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Pore Morphology of Heavily Doped P-Type Porous Silicon †

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Abstract: Tuning pore diameter of porous silicon (PS) is essential for some applications such as biosensing, where pore size can filter the entrance of some analytes or increase its sensitivity. However, macropore (>50nm) formation on p-type silicon is still poorly known due to the strong dependence on resistivity. Electrochemically etching heavily doped p-type silicon usually forms micropores (<5nm), but it has been found that bigger sizes can be achieved by adding an organic solvent to the electrolyte. In this work, we present the results of using dimethylformamide (DMF), dimethylsulfoxide (DMSO), potasium hydroxide (KOH) and sodium hydroxide (NaOH) for macropore formation in p-type silicon with resistivities between 0.001 and 0.02 Ω·cm, achieving pore sizes from 5 to 100nm.

Keywords: porous silicon; pore diameter; macropore; dimethylformamide; dimethylsulfoxide

1. Introduction

Porous silicon (PS) is a nanostructured material generated by electrochemically etching silicon (Si) in electrolytes containing hydrofluoric acid (HF) [1]. The growth of the pores is a combination of two chemical reactions: a direct dissolution of Si in fluoride and the oxidation of Si in the presence of oxygen and its later dissolution [2]. Both reactions are strongly dependent on etching conditions, both chemical and electrical [3].

PS has many potential application areas such as optoelectronics and biosensing [4, 5, 6], mainly because it retains the advantages of silicon technology while adding the ability of controlling optical properties. Porosity, thickness, pore diameter, pore morphology and distance between pores are some of the tunable properties during fabrication [7]. High porosities combined with small pore diameters commonly lead too high sensitivity sensors. Contrarily, high pore diameters allow a better adsorption ability. On the other hand, when using PS membranes for sensing, longer distances between pores are preferred for a better endurance. Unfortunately, not all combinations of parameters are possible or at least different approximations must be carried out to overcome the initial limitations.

The macropore (pores with average diameter greater than 50 nm) formation mechanism on n-type silicon is well known [3, 8]. Low-doped p-type silicon wafers have also been used for macropore formation [9]. However, achieving mesopores (5 – 50 nm) and macropores in moderately-doped and heavily-doped silicon is more challenging. Aqueous HF-based electrolytes (HF diluted in water and optionally surfactants such as alcohols) will yield only micropores (<5 nm) and mesopores if no additional fabrication step is introduced [10, 11]. In order to overtake this limitation, several approaches have been developed:

- PS oxidation and HF dissolution. When PS is thermally oxidized, a SiO_2 layer is formed on its surface. Dissolution of this oxide in HF can increase the pore diameter up to half the SiO_2 layer thickness [12]. This process can be repeated but doing so will reduce the pore walls and jeopardize the structure stability.
- Post-treatment with alkaline mixtures. KOH and NaOH solutions anisotropically etch Si and can be used to expand the pores after fabrication [13], although this method has the same limitations as the previous one. They have also been used for dissolving partially the PS film and obtaining a pattern that - if used afterwards in a new electrochemical etching - can yield macropores [6].
- Organic electrolytes. The combination of HF-based solutions with non-aqueous electrolytes, e.g., dimethylformamide and dimethylsulfoxide, facilitates the Si dissolution during anodization [14, 15]. This method offers more control of PS properties.

Even though numerous studies have reported the obtainment of macropores on heavily-doped p-type silicon, there is still a lack of analysis for certain ranges of resistivities.

2. Methods

PS was prepared by electrochemically etching p-type silicon wafers (boron doped, <100> oriented) with different resistivities: 0.001-0.005 Ω·cm and 0.01-0.02 Ω·cm, both purchased from MicroChemicals GmbH (Germany). Aqueous electrolytes were prepared with Ethanol (EtOH) obtained from Scharlab S.L. (Spain) and hydrofluoric acid (HF) (48% solution in water) purchased from BASF (Germany). For organic electrolytes, N,N-Dimethylformamide (DMF) from Sigma-Aldrich (USA) and Dimethylsulfoxide (DMSO) from Scharlab S.L. (Spain) were employed. In the cases where alkaline solutions were used, potassium hydroxide (KOH), obtained from Panreac S.L. (Spain), and sodium hydroxide (NaOH), from Scharlab S.L. (Spain), were mixed in different concentrations with deionized water (DIW) produced in house by a Millipore water purification system.

For cleaning purposes, all samples were pretreated for 30 min in a 3:1 volumetric mixture of sulfuric acid (H_2SO_4) and hydrogen Peroxide (H_2O_2), both purchased from BASF (Germany), for removing organic residues off the substrate. Afterward, they were dipped into a solution of <5% HF for 30 s in order to eliminate the native oxide layer.

Electrochemical etching of Si was performed under galvanostatic conditions in a vertical cell in which a Pt electrode worked as a cathode and the Si itself as anode. Different aqueous and organic solutions have been used as electrolytes.

Field emission scanning electron microscopy (FESEM) was performed using both a Hitachi S-4500 SEM and a Zeiss Ultra 55 microscope.

3. Results and Discussion

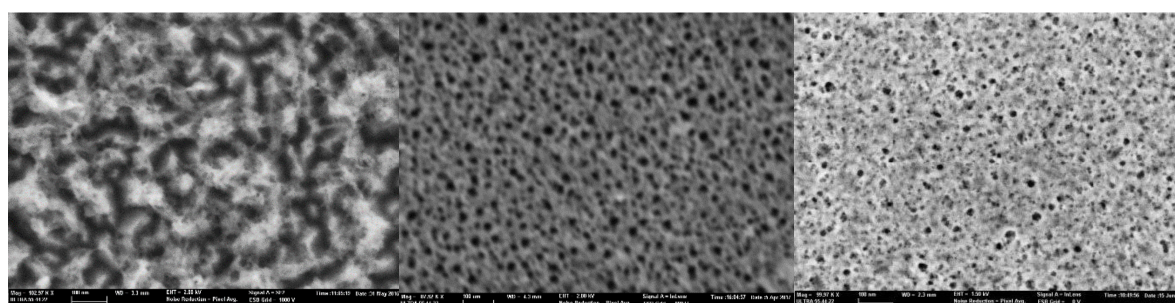
The results of the pore morphology dependence with different etching parameters for resistivities of 0.01-0.02 Ω·cm are summarized in Table 1.

The lower the HF concentration in the electrolyte, the bigger the pore will be. However, etching heavily doped silicon wafers with very low HF concentrations (Figure 1 (a)) leads to pore interconnection. This implies thin walls and a slow vertical growth. PS films created this way will be structurally weak and only a small range of porosities can be achieved. Rising the HF concentration reduces the pore diameter but strengthens the structure. PS films formed this way are not appropriate to be used as membranes but they might be suitable for sensing gas or humidity, due to its high sensitivity.

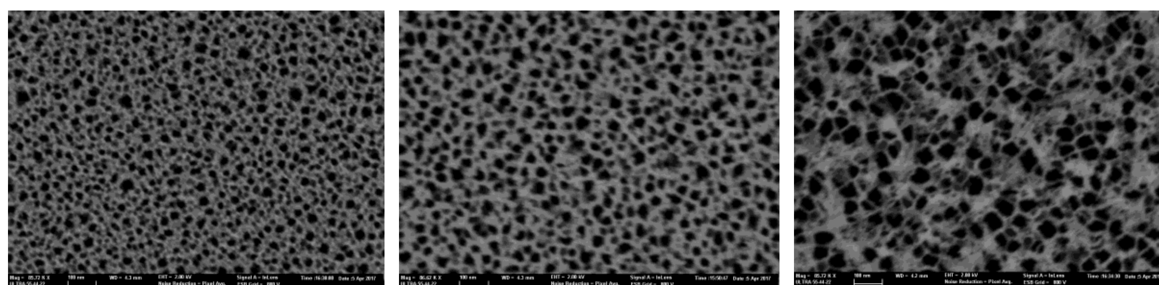
Comparing Figure 1 (b) and (c), we can see that both samples have similar pore diameters. The difference between those two images is pore interspacing, being higher in the case of the KOH etching of the PS film. This effect is caused due to the deposition of the Si on the surface and can be reduced if agitation is added.

Table 1. Influence on pore morphology of fabrication parameters for resistivities of 0.01-0.02 Ω·cm.

Electrolyte	**HF:EtOH 1:9**	**HF:EtOH 1:2 + Oxidation**	**HF:EtOH 1:2 + KOH**	**HF:DIW: DMF 1:1:4**	**HF:DIW: DMF 1:1:9**	**HF:DIW: DMSO 1:1:9**
Resistivity of the electrolyte	150 Ω·cm	100 Ω·cm	100 Ω·cm	750 Ω·cm	1300 Ω·cm	1500 Ω·cm
Current range of PS formation	<18 mA/cm^2	<130 mA/cm^2	<130 mA/cm^2	<25 mA/cm^2	<18 mA/cm^2	<18 mA/cm^2
Pore surface shape	Pores inter-connected	Holes	Holes	Holes	Holes	Hexagons
Pore section shape	Random and short branches	Secondary branches only	Secondary branches only	Secondary branches only	Secondary branches only	Smooth pore wall
Pore diameter	~20 nm	~25 nm	~25 nm	~25 nm	~30 nm	~50 nm
Etch rate	~0.5 nm/s, I=5 mA/cm^2, T=310 s	~8 nm/s, I=6 mA/cm^2, T=100 s	~8 nm/s, I=6 mA/cm^2, T=120 s	~20 nm/s, I=22 mA/cm^2, T=90 s	~8 nm/s, I=11 mA/cm^2, T=90 s	~5 nm/s, I=11 mA/cm^2, T=90 s
Spacing between pores	~50 nm	~30 nm	~60 nm	~40 nm	~20 nm	<10 nm
Micropore layer on top	No	No	No	No	No	No



(**a**) (**b**) (**c**)



(**d**) (**e**) (**f**)

Figure 1. FESEM images of electrochemically etched p-type Si 0.01-0.02 Ω·cm (**a**) HF:EtOH 1:9, I=22mA/cm^2, T=90s, (**b**) HF:EtOH 1:2, I=6mA/cm^2, T=100s, oxidized for 30min and dipped in HF, (**c**) HF:EtOH 1:2, I=6mA/cm^2, T=120s, etched with 45mg of KOH in 100ml of DIW for 5min, (**d**)

HF:DIW:DMF 1:1:4, I=22mA/cm^2, T=90s (**e**) HF:DIW:DMF 1:1:9, I=11mA/cm^2, T=90s and (**f**) HF:DIW:DMSO 1:1:9, I=11mA/cm^2, T=90s.

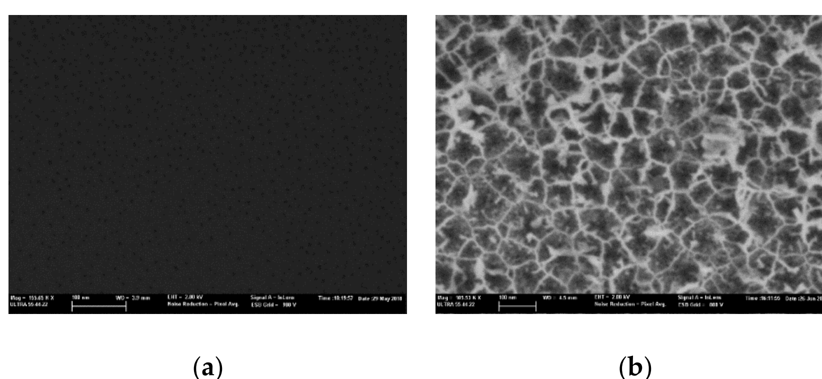
Adding DMF to the electrolyte yields higher pore diameters. It can be seen in Figure 1 (d) and (e) how increasing DMF proportion directly increases the pore size. These PS samples are more convenient than the ones etched with aqueous electrolytes for applications such as biodetection since the pore size allow the entrance of molecules and proteins. Instead, anodization with DMSO have resulted in pores extremely close to adjacent pores, creating a hive-like structure (see Figure 1 (f)) and adopting a hexagonal form instead of the typical circular one. PS films formed with 1:1:9 DMF and DMSO are structurally more fragile than for other electrolytes and also organic electrolytes have a negative impact on vertical uniformity but pore diameters up to 50 nm can be achieved.

In Table 2, the results for resistivities of 0.001-0.005 Ω·cm are shown. Oxidation of PS films and removal dipping in HF as well as alkaline etching are omitted for they yield intermediate pore sizes.

In this case, for some HF concentrations, a small layer of micropores appears on top of the desired layer. It can be easily removed by dipping the sample in a 1M NaOH dissolution in order to achieve PS films with pore diameters up to 100nm. These sensors display lower sensitivities but are preferred in some applications for its adsorption ability.

Table 2. Influence on pore morphology of fabrication parameters for resistivities of 0.001-0.005 Ω·cm.

Electrolyte	**HF:EtOH 2:1**	**HF:EtOH 2:1 + NaOH**
Resistivity of the electrolyte	10 Ω·cm	10 Ω·cm
Current range of PS formation	<750 mA/cm^2	<750 mA/cm^2
Pore surface shape	Holes	Holes
Pore section shape	Secondary branches only	Secondary branches only
Pore diameter	<10 nm	~100 nm
Etch rate	~400 nm/s, I=650mA/cm^2, T=30s	~450 nm/s, I=730mA/cm^2, T=30s
Spacing between pores	~20 nm	~20 nm
Micropore layer on top	Yes	No



(**a**) (**b**)

Figure 2. FESEM images of electrochemically etched p-type Si 0.001-0.005 Ω·cm (**a**) HF:EtOH 2:1, I=650mA/cm2, T=30s, (**b**) HF:EtOH 2:1, I=730mA/cm2, T=30s, dissolved 2min in 0.1M NaOH.

4. Conclusions

Pore morphology and fabrication properties for PS formed in heavily doped p-type Si (100) have been presented. The effect of organic electrolytes such as DMF and DMSO and alkaline etchants e.g. KOH and NaOH has been reported. The use of organic electrolytes on Si wafers with resistivities of 0.01-0.02 Ω·cm have proven the increase the pore diameter up to 50 nm. On the other hand, pore sizes

or around 100 nm can be achieved on wafers with lower resisitivity. Macropores can be formed in heavily doped p-type Si, which allows a wider range in the design of PS based sensors for different applications.

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References

1. Pacholski, C. Photonic crystal sensors based on porous silicon, *Sensors*, **2013**, 13, 4697-4713, DOI: 10.3390/s130404694.
2. Föll, H.; Christophersen, M.; Carstensen, J.; Hasse, G. Formation and application of porous silicon, *Mater. Sci. Eng. R.*, **2002**, 39, 93-141, DOI: 10.1016/S0927-796X(02)00090-6.
3. Zhang, G.X. Porous silicon: morphology and formation mechanisms, In *Modern Aspects of Electrochemistry*, Vayenas, C.; Gamboa-Adelco, M.E., Springer, Boston, USA, 2006, 39, 65-133, ISBN 0076-9924.
4. Caroselli, R.; Ponce-Alcántara, S.; Prats-Quílez, F.; Martín- Sánchez, D.; Torrijos-Morán, L.; Griol-Barres, A.; Bellieres, L.; Bandarenka, H.; Girel, K.; Bondarenko, V.; García-Rupérez, J. Experimental study of the sensitivity of a porous silicon ring resonator sensor using continuous in-flow measurements, *Opt. Express*, **2017**, 25, 31651-31659, DOI: 10.1364/OE.25.031651.
5. Hutter, T.; Horesh, M.; Ruschin, S. Method for increasing reliability in gas detection based on indicator gradient in a sensor array, *Sens. Actuators B*, **2011**, 152- 29-36, DOI: 10.1016/j.snb.2010.09.058.
6. Mariani, S.; Strambini, L.M.; Barillaro, G. Femtomole detection of proteins using a label-free nanostructured porous silicon interferometer for perspective ultrasensitive biosensing, *Anal. Chem.*, **2016**, 88, 8502-8509, DOI: 10.1021/acs.analchem.6b01228.
7. Canham, L.T.. Tunable properties of porous silicon, In *Handbook of porous silicon*, Canham, L.T., Springer International Publishing, Switzerland, 2014, 201-206, ISBN 978-3-319-05744-6.
8. Lehman, V.; Föll, H. Formation mechanism and properties of electrochemically etched trenches in n-type silicon, *J. Electrochem. Soc.*, **1990**, 137, 653-659, DOI: 10.1149/1.2086525.
9. Lehman, V.; Rönnebeck, S. The physics of macropore formation in low-doped p-type silicon, *J. Electrochem. Soc.*, **1999**, 146, 2968-2975, DOI: 10.1149/1.1392037.
10. Lehman, V.; Stengl, R.; Luigart, A. On the morphology and the electrochemical formation mechanism of mesoporous silicon, *Mater. Sci, Eng. B*, **2000**, 69-70, 11-22, DOI: 10.1016/S0921-5107(99)00286-X.
11. Mariani, S.; Pino, L.; Strambini, L.M.; Tedeschi, L.; Barillaro, G. 10000-fold improvement in protein detection using nanostructured porous silicon interferometric aptasensors, *ACS Sens.*, **2016**, 1, 1471-1479, DOI: 10.1021/acssensors.6b00634.
12. Lau, H.W.; Parker, G.J.; Greef, R. High-aspect ratio silicon pillars fabricated by electrochemical etching and oxidation of macroporous silicon, *Thin. Solid. Films*, **1996**, 276, 29-31, DOI: 10.1016/0040-6090(95)08042-2.
13. Chernienko, A.V.; Astrova, E.V.; Zharova, Y.A. Zigzag structures obtained by anisotropic etching of macroporous silicon, *Tech. Phys. Lett.*, **2013**, 39, 990-993, DOI: 10.1134/S1063785013110175.
14. Ponomarev, E.A.; Lévy-Clément, C. Macropore formation on p-type silicon, *J. Porous Mat.*, **2000**, 7, 51-56, DOI: 10.1023/A:1009690521403.
15. Haldar, S.; De. A.; Chakraborty, S.; Ghosh, S.; Ghanta, U. Effect of dimethylformamide, current density and resistivity on pore geometry in p-type macroporous silicon, *Procedia Mater. Sci.*, **2014**, 5, 764-771, DOI: 10.1016/j.mspro.2014.07.326.

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