositions

Figure 4-c and 5-c represent P<sub>Si</sub> layers for two different HF: ETOH (1:3) and HF: ETOH: H<sub>2</sub>O (1:2:2) etchant compositions, respectively. The average pores size for (1:3) solution is 16 nm and for (1:2:2) solution is 35 nm. This result demonstrates that the three component etchant solution is more efficient than two component solution at the fixed applied current density. Moreover,

by varying the ratio of composition for three component solution from 1:2:2 to 1:1:1, the average pore size changes to 38 nm due to the high reaction rate of etchants.

#### 4. CONCLUSION

The results show that the morphology of PSi is extremely dependent on the etching parameters. Varying current density leads to different amount of pores size while etching time gives rise to different amount of pores depth. The pores size increased monotonically with current density increment for two component solutions and exponentially for three components solutions. Such tuning process due to self-assembly electrochemical process via controlling etching parameters is applicable in fabrication of porous thin films.

#### 5. ACKNOWLEDGMENT

The authors acknowledge the Materials and Energy Research center (MERC) for funding this research.

#### REFERENCES

1. Zhang, X.G., "Electrochemistry of Silicon and its Oxide", Springer, NY, (2001).
2. Lehmann, V., "Electrochemistry of silicon: instrumentation, science, materials and applications, by Volker Lehmann, Wiley-VCH, April (2002) 286.
3. Poole, Ch.P., Owens, F.J., "Introduction to Nanotechnology", John Wiley and Sons Inc., Hoboken, 38 (2003).
4. Uhler, A., "Electrolytic shaping of germanium and silicon", *Bell System Technical Journal*, Vol. 35, (1956), 333-347.
5. Turner, D.R., "Electropolishing silicon in hydrofluoric acid solutions", *Journal of the Electrochemical Society*, Vol. 105 (1958), 402-408.
6. Canham, L.T., "Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers", *Applied Physics Letters*, Vol. 57, (1990), 1046-1048.
7. Zhao, H.P., Jiang, C.-Y., He, X.-M., Ren, J.-G., "A new process of preparing composite microstructure anode for lithium ion batteries", *Journal of Power Sources*, Vol. 184, (2008), 532-537.
8. Zhao, Y., Liu, X, Li, H., Zhai, T., Zhou, H., "Hierarchical micro/nano porous silicon Li-ion battery anodes", *Chemical Communications*, Vol. 48, (2012), 5079-5081.
9. Khoshnevis, S., Dariani, R.S., Azim-Araghi, M.E., Bayindir, Z. and Robbie, K., "Observation of oxygen gas effect on porous silicon-based sensors", *Thin Solid Films*, Vol. 515, (2006), 2650-2654.
10. Kim, J.H., Kim, K.P., Lyu, H.K., Woo, S., Seo, H.S. and Lee, J.H., "Three-dimensional Macropore Arrays in p-type Silicon Fabricated by Electrochemical Etching", *Journal of the Korean Physical Society*, Vol. 55, (2009), 5-9.
11. Kang, C.G., Kang, M.S., Yang, J.H. "Comparision of nanoporous silicon prepared by photoelectrochemical etching in HF-ethanol and HF-acetonitrile solutions", *Journal of the Korean Physical Society*, Vol. 42, (2003), S693-S697.
12. Kim H., and Cho N., "Morphological and nanostructural features of porous silicon prepared by electrochemical etching" *Nanoscale Research Letters*, Vol. 7, (2012), 408.
13. Lee, J.S. and Cho, N.H., "Structural and optical features of nanoporous silicon prepared by anodic etching", *Journal of the Korean Physical Society*, Vol. 39, (2001), S134-S137.
14. Kumar, P., and Huber, P., "Effect of etching parameter on pore size and porosity of electrochemically formed nanoporous silicon", *Journal of Nanomaterials*, Vol. 2007, (2007), 1-4