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Effects of Electrochemical Etching Conditions on the Formation and Photoluminescence Properties of P-Type Porous Silicon

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Abstract. Porous silicon has been widely used in sensors, microelectronics and other fields. This material retains the characteristics of the original silicon-based material, while having good optical, electrical and mechanical properties. How to make porous silicon efficient and controllable by means of anodization has become the focus of research. This article mainly studied the influence of different current conditions and electrolytes on the pore formation and performance of porous silicon in the electrochemical etching process of p-type silicon. It was found that porous silicon structures with controllable morphologies can be prepared by changing the etching current densities. Moreover, adding oxidants (H₂O₂) and dimethylformamide (DMF) into the electrolytes will significantly enlarge the etching parameter window of porous silicon and improve its photoluminescence properties. This will help to expand the applications of porous silicon in the field of microelectronics such as biosensors.

1. Introduction

With the rapid development of microelectronics technology, many excellent properties of porous silicon have been widely applied in various biosensors [1], micro batteries [2-4], photoelectric integrated devices [5] and other fields. At the same time, the high surface area of porous silicon has opened the possibility of a wide range of applications of porous silicon in biosensors such as drug delivery carriers [6-7].

In order to guide the controllable preparation of porous silicon, hoping that the structure and properties can be optimized during the preparation process. In the past several decades, a series of quite different models has been put forward to explain the formation of n-type porous silicon, including the famous space charge region (SCR) model, and the current burst model [8]. However, for p-type silicon, it's hard to produce and explain the pore-forming, especially the macropore formation [9]. Therefore, at present, passivation of p-type porous silicon surface or composite of other materials to improve its performance is the focus of researchers [10-12]. The disadvantage of these approaches is that operations are generally complex and require high cost and technology. For these reasons, a method for preparing P-type porous silicon with superior performance by controlling electrolyte and corrosion conditions, can not only promote the research of the formation process of the P-type porous



silicon, but also greatly reduce the cost and conducive to the realization of its industrial application.

In this paper, the effects of different current densities and electrolytes on the pore formation of p-type porous silicon were systematically investigated by a series of anodization experiments. Moreover, the HF/ethanol-containing electrolyte was modified with strong oxidizer (H_2O_2) and organic solvent (DMF), and special attention was paid on exploring the roles of electrolyte components and proportions in the pore morphologies and properties. We have found that the parameter window of pore formation was enlarged under the condition of oxidants and organic solvents, along with greatly enhanced photoluminescence (PL).

2. Experiment

Porous silicon samples were fabricated by electrochemical etching of p-type silicon (1-10 $\Omega\cdot\text{cm}$ resistivity, <100>-oriented, 450 ± 25 μm thick). The electrolyte solutions for anodization consisted of 40 wt% aqueous hydrofluoric acid (HF) and 99.7 wt% ethanol solutions with the volume ratio of 1:1 as a basic solvent. This HF-ethanol-based electrolyte was modified with two kinds of solutions, H_2O_2 and DMF. The concentration of electrolyte component is expressed in volume unless otherwise stated. Galvanostatic conditions of 30–100 mA cm^{-2} were applied from a computer controlled current source (tianjin lanli LK2500) with a tolerance down to 0.001 mA. All samples were prepared in the dark on an electrochemical etching platform in a standard decontamination chamber at room temperature (18 ± 1 $^\circ\text{C}$), with the etching area of 1 cm^2 . After anodization, the samples were rinsed repeatedly with deionized water and dried with nitrogen gas.

Field Emission Scanning Electron Microscopy (Shimadzu SPM9700) was used to characterize the microstructure of etched pores. Plan-view micrographs show the (1 0 0) planes, and the cross-section view micrographs, after cleaving the samples, show the pores in the (1 1 0) cleavage planes. The PL spectrums of the PS samples were measured at room temperature using an UV light from a Cary Eclipse Fluorescence Spectrophotometer.

3. Results and Discussion

First the dependence of pore size and etching rate on the applied current has been studied. For the given HF-ethanol basic electrolyte, a set of electrochemical etching experiments were performed for 5 min at different current densities ranging from 30 to 100 mA/cm^2 . The results are shown in figure 1. It can be seen that uniform pores with straight pore walls can be obtained and the pore-wall roughness decreases with the increase of current density.

At 30 mA cm^{-2} , branched pores were obtained and the average diameters were about 78 nm (Fig. 1a). The depth of pores was about 3.5 μm , corresponding to the etching rate of 0.7 $\mu\text{m min}^{-1}$. While current density increased to 50 mA cm^{-2} , straight pores with average diameters of 88 nm were obtained (Fig. 1b). The pore walls were relatively straight and smooth. The pore depth was about 5.3 μm after 5 min anodization, with the etching rate increased up to 1 $\mu\text{m min}^{-1}$. Increasing current densities to 80 mA cm^{-2} , the pore diameters increased to 80 nm while the etching rate increased to 1.37 $\mu\text{m min}^{-1}$, corresponding to the etching depth of 6.8 μm (Fig. 1c). At 100 mA cm^{-2} , well-defined pores with smooth pore-walls were obtained, and the pore diameters were about 85 nm (Fig. 1d). The pore depth was about 11.9 μm , corresponding to the aspect ratio and the etching rate 170 and 2.4 $\mu\text{m min}^{-1}$, respectively. One trend is that the pore diameters increase with the increase of applied current density, and the etching rate increases from 0.7 to 2.4 $\mu\text{m min}^{-1}$ when the current density increases from 30 to 100 mA cm^{-2} . Besides, some pore walls were broken or even collapsed during the etching process especially when the current density increased up to 50 mA cm^{-2} . This phenomenon became increasingly serious with the increase of the current density, and a large amount of collapse occurred when the current density reached 100 mA cm^{-2} . Therefore, it can be seen that the current parameter window for straight pore formation with the conventional HF/ethanol electrolyte is less than 100 mA/cm^2 .

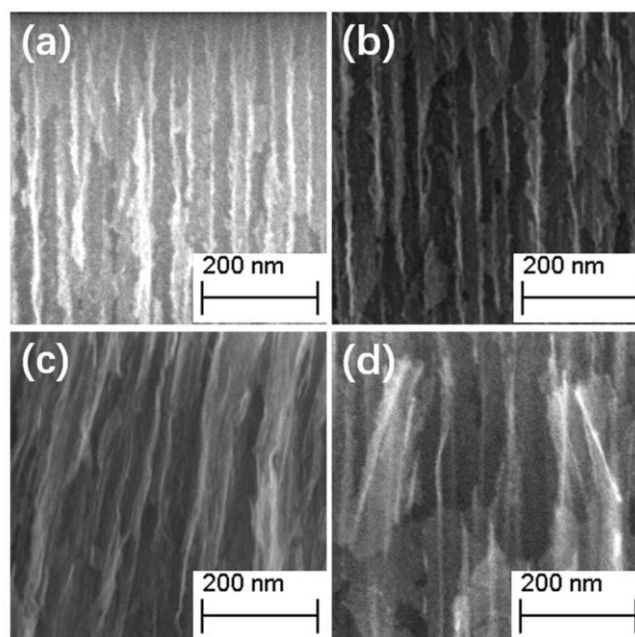


Figure 1. Cross-section SEM micrographs of pores formed on different current densities: (a) 30, (b) 50, (c) 80, (d) 100 mA cm⁻². All samples were anodized in HF-ethanol basic solution for 5 min.

Then, the dependence of pore formation and properties on electrolyte was investigated in detail. Two kinds of solvents, strong oxidizing agent (H₂O₂) and organic solvent (DMF), were added into the HF-ethanol based electrolyte respectively, with a volume ratio of 1:1:1. Figure 2 shows the top-view SEM images of the porous silicon formed with these two modified electrolytes at an etching current density of 100 mA cm⁻². It can be seen that the surface of the porous silicon was completely intact without any collapse after 5 min anodization both in H₂O₂ and DMF based electrolytes. It indicates that the addition of H₂O₂ or DMF can effectively improve the parameter window for the p-type porous silicon formation. Moreover, it is also apparent from Fig. 2a that the surface of the porous silicon formed by the H₂O₂-contained electrolyte is covered with a translucent film. This interesting phenomenon is probably due to the oxidation effect. A translucent oxide layer was formed on the porous silicon surface due to the existence of the strong oxidant, and the porous structure can be clearly observed through the oxide film. As a comparison, no similar oxide layer was formed under the condition of organic solvent modified electrolyte, shown in Fig. 2b.

Finally, the PL spectrums of porous silicon formed by different electrolytes were carried out at an excitation wavelength of 320 nm, and the results are shown in Figure 3. It can be seen from Fig. 3 that the porous silicon prepared in the HF/ethanol based electrolyte shows relatively weak luminescence intensity, with the luminescence peak located at 750 nm. However, the PL intensity of porous silicon obtained in H₂O₂ or DMF modified electrolytes was greatly improved, with the same current density. The PL intensity of the porous silicon obtained in H₂O₂ modified solution is about 15 times higher than that in basic electrolyte. Besides, the position of the luminescence peak was blue-shifted to 600 nm.

We believe that the change in porous silicon structure caused by changes in the etching solution system is the main cause of changes in photoluminescence properties. According to the "inrush current model", the formation process of porous silicon is essentially the dissolution process of silicon. The rate of electrochemical etching in the HF/C₂H₅OH electrolyte is slow due to the indirect dissolution, which is the process of first forming silicon oxide and then dissolving. However, the addition of a strong oxidant accelerates the oxidation process and shortens the overall reaction time to speed up the etching process. The addition of an organic solvent is just the opposite. It can inhibit the indirect dissolution process during the reaction and effectively reduce the pore-forming time of the porous silicon.

The modification of oxidant and organic solvent accelerates the pore-forming process of porous silicon, forming porous silicon with larger porosity under the same current conditions, and the larger void ratio brings more refined silicon nanowire and silicon nanoparticles. According to the quantum size effect, the corresponding photoluminescence efficiency increases, and the refinement of the silicon nanowires and nanoparticles causes the band gap to increase the PL spectrum peak to move toward high energy, which is represented by the blue shift of the luminescence peak position. With the addition of strong oxidizing agent, the Si-H bond of the porous silicon is replaced by a more stable Si-O bond, and a layer of oxide film is formed on the surface of the porous silicon as showing in Figure 2(a), which effectively passivates the porous silicon and makes the surface of the porous silicon form more luminescent center so that the formed porous silicon has higher photoluminescence efficiency.

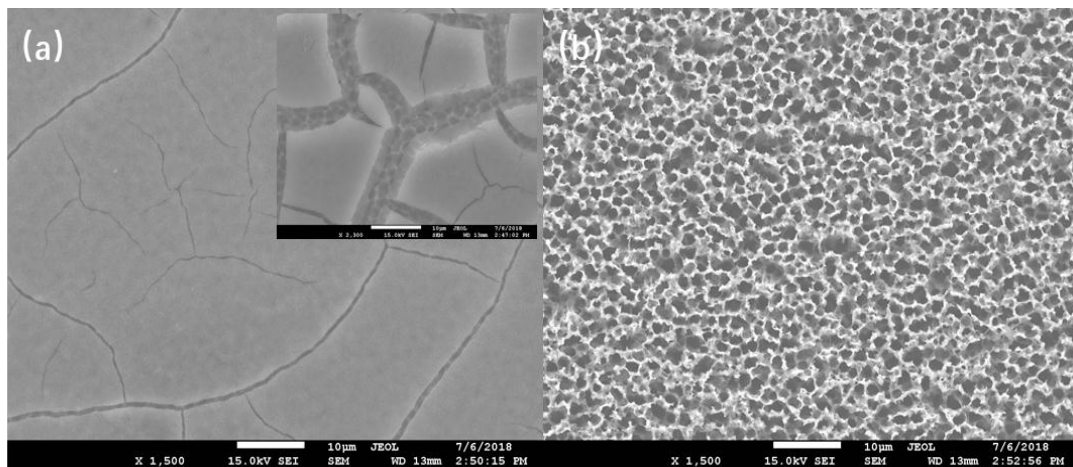


Figure 2. Porous silicon surface after addition of oxidant and organic solvent: (a) HF: ethanol: H₂O₂= 1: 1: 1; (b) HF: ethanol: DMF= 1: 1: 1. All samples were anodized at 100 mA cm⁻² for 5 min.

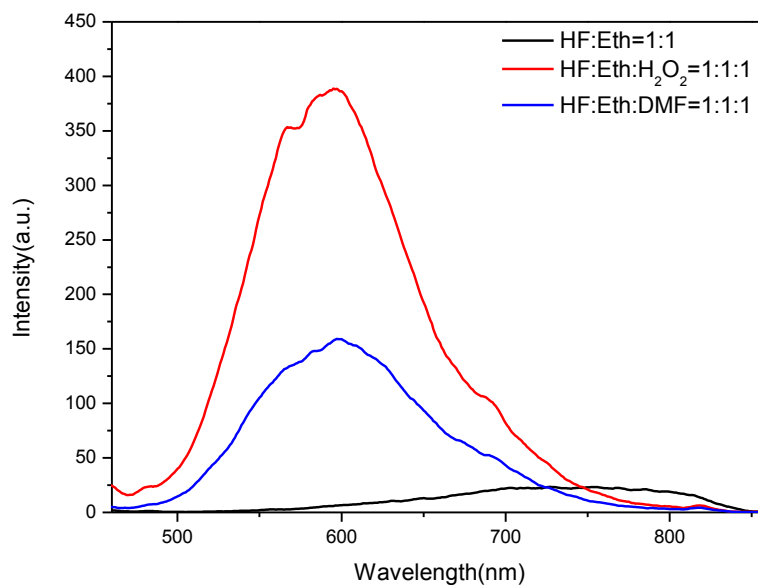


Figure 3. PL spectrum of porous silicon anodized in different electrolytes

4. Conclusion

In conclusion, straight pores were prepared on p-type silicon substrate with different current densities and electrolytes. The parameter window for pore formation is relatively small in the traditional HF/ethanol electrolyte, as well as poor PL efficiency. It is found that the addition of H₂O₂ and DMF into the electrolyte can obviously enlarge the parameter window and improve the PL. The PL intensity of the porous silicon obtained in H₂O₂ modified solution was observed 15 times higher than that in basic electrolyte. This result demonstrates an important method to enhance the PL of porous silicon and is expected to promote the application of p-type porous silicon in high-efficiency sensors and optoelectronic devices.

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6. References

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