Photoelectrochemical etching of uniform macropore array on full 5-inch silicon wafers*

Zhao Zhigang(赵志刚)[1,2], Guo Jinchuan(郭金川)[1], Lei Yaohu(雷耀虎)[1], and Niu Hanben(牛憨笨)[1,†]

(1 Institute of Optoelectronics Engineering, Shenzhen University, Shenzhen 518060, China)
(2 Institute of Optoelectronics Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China)

Abstract: We analyze the two main factors causing non-uniformity of the etched macropore array first, and then a novel photoelectrochemical etching setup for large area silicon wafers is described. This etching setup refined typical etching setups by a water cooling system and a shower-head shaped electrolyte circulator. Experimental results showed that the uniform macropore array on full 5-inch n-type silicon wafers could be fabricated by this etching setup. The morphology of the macropore array can be controlled by adjusting the corresponding etching parameters.

Key words: photoelectrochemical etching; macropore array; large area; non-uniformity; current density
DOI: 10.1088/1674-4926/31/7/076001 **EEACC:** 2575F; 4145

1. Introduction

Silicon macropore arrays are important materials in many applications, such as microchannel plates (MCP)[1,2], pixelated X-ray scintillators[3,4] and photonic crystal[5−7]. Traditional methods of fabricating the macropore array, including laser drilling, DRIE (deep reaction ion etching) or ICP (inductively coupled plasma), need complex equipments and the fabrication costs are very high. Furthermore, these methods all have their respective defaults, so it is difficult to fabricate a deep macropore array with a high aspect ratio of larger than 100. In 1990, Lehmann[8] reported that the periodic macropore array could be formed by electrochemical etching in prepatterned n-type silicon. In the following years, the photoelectrochemical etching of silicon has been investigated widely as a low-cost and effective method of fabricating a high aspect ratio macropore array.

However, in most cases, the area of silicon used in photoelectrochemical etching is no larger than 2 cm^2, which is not suitable for manufacturing practical components[9−12]. For example, the area of pixelated X-ray scintillators in a digital medical imaging system needs to be 100 cm^2 at least. Some works have been done with electrochemical etching of large area full silicon wafers, but there are still two major problems left undiscussed[13,14]. The first problem lies with the fact the temperature of the electrolyte will be heated up by the high power light source used in the etching system. The second problem comes from hydrogen bubbles generated during silicon dissolving, which can locally prevent electrolyte participating in reactions. Both the two problems can cause non-uniformity of the fabricated microstructures.

In this paper, we will first analyze factors causing non-uniformity in a typical photoelectrochemical etching setup. Then a novel large area etching setup will be introduced, which can overcome both of the two problems in large area silicon wafers' etching. Finally, uniform macropore array with high aspect ratio were fabricated on full 5-inch n-type silicon wafers by the novel photoelectrochemical etching setup.

2. Typical experimental setup and the non-uniformity

Silicon photoelectrochemical etching is essentially anodic dissolution of silicon in HF electrolyte. A typical experimental setup of photoelectrochemical etching is sketched in Fig. 1. The electrochemical reaction cell is made of Teflon and has a volume of 6000 cm^3. Silicon wafer is fixed on bottom of the cell by an aluminum ring holder, which provides the electrical contact between the wafer and the DC power supply. A Pt (platinum) electrode, working as counter electrode, is mounted 5 mm above the silicon wafer. Light source is a halogen lamp, which is placed about 6 cm from the bottom of the wafer to provide photo-exited holes in silicon.

The silicon sample used in this experiment is n-type 5-inch two-side polished silicon wafer, ⟨100⟩ oriented, with a resistivity of 3–6 Ω·cm. The electrolyte used for etching is HF (40%) : C_2H_5OH (99.9%) : H_2O, 2 : 4 : 14 by volume. C_2H_5OH is added to reduce hydrogen bubble formation. All the experiments should be performed at constant room temperature. To guarantee a uniform electrical field along the whole silicon

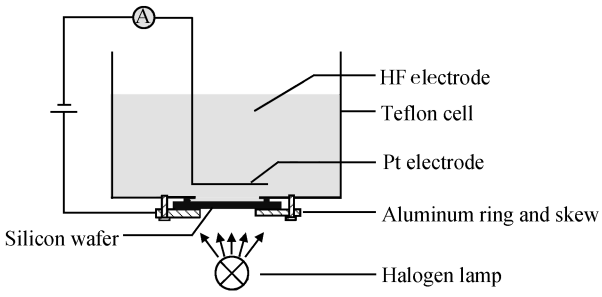


Fig. 1. Schematic of typical experimental setup.

* Project supported by the Key Program of the National Natural Science Foundation of China (No. 60532090).
† Corresponding author. Email: hbniu@szu.edu.cn
Received 21 January 2010, revised manuscript received 23 February 2010

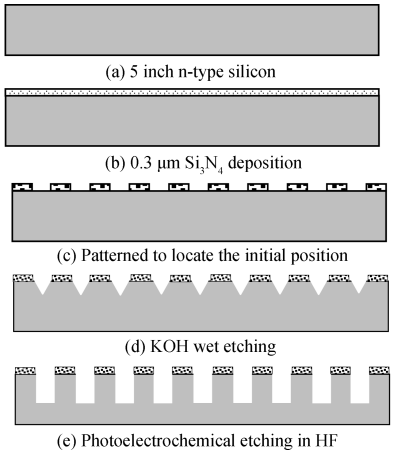


Fig. 2. Procedure flow of macropore arrays formation.

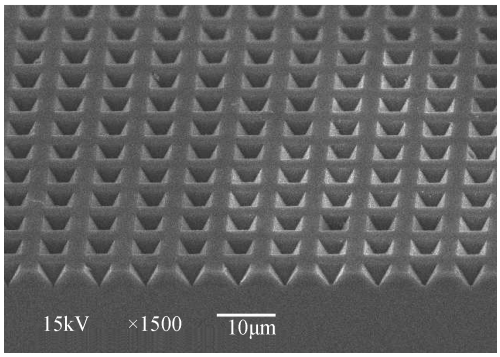


Fig. 3. SEM micrographs of inverted pyramid initial pits formed by KOH wet etching.

wafer, a layer of aluminum grid has already been deposited on the backside of the wafer.

The process flow is shown in Fig. 2. A 0.3-μm silicon nitride layer was deposited on the front side of the wafer (Fig. 2(b)). Then the silicon nitride layer was patterned by photolithography and RIE to define position of inverted pyramid initial pits (Fig. 2(c)). Inverted pyramid initial pits were formed by a KOH anisotropic wet etching at a temperature of 80 °C (Fig. 2(d)). Finally, macropore array were fabricated in HF solution by photoelectrochemical etching (Fig. 2(e)).

Initial pattern used in our experimental was square array with 5 mm side and 8 mm pitch. As shown in the SEM (scanning electron microscope) micrograph in Fig. 3, uniform inverted pyramid initial pits could be formed by this process. Morphology of inverted pyramid on the whole the silicon wafer was almost the same.

But morphology of macropore array etched in HF electrolyte was not so good. Figure 4 shows macropore array of three different regions in 5-inch etched silicon wafer. The etching time was 70 min, current density was 5.1 mA/cm^2, and electrolyte temperature went up from 23.8 to 31.7 °C almost linearly. Morphology of macropore array in one region differed clearly from other regions'. At the same time, non-uniformity can also be seen in every macropore along its depth direction in one region.

In fact, the non-uniformity was foreseeable by some phenomenons. One obvious example was that a big bubble could be seen moving out from Pt electrode every 2 or 3 min, correspondingly the etching current jumping from 0.5 to 2 A. Another example was also obvious, because surface of different parts on the 5-inch etched silicon wafers exhibited different colors.

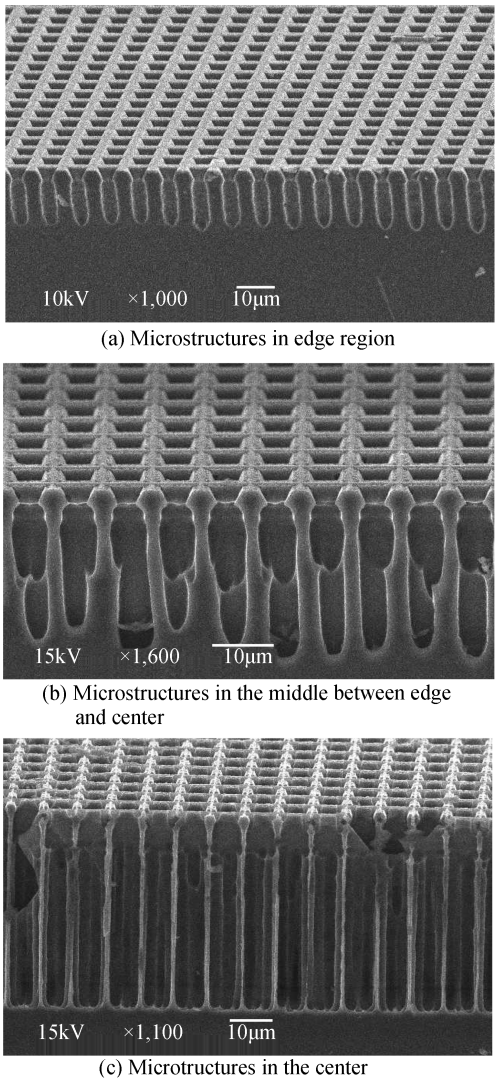


Fig. 4. SEM micrographs of microstructures in three different parts of the etched silicon wafer by the typical etching setup.

3. Factors causing non-uniformity on large area silicon wafer etching

There are two main factors which are inevitable on large area silicon wafer electrochemical etching, causing non-uniformity of macropore array in time domain and in space domain respectively.

(1) Electrolyte temperature heated up by the high power light source

To provide a high and uniform light intensity on the backside of the whole wafer, not one only halogen lamp, but more halogen lamps forming a lamp array are used for the light source. For example, number of lamps used in our 5-inch experimental setup was 14. Each lamp has a power of 250 W, so

the total power energy of the halogen lamps can be as high as 3500 W. Although four electric fans are placed near the lamps to take away much heat generated by the light source, temperature of the electrolyte still can be heated up from 20 to 60 °C if the etching time is longer than 2 h.

Increase of temperature can remarkably cause non-uniformity of the etched silicon structures. The relationship between peak etching current density J_{ps} (in A/cm^2) and electrolyte temperature T (in ℃) can be expressed by Eq. (1)[15]:

$$J_{ps} = Cc^{1.5} \exp(-E_a/KT), \tag{1}$$

where $C = 3300$ A/cm^2, c represents concentration of the HF solution, $E_a = 0.345$ eV. It can be seen from Eq. (1) that temperature T influences current density J_{ps} seriously by the form of exponential.

Therefore, as electrolyte temperature increases rapidly with the advance of etching time, morphology of macropore array changes seriously. Because electrolyte temperature goes up as time advancing, non-uniformity caused by this factor is in time domain.

(2) Hydrogen bubbles staying between silicon and Pt electrode

Hydrogen is one production of silicon dissolution reaction. The reaction is expressed by Eq. (2):

$$\mathrm{Si} + 6\mathrm{HF} + 2\mathrm{h}^+ \rightarrow \mathrm{SiF}_6^{2-} + \mathrm{H}_2 + 4\mathrm{H}^+. \tag{2}$$

It shows that large volume of hydrogen bubbles will be generated during the dissolution reaction. The generated hydrogen bubbles can cause non-uniformity in two ways. Firstly, small hydrogen bubbles, in micron scale, stick on the surface of the silicon wafer, each covering some etched macropore. Secondly, large hydrogen bubbles assemble in some local places between silicon wafer and Pt electrode. In both these states, hydrogen bubbles separate HF solution from silicon, and then the silicon dissolution will break down locally.

This problem is relatively more serious in large area silicon wafers' etching, because the area of Pt electrode must be large enough to obtain uniform electric field on silicon wafers. For example, in our 5-inch etching system, the Pt electrode is a round shaped panel with a radius of 50 mm. As pointed out before, the distance between Pt electrode and silicon wafer is only 5 mm, so the hydrogen bubbles can hardly move out from the region trapped by Pt electrode and silicon wafer. For the same reason, fresh HF solution outside this region can hardly flow into the surface of silicon wafer. Non-uniformity caused by this factor is in space domain.

Furthermore, local hydrogen bubbles on some regions can also affect morphology of macropore array outside these regions. Photoelectrochemical etching experiments are mostly carried out in constant current density mode by adjusting applied voltage or light intensity, where current density is an average value over the whole etching surface. If one or more local regions are occupied by hydrogen bubbles, other regions actually take up larger current density, therefore morphology of macropore array changes accordingly.

In order to fabricate uniform macropore array, we must overcome the problems existing in the experimental setup firstly.

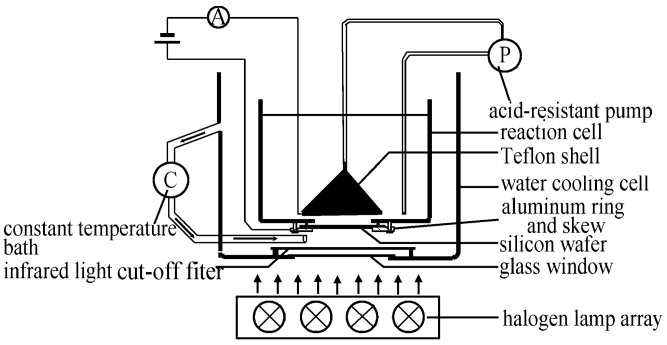


Fig. 5. A novel large area photoelectrochemical etching setup.

4. A novel setup for uniform etching

Traditionally, a constant temperature bath is used in the etching system to cool the electrolyte directly. It is unfortunately that the electrolyte in silicon photoelectrochemical etching is HF contained, and the aqueous HF is strongly corrosive to mental made constant temperature bath. So directly cooling of the electrolyte by a constant temperature bath does not work here. Nevertheless, we should notice the fact that light source is the only heat source responsible for heating up the electrolyte. If we block off heat transmission from halogen lamps to electrolyte, then electrolyte will not be heated up by the light source. In our novel etching system, a water cooling system settled between silicon wafer and light source can block off the heat transmission effectively.

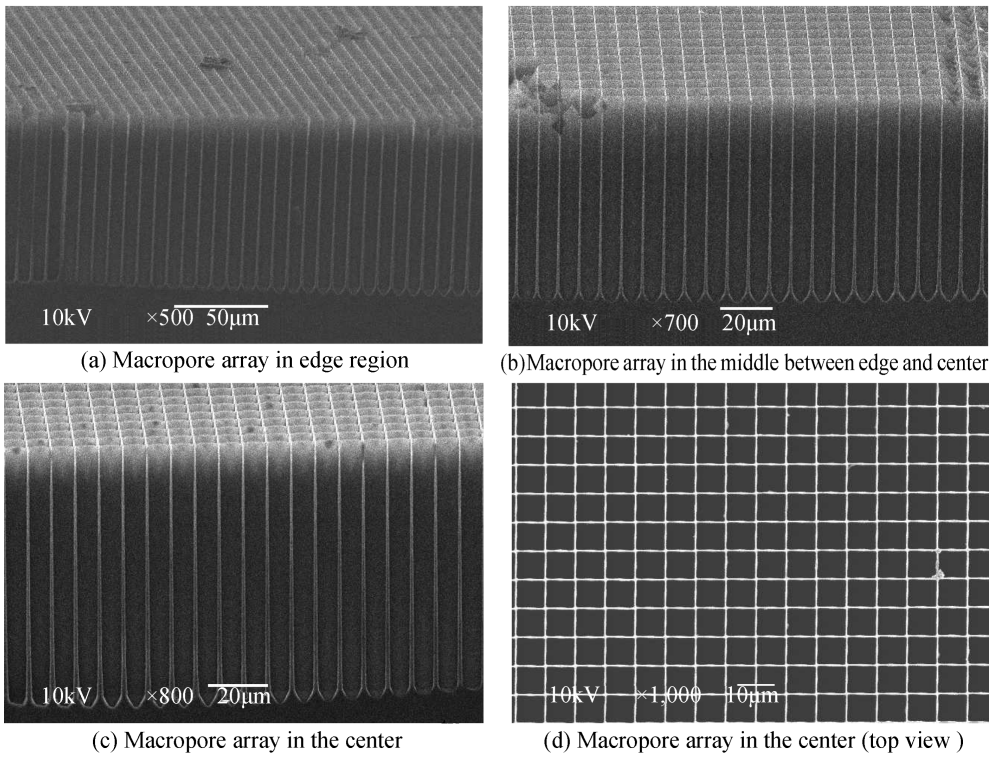
As for the problem of hydrogen bubbles, traditional way is to stir the electrolyte by a HF-resistant stirrer, or circulating the electrolyte by a HF-resistant circulating pump. But in the 5-inch etching system, the area of Pt electrode is so large, and the distance between Pt electrode and wafer is so short, so the electrolyte between Pt electrode and wafer cannot be stirred or circulated equally, especially the inner part. To increase the circulation area, a pump with two output pipes have been designed by Mlcak[16]. But it is essentially still in the form of point circulation, because there are only two points or two local places can be circulated. In our novel etching system, a shower-head shaped circulator is manufactured, which can circulate the whole silicon wafer uniformly in the form of plane circulation.

The novel 5-inch etching system with a water cooling system and a shower-head shaped electrolyte circulator is sketched in Fig. 5.

5. Results and discussion

The water cooling system consists of a water cooling cell and a constant temperature bath. A glass window is water-tight sealed on bottom of the water cooling cell. The water cooling cell is filled with transparent water, and located outside the reaction cell. The constant temperature bath cools the water flowing out from the water cooling cell, and circulates it back again. Because water between glass window and silicon wafer can absorb the light with the wavelength of greater than 1.1 μm, therefore heat generated by light source cannot reach silicon wafer.

To circulate the electrolyte uniformly, outlet of the acid-



(a) Macropore array in edge region (b)Macropore array in the middle between edge and center

(c) Macropore array in the center (d) Macropore array in the center (top view)

Fig. 6. SEM micrographs of macropore array etched by the novel large area photoelectrochemical etching setup. (a)–(c) Cross section. (d) Top view.

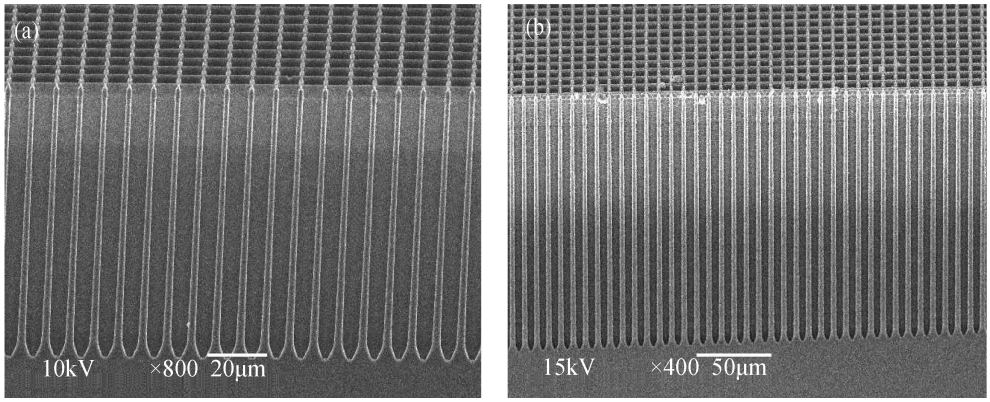


Fig. 7. SEM micrographs of modified macropore array etched in different current densities. (a) Applied voltage was 2.4 V, and current density was 8.4 mA/cm^2. (b) Applied voltage was 1.9 V, and current density was 5.7 mA/cm^2.

resistant pump was connected by a cone cavum with the Pt electrode mounted on its bottom, forming a shower-head shaped electrolyte circulator. Pt electrode is the key component in the circulation system, which is not a Pt mesh or integrated Pt plane plate, but a plate with equally distributed holes. Diameter of the holes is 0.4 mm, and the distance of two adjacent holes is 1.5 mm. By this design, circulated HF electrolyte can flow out from the Pt electrode and erode the whole silicon wafer uniformly.

A series of experiments have been done to test the novel large area silicon wafer etching setup. Experimental tests showed that the temperature changes of the electrolyte could be controlled within the range of ± 1 ℃, during the whole etching time of 2 h or more. Tiny hydrogen bubbles generated by silicon dissolution reaction dispersed in the electrolyte immediately, and no big hydrogen bubbles were found. The phenomenon of etching current fluctuation did not happen anymore, and constant current density photoelectrochemical etching could be sustained.

Figure 6 shows the uniform macropore array fabricated by the novel etching setup. The photoelectrochemical etching experiment was carried out in constant current mode, where current density was 11.3 mA/cm^2, etching time was 90 min, electrolyte temperature kept almost constant at 29.3 °C, and the applied voltage was 2.8 V. Morphology of macropore array was almost the same in different regions of the whole silicon wafer.

But there still one question left. As we can see from Figs. 6(a) to 6(d), thickness of the macropore walls was only about 1 μm, which was much less than the value of 3 μm in initial pattern. Morphology of macropore array depends on many pa-

rameters, such as applied voltage across the wafer, HF concentration, light wavelength and intensity, silicon wafer character, and so on. Plenty of researches have been done on these topics in detail[17−19].

To increase the thickness of macropore walls, we changed the applied voltage only to adjust photoelectrochemical etching current density. Figures 7(a) and 7(b) show morphology of macropore array fabricated at different current densities. When current density was decreased to as low as 5.7 mA/cm^2, thickness of macropore walls can be increased to a little less than 3 μm.

6. Conclusion

Factors causing non-uniformity in large area silicon wafer photoelectrochemical etching have been investigated. To resolve the problems in the typical photoelectrochemical etching setup, a novel large area photoelectrochemical etching setup with a water cooling system and a shower-head shaped circulator was manufactured. Uniform macropore array can be fabricated on whole 5-inch silicon wafers by the novel etching setup. Based on the fact that current density is equal on the whole large area silicon wafer, further researches concerning parameters such as applied voltage and HF concentration, can also be performed on this universal experimental platform.

Acknowledgements

We would like to thank Engineers Li Guoyan and Bai Caili from Shenzhen SI Semiconductor Co, LTD for providing much support for the fabrication of initial patterns on 5 inch silicon wafers, and Ms Xu Guiwen in Test Center of our Institute for giving great help in SEM testing ever since 2006.

References

[1] Gao Yanjun, Duanmu Qingduo, Wang Guozheng, et al. Formation of a silicon micropore array of a two-dimension electron multiplier by photo electrochemical etching. Journal of Semiconductors, 2009, 30(2): 022001

[2] Yuan D, Ci P, Tian F, et al. Large-size P-type silicon microchannel plates prepared by photoelectrochemical etching. J Micro/Nanolith, 2009, 8(3): 033012

[3] Bade X, Norlin B, Kleimann P, et al. Performance of scintillating waveguides for CCD-based X-ray detectors. IEEE Trans Nucl Sci, 2006, 53(1): 3

[4] Bade X, Linnros J, Kleimann P, et al. Metallized and oxidized silicon macropore arrays filled with a scintillator for CCD-based X-ray imaging detectors. IEEE Trans Nucl Sci, 2004, 51(3): 1001

[5] Lehmann V, Ronnebeck S. MEMS techniques applied to the fabrication of anti-scatter grids for X-ray imaging. The 14th IEEE International Conference on Micro Electro Mechanical Systems, 2001: 84

[6] Garin M, Trifonov T, Rodriguez A, et al. Optical properties of 3D macroporous silicon structures. Mater Sci Eng B, 2008, 149(3): 275

[7] Matthias S, Matthias S, Müller F, et al. Macroporous silicon: homogeneity investigations and fabrication tolerances of a simple cubic three-dimensional photonic crystal. J Appl Phys, 2006, 99(11): 113102

[8] Lehmann V, Foll H. Formation mechanism and properties of electrochemically etched trenches in n-type silicon. J Electrochem Soc, 1990, 137(2): 653

[9] Tao Y, Esashi M. Local formation of macroporous silicon through a mask. J Micromech Microeng, 2004, 14: 1411

[10] Tao Y, Esashi M. Macroporous silicon-based deep anisotropic etching. J Micromech Microeng, 2005, 15: 764

[11] Grigoras K, Niskanen A J, Franssila S. Plasma etched initial pits for electrochemically etched macroporous silicon structures. J Micromechan Microeng, 2001, 11: 371

[12] Bade X, Kumar R R T, Kleimann P, et al. Formation of ordered pore arrays at the nanoscale by electrochemical etching of n-type silicon. Superlattices and Microstructures, 2004, 36: 245

[13] Van den Meerakker J E A M, Elfrink R J G, Roozeboom F, et al. Etching of deep macropores in 6 in Si wafers. J Electrochem Soc, 2000, 147(7): 2757

[14] Foll H, Izuo S, French P J, et al. Macroporous-based micromachining on full wafers. Sensors and Actuators A, 2001, 92: 384

[15] Lehmann V. The physics of macropore formation in low doped n-type silicon. J Electrochem Soc, 1993, 140(10): 2836

[16] Mlcak R, Tuller H L. Electrochemical etching process. United States Patent, No. 5338416. 1994

[17] Bao Xiaoqing, Ge Daohan, Jiao Jiwei. Observation of a diverse deviation from macropore-formation theory in silicon electrochemistry. Chin Phys B, 2008, 17(8): 3130

[18] Carstensen J, Christophersen M, Hasse G. Parameter dependence of pore formation in silicon within a model of local current bursts. Phys Status Solidi A, 2000, 182(1): 63

[19] Jehng W D, Lin J C, Lee S L. Concentration effect of HF on energy band diagram for n-Si(100)/HF photoelectrochemical etching system. J Electrochem Soc, 2005, 152(3): C124