

Morphologies of porous silicon etched by the electrochemical etching method with alcohols additives



Yibin Zhang, Minghui Yuan, Bin Cai, Dongsheng Zhang, Hongyan Chen, Yiming Zhu*

Cooperative Innovation Centre of Terahertz Science, Engineering Research Center of Optical Instrument and System, Ministry of Education, Shanghai Key Lab of Modern Optical System, Institute of Optical-Electrical Engineering, University of Shanghai for Science and Technology, No. 516 Jungong Rd., Shanghai 200093, China

ARTICLE INFO

Article history:

Received 24 July 2015

Accepted 7 December 2015

Keywords:

Electron microscopy

Porous materials

Morphology

Alcohol

ABSTRACT

Several porous silicon (PS) films with macropores are fabricated by electrochemical etching method using five different monohydric normal alcohol additives without any illumination. The experiment results show that as the number of carbon atoms increases, the branch length elongates, the pore density decreases because the ability of anisotropic etching of the solution is enhanced gradually and the space charge region (SCR) width of PS becomes larger. Furthermore, except for methanol (MeOH) and *n*-pentanol (*n*-PeOH), with the increasing number of carbon atoms in alcohol, the main pore size decreases and the depth increase because the isotropy becomes weaker. PS in MeOH has small main pore size and large depth because most of charges accumulated at the bottom of pores and promote the growth of the depth. PS in *n*-PeOH has a small depth because of its strong hydrophobicity property, which hinders the etching at the length direction. These experimental results demonstrate the important role of alcohols on the dissolution kinetics with silicon, which has a direct impact on the pore growth process.

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1. Introduction

Since the porous silicon (PS) film is first fabricated by the electrochemical etching method in 1950s [1–3], it has been widely used in many fields, such as sensors [4], photoluminescence [5], solar cells [6], and so on. Particularly, by using ultra-high order mode [7,8], a label-free porous silicon membrane waveguide biosensor with very high sensitivity can be achieved due to the utilization of an ultra-high order mode for sensing. And its design can easily expand to regular photonic crystal design [9,10]. Up to now, it has been investigated in details on many technical parameters of the etching process such as the doping, resistivity of the silicon (Si) substrate, temperature, current density, illumination intensity (in *n* type silicon), the concentration of the electrolyte, and different kinds of composition of the electrolyte [11]. In those investigations, electrolyte solutions containing HF and organic solvent or some strong oxidizers like H₂O₂, HCl and H₂SO₄ have been studied [12–14]. As a result, it is well accepted that the alcohol can reduce surface tension and help H₂ be escaped from the porous layer, where the alcohol does not react with silicon directly [15]. According to recent researches, the additive of alcohol can improve

the degree of surface wetting and lead to a more robust oxides homogenous etching. Essentially, alcohol plays an important role on the dissolution kinetics of the SiO₂ [16]. However, little attention has been paid to the effect of alcohol upon the pore formation.

In our work we address these issues by etching macropores in *n*-Si and investigate their feature sizes. Furthermore, the study tries to find out some rules of fabricating PS with different alcohol additives and without any illumination.

2. Experiment

Wafers of *n*-Si with low doping levels corresponding to a resistivity of 1–10 Ω cm are used for etching macro-pores without light illumination. The lattice orientation is (100). The electrolyte consists of 40 wt.% HF, 30 wt.% H₂O₂, and different monohydric alcohol additives with the volume ratio of 1:2:2. H₂O₂ provides a large amount of holes and accelerates the oxide dissolution of silicon so that the large pores can be formed without illumination [17]. The monohydric alcohol additives we used are: methanol (MeOH), ethanol (EtOH), *n*-propanol (*n*-PrOH), *n*-butanol (*n*-BuOH), and *n*-pentanol (*n*-PeOH), respectively. Before the electrochemical etching process, a 1 μm-thick Al film is plated on the no *n*-polished surface of Si wafer as the anode after RCA cleaning process. After the electrochemical etching process, PS is applied reverse current

* Corresponding author. Tel.: +86 18916018187; fax: +86 2133773176.
E-mail address: shyimingzhu@hotmail.com (Y. Zhu).

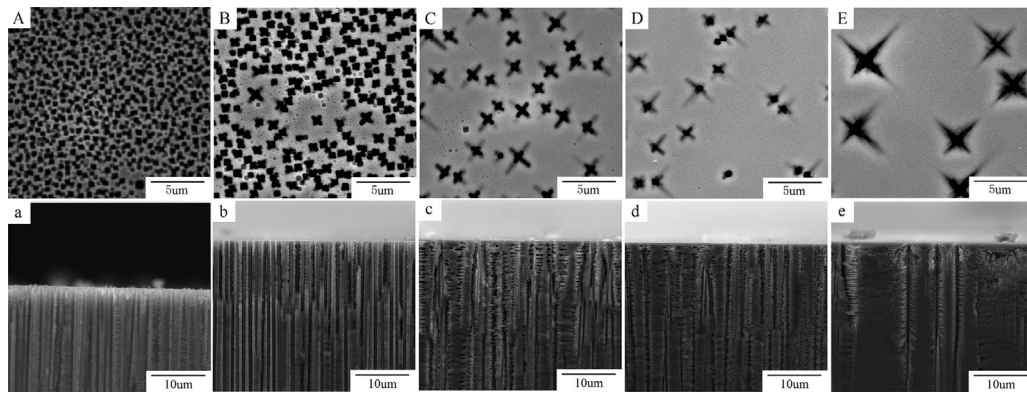


Fig. 1. Scanning electron microscope (SEM) images (top view ((A)–(E)) and cross-section ((a)–(e))) of the porous silicon produced by different alcohol additives: methanol ((A) & (a)), ethanol ((B) & (b)), *n*-propanol ((C) & (c)), *n*-butanol ((D) & (d)) and *n*-pentanol ((E) & (e)).

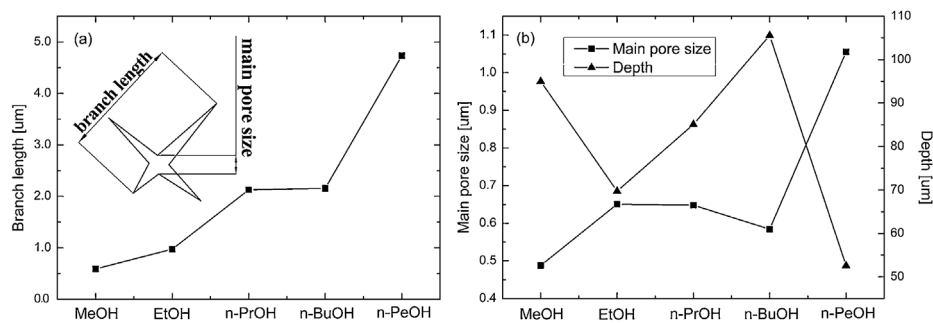


Fig. 2. (a) Average branch length of PS versus different alcohols; (b) average main pore size and depth of PS versus different alcohols.

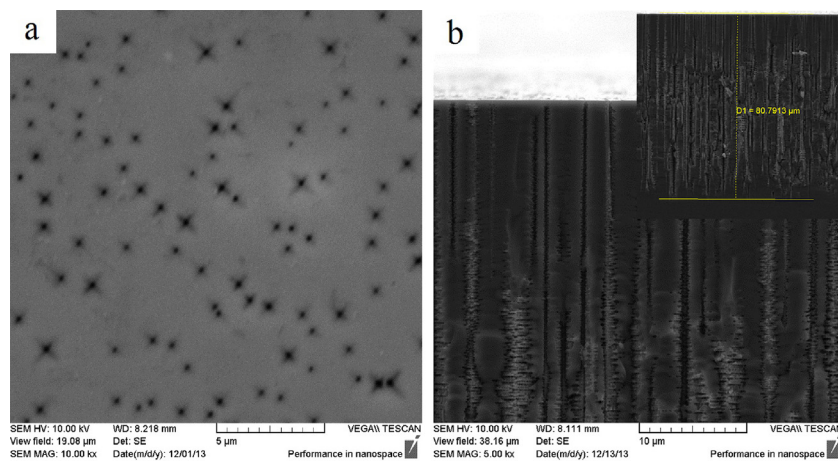


Fig. 3. SEM images of the porous silicon produced by HF/H₂O₂ solution.

for 2 min to treat the wafer surface in order to passivate the silicon surface.

The porous structures are observed by using a scanning electron microscope (TFSEM Tescan Vega2). Pla *n*-view micrographs show the (1 0 0) plane, whereas after cleaving the samples, cross-section view micrographs show the pores in the (1 1 0) cleavage planes.

3. Result and discussion

Fig. 1 shows scanning electron microscope (SEM) images of PS anodized in aqueous HF/H₂O₂ solution with five different monohydric alcohol additives. First, we can see that most of the pores have four-branching structures along the orientation, which the feature sizes of the pores are shown in **Fig. 2**. It is obtained that the branch length in a range from 0.77 μm to 4.7 μm and the

main size in a range from 0.46 μm to 1.05 μm. The pore formation can be explained by the dissolution process of silicon in HF solution. At the beginning of the dissolution, the Si–H bond of silicon surface is substituted by the Si–F bond. The bonded fluorine atom induces a weakening of the Si–Si bond on the back of Si atom. The Si–Si along the orientation with two F[−] are more easily reacted than the Si–Si along (1 1 1) with only one F[−]. So the etching speed is fast in the direction of lattice orientation and the pore shape is crosswise at first, where the etching in the direction of amorphous orientation keeps constant. Second, the pore density decreases obviously with the increasing number of carbon atoms in alcohol, which means the SCR width becomes larger. Previous studies show that if the PS has enough SCR width, the branches at the pore tip or pore wall would be easier to be formed because it has more opportunities to get holes [18]. Besides, high concentration

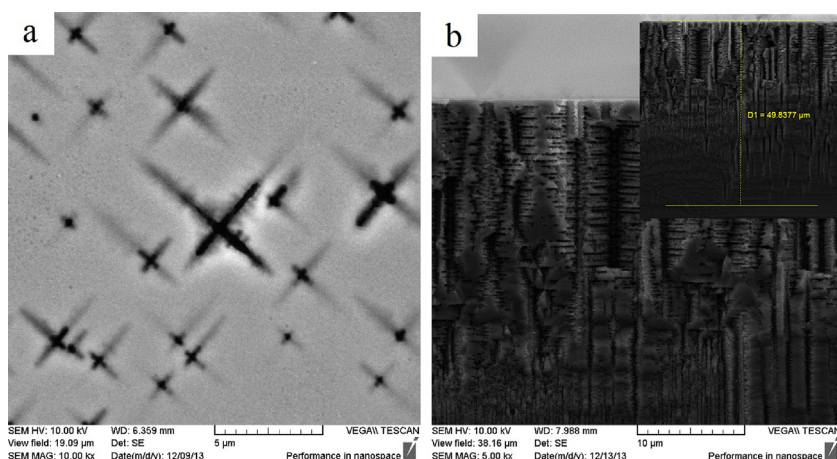


Fig. 4. SEM images of the porous silicon produced by the mixture solution of 1 ml *n*-PeOH and HF/H₂O₂.

of HF [19], low concentration of H₂O₂ [20] and low current density [21] can also promote the growth of branch. In our experiments, Fig. 2(a) shows that the branch length of PS increases gradually with the increasing number of carbon atoms in alcohol, which the major reason is that the SCR width of the PS becomes larger. Especially, Fig. 2(a) shows that the *n*-PrOH and *n*-BuOH have the similar branch length. This is because the solubility of *n*-BuOH in water is low due to large alkyl group and the concentration of HF and H₂O₂ solution increases. Therefore these two factors offset each other.

Although the change of branch length has a significant regularity, changes of main pore size and depth are not so (Fig. 2(b)). The only obvious rule is that the main pore size is always contrary with the depth. This is because all experiments have the same current density and etching time. Meanwhile, the main pore and the depth always have a competition for consuming charges. In common sense, with the increasing number of carbon atoms in alcohol, average main pore size would decrease and depth would increase because the isotropy etching becomes weaker. But PSs in MeOH and PeOH solution are not so. PS in MeOH has a very small SCR width and wall thickness. This leads the pores has no enough space and charge to grow the branch and the main pore during the later etching. Most of charges accumulate at the bottom of pores and promote the growth of the depth. Moreover, in order to understand the etching in *n*-PeOH solution better, additional experiments have been designed.

Two comparative experiments with little (1 ml) *n*-PeOH and without *n*-PeOH are performed, which the results are shown in Figs. 3 and 4, respectively. In Fig. 3, macropores with diameters around 200 nm, depth around 80 μm and small cross-shaped pores can be observed. In Fig. 4, macropores with diameters around 500 nm, depth around 60 μm and very large cross-shaped pores can be observed. The two experiments have a similar concentration of solution. But compared with the sample without *n*-PeOH, we can see that the sample with little *n*-PeOH has lower depth, larger main pore size and larger branch. This means *n*-PeOH can enlarge SCR width effectively, which makes the large branch. But the hydrophobic property of the *n*-PeOH already becomes very strong and hinders the escape of H₂. It has a significant impact on the gradient of concentration in the depth direction. In addition, the degree of uniformity of *n*-PeOH in the solution has a big impact on the morphology. Compare with Figs. Fig. 4 and 1(e) and (E), though the concentration of HF and H₂O₂ are similar because of the little solubility of the *n*-PeOH, the uniformity of *n*-PeOH can be improved by add more *n*-PeOH, which the surface morphology of the PS becomes more uniformity.

4. Conclusion

The experiments show that the cross-shaped pores can be observed on the surface of PS, which are etched by the electrolyte with different alcohols additives and without illumination. As the order of alcohols increases, the density decreases and branch length increases. The changes of the main pores size are contrary to its own depth. Especially, PS in MeOH has small main pore size and large depth because it has no enough space and charge to etch laterally and most of charges accumulate at the bottom of pores and promote the growth of the depth. Moreover, when *n*-PeOH is added in the solution, it can make the large branch and hinder the etching in the depth direction due to its hydrophobic properties. In short, our experiments results obtained in this study highlight the role of alcohols on the dissolution kinetics of the silicon, which has a direct impact on the pore growth process.

Acknowledgments

This work was partly supported by National Program on Key Basic Research Project of China (973 Program, 2012CB934203), National Natural Science Foundation of China (11104186, 61138001, 11174207, 51202238), Shanghai Basic Research Key Project (12JC1407100) and the Science Foundation of Shanghai (11ZR1424900).

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