Study on Silicon Microstructure Processing Technology Based on Porous Silicon

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Abstract. Aiming at the heterogeneity of micro - sealed cavity in silicon microstructure processing technology, the technique of preparing micro - sealed cavity of porous silicon is proposed. The effects of different solutions, different substrate doping concentrations, different current densities, and different etching times on the rate, porosity, thickness and morphology of the prepared porous silicon were studied. The porous silicon was prepared by different process parameters and the prepared porous silicon was tested and analyzed. For the test results, optimize the process parameters and experiments. The experimental results show that the porous silicon can be controlled by optimizing the parameters of the etching solution and the doping concentration of the substrate, and the preparation of porous silicon with different porosity can be realized by different doping concentration, so as to realize the preparation of silicon micro-sealed cavity, to solve the sensor sensitive micro-sealed cavity structure heterogeneous problem, greatly increasing the application of the sensor.

1. Introduction
The traditional sensor seal cavity is achieved by the bonding of silicon glass, which makes the sensor sealed cavity heterogeneous structure, resulting in the sensor by stress, reduce the performance of the sensor and limit the use of the sensor environment. Therefore, it is proposed to use porous silicon as the sacrificial layer to realize the processing of silicon microstructure. Solve the heterogeneous problem of micro-sealed cavity. Porous silicon is a unique nano-silicon cluster skeleton of the "quantum sponge" or "branch" microstructure silicon-based materials, is an important micro-machining material, the tower has a large surface area, good biocompatibility, room temperature can be Luminous and refractive index adjustable features, in the micro-sensor and actuator manufacturing has been widely used. Porous silicon due to its pore structure characteristics, has a very large surface area, its surface activity is high, the hole surface adsorption of organic gases, inorganic gases and water vapor. So it can be used for sensitive materials of gas and humidity sensors. Porous silicon, although filled with porous silicon thickness, but its structure is still showing a single crystal, the use of its single crystal properties, it can grow epitaxial silicon on it. The thickness of porous silicon is larger and can be precisely controlled, and the removal rate is high, so it can be used as a sacrificial
layer material in surface micromachining technology. At the same time, porous silicon is also a good insulation material, rich holes can absorb air to reduce thermal conductivity, improve the insulation performance, it can be used as a thermal sensor base material. Porous silicon was discovered as early as 1956[1], but in 1990 it made much progress in its research[2-5]. With the rapid development of MEMS theory and the rapid development of process technology, porous silicon in the field of micromachining has shown great prospects for development. So far, the theoretical study on porous silicon has focused on the preparation methods, formation mechanism, microstructure, luminescence mechanism, biotechnology, photo catalysis and super capacitor[6]. In the field of sensors, the use of porous silicon as a sacrifice layer has great advantages. The traditional sacrificial layer material thickness is only a few microns, limiting the fabrication of many microstructures and microsensors. The formation rate of the porous silicon film is faster than the conventional material, and can reach several microns per minute and has a thickness of up to 100 μm. The film or epitaxial silicon film can be prepared on porous silicon, which can form porous silicon within a particular region by a suitable mask, KOH at 1% concentration at room temperature can rapidly etch the porous silicon layer, and the preparation process can be compatible with the CMOS process[7,8].

2. Preparation principle of porous silicon
Preparation of stable porous silicon is the basis and key of the study. There are many ways to prepare porous silicon at home and abroad, which are mainly chemical corrosion, electrochemical corrosion, photochemical corrosion, hydrothermal corrosion, laser ablation. Chemical etching method for the preparation of porous silicon is the simplest method, which is prepared by the appropriate composition of the etching solution directly on the base monocrystalline silicon wafer for general chemical corrosion and preparation of porous silicon. However, the preparation of porous silicon in this process is difficult to control the process, the prepared porous silicon has poor homogeneity and has a limited thickness. Photochemical etching is a kind of porous silicon which reacts with the etching solution under the action of light, however, the light-assisted preparation of porous silicon requires very high wavelengths for incident light wavelength is too long to produce electron-hole pairs, Light waves too short will affect the electron-hole pair generation rate, porous silicon must be prepared using incident light of the appropriate wavelength. Hydrothermal corrosion method needs to be carried out in high pressure liquid system, and the preparation process temperature is higher. Electrochemical corrosion method has the advantages of simple operation and controllable preparation, and it is a relatively common preparation method. The use of electrochemical corrosion method to prepare porous silicon, not only to maintain the advantages of anisotropic corrosion, but also to avoid the high concentration of corrosive materials doped and high stress and other shortcomings. The reaction equation for the silicon surface is:

\[ Si + 2HF + (2-n)e^- \rightarrow SiF_2 + 2H^+ + ne^- \]  \hspace{1cm} (1)

\[ 2SiF_2 \rightarrow Si + SiF_4 \]  \hspace{1cm} (2)

\[ SiF_4 + 2HF \rightarrow H_2SiF_6 \]  \hspace{1cm} (3)

Where n <2, e + denotes a hole, and e - denotes an electron.
In the pores of the porous silicon, the reaction is carried out in two ways, respectively, for the divalent and tetravalent reactions. The bivalent reaction is:

\[ Si + 2HF + (2-n)e^- \rightarrow SiF_2 + 2H^+ + ne^- \]  \hspace{1cm} (4)

\[ 2SiF_2 + HF \rightarrow SiF_4 \]  \hspace{1cm} (5)

\[ SiF_4 + H_2 + 2HF \rightarrow H_2SiF_6 \]  \hspace{1cm} (6)

The tetravalent reaction is:

\[ Si + 4HF + (4-n)e^- \rightarrow SiF_4 + 4H^+ + ne^- \]  \hspace{1cm} (7)
3. Preparation of porous silicon

There are two factors that affect the structure of porous silicon, one is the silicon itself, including the silicon type, doping concentration and crystal orientation, the second is the process parameters, including the composition of the corrosive liquid, current density and corrosion time. In this paper, the electrochemical corrosion method was used to prepare porous silicon, and the relationship between different solutions, different types of silicon wafers, different current densities, different etching times and the rate, porosity, thickness and morphology of prepared porous silicon was studied. Experiments were carried out using a <100> crystal wafer with a thickness of 400 μm. The preparation of porous silicon is accomplished by double-channel electrochemical etching. Experiments were carried out with different corrosion solutions (HF and H₂O mixed solution, HF and C₂H₅OH mixed solution and HF, C₂H₅OH and H₂O₂ mixed solution), different substrates (p⁺ silicon and p-type silicon), different current densities (5 mA / cm², 10 mA / cm², 15 mA / cm², 20 mA / cm², 25 mA / cm²), different etching time (40min, 80min, 90min, 100min, 140min) for porous silicon. Finally, the porous silicon was etched with 1% KOH solution, the effects of different solutions, different substrate doping concentration, different current density and different etching time on the rate, porosity, thickness and morphology of the prepared porous silicon were analyzed.

4. Results and discussion

4.1. Effect of Corrosion Solution on Microstructure, Porous Silicon Thickness and Porosity of Porous Silicon

Aiming at the preparation principle of porous silicon, the surface morphology of porous silicon and the surface state of silicon wafer after etching were studied. The main components of the corrosion solution are HF, using different mixed solution (HF and H₂O mixed solution, HF and C₂H₅OH mixed solution and HF, C₂H₅OH and H₂O₂ mixed solution) as the etching solution. Porous silicon was prepared on an undoped p-type silicon wafer using a different ratio, corrosion time is 5min, current density 10mA / cm². After the process is completed, the porous silicon microstructure is tested. The prepared porous silicon was removed by 1% KOH solution, the surface morphology of the silicon wafer was tested, and the porous silicon thickness and porosity were calculated. Corrosion solution ratio is shown in Table 1. Preparation of porous silicon microstructure is shown in Figure 1. The surface state of the silicon wafer after removing the porous silicon is shown in Figure 2. Corrosion solution and porous silicon thickness and porosity relationship is shown in Figure 3.

Table 1. Corrosion solution ratio.

| Corrosion solution | Corrosion solution ratio |
|--------------------|--------------------------|
| HF: H₂O            | 3:1                      |
| HF: C₂H₅OH         | 3:1                      |
| HF: C₂H₅OH: H₂O₂   | 1:1:1                    |

Figure 1. The same ratio of different corrosive solutions prepared porous silicon microstructure.

SiF₄ + 2HF → H₂SiF₆
Figure 2. The surface state of the silicon after removing the porous silicon.

Figure 3. The relationship between the different corrosion solutions of the same ratio and the thickness and porosity of the porous silicon.

The above test results show that HF and H₂O mixed solution prepared porous silicon pore size is inconsistent, the surface is not uniform, HF, C₂H₅OH and H₂O mixed solution prepared porous silicon, the silicon surface has obvious hills after remove the porous silicon, HF and C₂H₅OH mixed solution prepared the porous silicon effect is relatively good, and the silicon surface smooth after remove the porous silicon. As a result of the preparation of porous silicon from different solutions, the thickness of porous silicon decreases with the decrease of HF concentration, and the porosity increases with the decrease of HF concentration. When H₂O₂ was added to the solution, the porosity increased first and then decreased with the increase of H₂O₂ concentration.

4.2. Effect of Silicon Type on Porous Silicon Microstructure, Porous Silicon Thickness and Porosity

Experiments were carried out using the mixed solution of etchant HF and C₂H₅OH, the etching time was 10min, and the current density was 10mA / cm² as the preparation method of porous silicon.
preparation of porous silicon was carried out using p-type and p⁺-type silicon as substrates. After the process is completed, the microstructure of the porous silicon is tested, as shown in Figure 4. The prepared porous silicon was removed by 1% KOH solution. The surface morphology of the tested silicon wafer was shown in Figure 5, and the calculated porous silicon thickness and porosity, the relationship between the silicon type and the porous silicon thickness and porosity is shown in Figure 6.

Figure 4. Preparation of porous silicon microstructure by different types of wafers.

Figure 5. The surface state of the silicon after removing the porous silicon.

Figure 6. The relationship between different types of silicon and porous silicon thickness and porosity.

The above test results show that the porous silicon of p⁺-type silicon is uniform. Compared with p-type silicon, porous silicon is prepared by p⁺-type silicon that porosity is low, the thickness of porous silicon is thick.

4.3. Influence of Current Density on Microstructure, Porous Silicon Thickness and Porosity of Porous Silicon
Experiments were carried out using p-type silicon wafers, the etching solution was mixed with HF and C₂H₅OH, and the etching time was 10min. The current densities were set to 5 mA / cm², 10 mA / cm², 15 mA / cm², 20 mA / cm² and 25 mA / cm², respectively. After the completion of the process, the
The microstructure of the porous silicon is shown in Figure 7. The prepared porous silicon was removed by using 1% KOH solution to test the surface morphology of the silicon wafer. As shown in Figure 8, the porous silicon thickness and porosity were calculated. The relationship between current density and porous silicon microstructure, porous silicon thickness and porosity is shown in Figure 9.

Figure 7. Preparation of porous silicon microstructure by different current densities.

Figure 8. The surface state of the silicon after removing the porous silicon.

Figure 9. The relationship between different current densities and porous silicon thickness and porosity.

The above test results show that the pore size of porous silicon increases with increasing current density. The thickness and porosity of the porous silicon increased first and then decreased with the current density. This is because the current density exceeds the critical current density, the occurrence of electrochemical polishing phenomenon.

4.4. Effects of Corrosion Time on Microstructure, Porous Silicon Thickness and Porosity of Porous Silicon

Experiments were carried out using p-type silicon wafers, the etching solution was mixed with HF and C2H5OH, and the current density was 10min. The etching times were set to 40min, 80min, 90min, 100min, and 140min, respectively. After the completion of the process, the microstructure of the porous silicon is shown in Figure 10. The prepared porous silicon was removed by using 1% KOH solution to test the surface morphology of the silicon wafer. As shown in Figure 11, the porous silicon...
thickness and porosity were calculated. The relationship between etching time and porous silicon microstructure, porous silicon thickness and porosity is shown in Figure 12.

![Figure 10. Preparation of porous silicon microstructure by different etching times.](image)

a) 40min  

b) 90min  

c) 140min

![Figure 11. The surface state of the silicon after removing the porous silicon.](image)

5. Conclusions

The results of the above tests show that the thickness and porosity of porous silicon increase first and then decrease with the increase of corrosion time, because of the phenomenon of excessive corrosion with the increase of corrosion time, porous silicon is dissolved. Resulting in porous silicon thickness and porosity continue to decrease.

5. Conclusions

The effects of etching fluid, current density, etching time and doping method on the preparation of porous silicon were studied. The effects of different process parameters were tested and tested. The relationship between the process parameters and the microstructure of porous silicon, the thickness of porous silicon and porosity was obtained. Optimize the process parameters, select different doping forms, can control the porous silicon pore size and porous silicon thickness. The use of porous silicon properties, the use of porous silicon as a sacrifice layer, silicon microstructure can be achieved, greatly increasing the application of the sensor.
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