ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 9, No. 4. 2003

Fabrication of Porous Silicon Microstructures using Electrochemical Etching

R. Jarimavičiūtė-Žvalionienė[1*], V. Grigaliūnas[2], S. Tamulevičius[1,2], A. Guobienė[1,2]

[1]*Kaunas University of Technology, K.Donelaičio 73, LT-3006 Kaunas*
[2]*Institute of Physical Electronics, Kaunas University of Technology, Savanorių 271, LT-3009 Kaunas*

Received 08 October 2003; accepted 22 October 2003

In this work an equipment was built and tested for the electrochemical etching of silicon in hydrofluoric acid electrolyte using aluminium anode and stainless steel cathode. Porous silicon layer was fabricated in n-type (100) oriented silicon using solution $HF : H_2O : C_2H_5OH$, 2 : 1 : 1 by volume. It was revealed, that current density determines geometry of the pores and etching anisotropy. Average depth of the obtained pores varied from 16 μm to 27 μm, when width of the pores varied from 2 μm to 5 μm. The depth of pores depended slightly on the current density, and anisotropy was high in the case of small diameter of the pores.
Keywords: electrochemical etching, porous silicon.

INTRODUCTION

Electrochemical etching of silicon in hydrofluoric acid (HF) electrolyte is a well-known technique for the formation of porous silicon [1-3]. Depending on the doping of the anodized silicon substrate, different pore morphologies can be obtained, ranging from nanometric pores made from p-type substrates, to micrometric pores obtained from illuminated n-type substrates. In the last case, by illuminating the rear surface of the wafer with sufficiently energetic photons, holes can be photogenerated in the bulk. Under anodic bias, these holes move toward the front silicon–electrolyte interface and silicon dissolution takes place. Initially, the electric field concentrates at sharp defects on the flat wafer surface. Surface defects therefore act as seeding points for macropores formation [2, 4, 5].

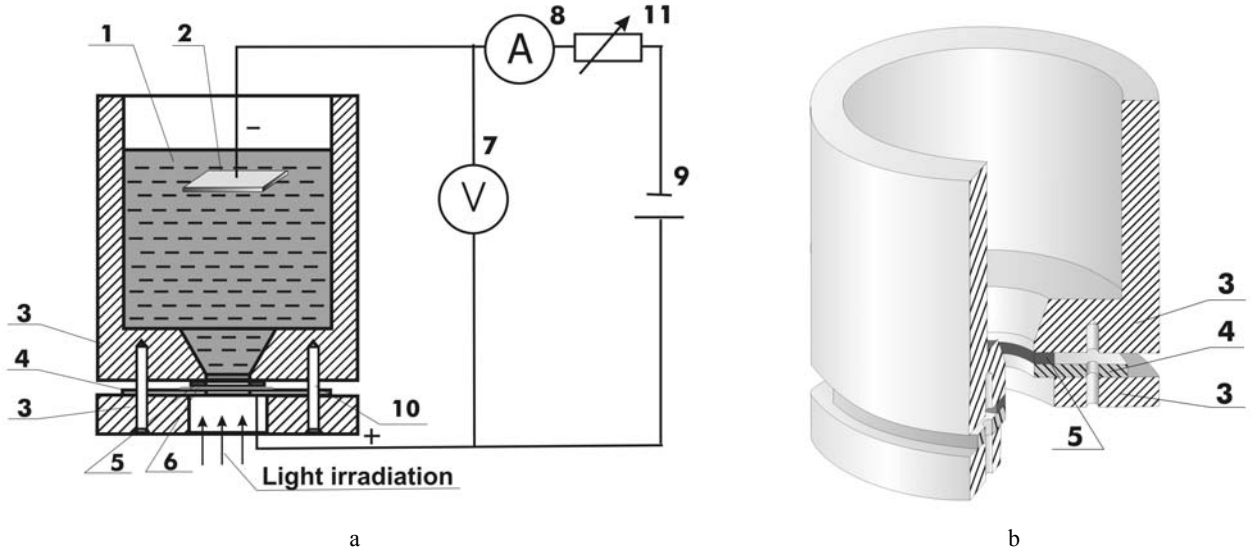
In [2, 6] it is suggested a formation mechanism of porous Si based on the measurement of the concentration of electrolytic solution in deep capilaries. Authors pointed out that the dissolution of Si in the form of H_2SiF_6 occurred at the bottom of the deep capillaries. This reaction can be represented by the folowing chemical formulas:

$$Si + 2HF + 2H \rightarrow SiF_2 + 4H^+, \quad (1)$$

$$SiF_2 + 2H_2O \rightarrow SiO + 2HF + H_2 + O^- , \quad (2)$$

$$SiO + 6HF \rightarrow H_2SiF_6 + 2H_2O. \quad (3)$$

Regarding the formation mechanism of macropores the authors reported that the growth of pore, particularly at the reacting point, begins from a pit as the nucleus caused by the fluctuation of electric curent.



a b

Fig. 1. Iliustration of the experimental setup: a) schematical view, b) crossection of the electrochemical etching tank (M 1 : 3.5 cm) 1 – electrolyte, 2 – stainless steel cathod, 3 – electrochemical etching tank (teflon), 4 – aluminium anode , 5 – seal, 6 – Si wafer, 7 – voltmeter, 8 – amperemeter, 9 – DC source, 10 – grips, 11 – rheostat

*Corresponding author. Tel.: + 370-37-313432; fax:+ 370-37-314423.
E-mail address: *renata@kauko.lt* (R. Jarimavičiūtė-Žvalionienė)

Porous silicon (PS) has been a material studied in the last years due to its photoluminescence in the visible light range at room temperature and its high surface-to-volume ratio [7 – 9]. Silicon, when anodized electrochemically or chemically in an HF-containing electrolyte, is etched in a manner which produces a sponge-like porous layer of silicon with pore dimensions that range from several microns in width to only a few nanometers. This phenomenon find scientific interest in the potential applications in the flat panel display technology [9].

The nanoporous silicon has potential applications for light-emiting diodes, waveguides, photodetectors, gas sensors, etc. [7, 9]

Another research field involves formation of silicon microstructures using selective etching masks. Due to high etching anisotropy electrochemical etching is very promising in the field of fabrication of microelectro-mechanical (MEMS) [2, 10] and optical devices [9, 10].

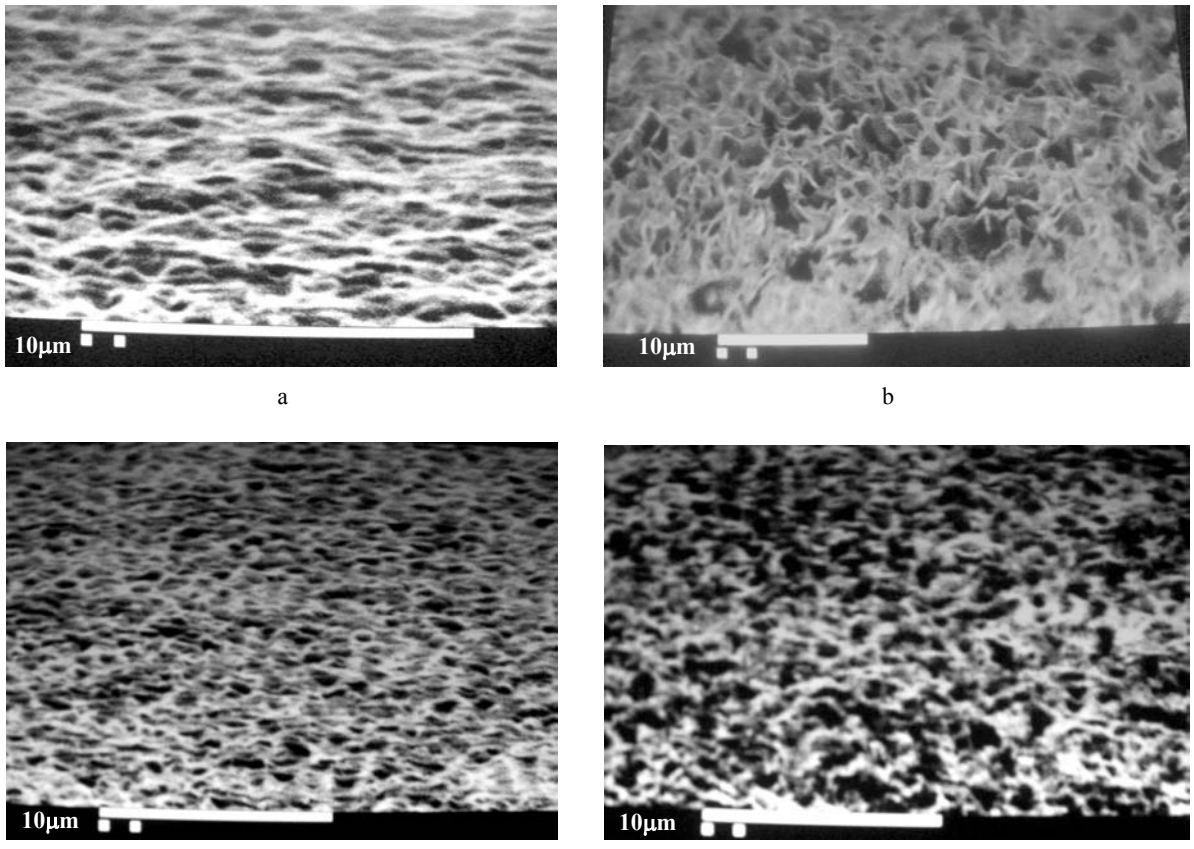
In this work we present an equipment that was built and tested for the electrochemical etching of silicon in hydrofluoric acid electrolyte using aluminium anode and stainless steel cathode (steel grade was 08Ch18N10 (GOST 5632-72). Regularities of the electrochemical etching in solution of $HF : H_2O : C_2H_5OH$ have been investigated experimentally.

EXPERIMENTAL

For electrochemical etching n-type (100) oriented silicon was used. The thickness of silicon wafer was 550 μm and resistivity $1 \div 1.5$ Ωcm. The initial silicon dioxide surface layer was removed in aqueous solution (30 % KOH). The solution for electrochemical etching was HF 48 % : H_2O : C_2H_5OH 96 %, 2 : 1 : 1 by volume.

Table 1. Specific features of the studied porous silicon layer

	Voltage, V	Current, mA	Current density, mA/cm^2	Time, min	Average depth of pores h, μm	Average width of pores d, μm	Anisotropy h/d
1.	1.0	50	13.2	5	16	3.5	4.57
2.	1.3	70	18.4	5	19	4	4.75
3.	1.8	100	26.3	5	24	5	4.80
4.	3.2	150	39.5	5	27	4	6.75
5.	9.5	200	52.6	5	24	2	12.0



a b c d

Fig. 2. SEM top view (scale bar 10 μm) of porous surface of silicon at current density: a) 13.2 mA/cm^2, b) 18.4 mA/cm^2, c) 26.3 mA/cm^2, d) 39.5 mA/cm^2

All the experiments were done at room temperature using working current of the etching process from 50 to 200 mA and the anodization voltage from 1 to 3 V. The corresponding current density varried from 13 mA/cm^2 to 55 mA/cm^2. The deep pairs were generated by illuminating the back side of the sample with a 50 W halogen lamp (range the back side of the sample with a 50 W halogen lamp (range of wavelength 380 – 750 nm), 40 cm from the sample, through a circular window in the electrochemical etching tank. Aluminium anode was used to provide the back electrical contact to the sample (Fig. 1).

Porous silicon microstructures were investigated by scanning electron microscope (SEM) JEOL JSM-IC25S The dependence of thickness of porous silicon layer and pores geometry on the parameters of etching process were established from the SEM photographs.

Average value of the width of pores was defined as arithmetical mean of 10 different pores (measured at the half depth of pore), i.e.: $d=\Sigma d_i/n$, where $n=10$. Average value of the depth was defined by the equation $h=\Sigma h_i/m$, where $m=10$. Measurements of d_i and h_i were performed by SEM.

RESULTS AND DISCUSSION

The porous layer of silicon was fabricated by means of the electrochemical etching in HF solution.

Fig. 2. shows the surface of porous silicon after etching at different current density. One can see, that increase of current density results in more porous silicon surface layer and corresponding pores are deeper. Geometry of the pores and etching anisotropy changes as well, when different current density is used, as it can be seen from Fig. 3. The dependence of the depth and width of pores and etching anisotropy on etching parameters is summarized in the Table 1. The density of pores and depth of the pores were small, when etching was performed at low current density (13.2 mA/cm^2). In this case only a small quantity of the charge carriers was generated at the fixed light irradiation resulting in the slow formation of rudiment in the silicon surface and slow etching of the pores. Increase of current density and concentration of charge carriers increased the silicon etching rate.

At low current density chemical etching prevails. Pore shape is more complex and branched, as it can be seen from Fig. 3 (a, b). Etching anisotropy increases with the current density and contribution of electrochemical etching starts to increase. The calculated dependence of etching anisotropy (ratio of pore depth versus width) via current density is presented in Fig. 4. It is important to note, that at high current density (52.6 mA/cm^2) the depth of pores changes only slightly, but anisotropy increases due to small diameter of the pores. Fig. 5 illustrates dependence of the average pore depth versus current density. The results

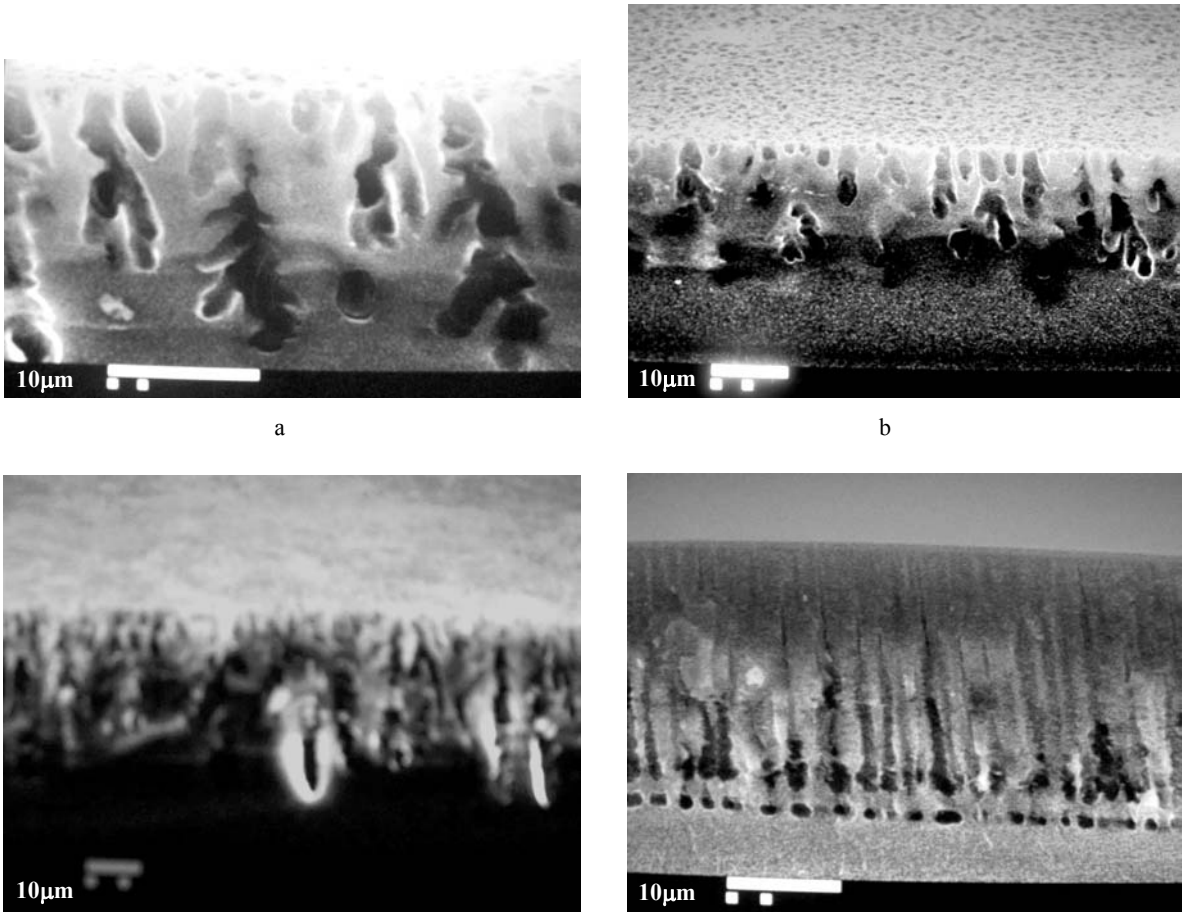


Fig. 3. SEM bulk view (scale bar 10 μm) of deep pores in silicon, at current density: a) 13.2 mA/cm^2, b) 26.3 mA/cm^2, c) 39.5 mA/cm^2, d) (sample contains SiO_2 on the top) 52.6 mA/cm^2

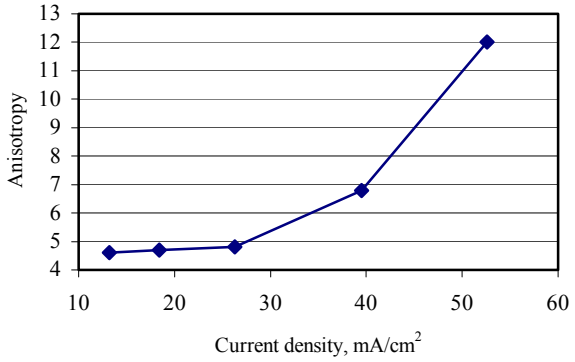


Fig. 4. Anisotropy of electrochemical etching of silicon vs current density

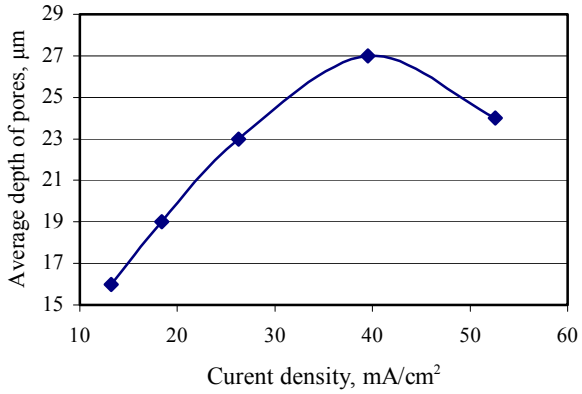


Fig. 5. Average depth of pores in silicon vs current density

indicate that maximal depth of pores was achieved when curent density was 39.5 mA/cm^2. That is 1.7 times higher than those find at curent density 13.2 mA/cm^2.

CONCLUSIONS

Increase of current density results in more porous silicon surface layer and the corresponding pores are deeper. Geometry of the pores and etching anisotropy changes, when different current density is used. Increase of current density and concentration of charge carriers increases the silicon etching rate.

At low current density chemical etching prevails and pores shape is more complex and branched.

Etching anisotropy increases with current density, at high current density (52.6 mA/cm^2) the depth of pores changes only slightly, but anisotropy is high due to small diameter of the pores.

The results indicate that maximal depth of pores was achieved when curent density was 39.5 mA/cm^2. That is 1.8 times higher than those find at curent density 13.2 mA/cm^2.

Acknowledgment

This work was partially supported by the NATO Colaborative Linkage Grant.

REFERENCES:

1. **Smith, R. L., Collins, S. D.** Porous Silicon Formation Mechanisms *J. Appl. Phys.* 71 1992: pp. R1 – R22.
2. **Grigoras, K.** Formation of Through-Holes on Silicon Wafer by Optical Excitation Electropolishing Method *Jpn. J. Appl. Phys.* 39 2000: pp. 378 – 386.
3. **Christopersen, M., Carstensen, J., Rönenbeck, S., Jäger, C., Jäger, W., Föll, H.** Crystal Orientation Dependence and Anisotropic Properties of Macropore Formation of p- and n-type Silicon *J. Electrochem. Soc.* 148 (6) 2001: pp. E267 – E272.
4. **Föll, H., Christopersen, M., Carstensen, J., Hasse, G.** A New View of Silicon Electrochemistry *Phys. Stat. Sol (a)* 182 (1) 2000: pp. 7 – 16.
5. **Föll, H., Christopersen, M., Carstensen, J., Hasse, G.** Formation and Application of Porous Silicon *Materials Science and Enginering, Review* 39 (4) 2002: pp. 93 – 141.
6. **Šimkienė I.** Semiconductor Nanocrystal Materials. *Proceedings of the School-Conference: Advanced Materials and Technologies* 2001: pp. 105 – 125 (in Lithuanian).
7. **Lee, J. - S., Cho, N. - H.** Nanostructural and photo-luminescence features of nanoporous silicon prepared by anodic etching *Applied Surface Science* 190 2002: pp. 171 – 175.
8. **Liu, Y., Xiong, Z. H., Liu, Y., Xu, S. H., Liu, X. B., Ding, X. M., Hou, X. Y.** A Novel Method of Fabricating Porous Silicon Material: Ultrasonically Enhanced Anodic Electrochemical Etching *Solid State Communications* 127 2003: pp. 583 – 588.
9. **Ehrfeld, W.** Electrochemistry and Microsystems. *Electrochimica Acta* 48 2003: pp. 2857 – 2868.
10. **Barillaro, G., Nannini, A., Piotto, M.** Electrochemical Etching in HF Solution for Silicon Micromachining *Sensors and Actuators A: Physical* 102 2002: pp.195 – 201.