

Influence of etching current density on the morphology of macroporous silicon arrays by photo-electrochemical etching*

Wang Guozheng(王国政), Chen Li(陈立), Qin Xulei(秦旭磊), Wang Ji(王薊), Wang Yang(王洋),
Fu Shencheng(付申成), and Duanmu Qingduo(端木庆铎)[†]

(School of Science, Changchun University of Science and Technology, Changchun 130022, China)

Abstract: Macroporous silicon arrays (MSA) have attracted much attention for their potential applications in photonic crystals, silicon microchannel plates, MEMS devices and so on. In order to fabricate perfect MSA structure, photo-electrochemical (PEC) etching of MSA and the influence of etching current on the pore morphology were studied in detail. The current–voltage curve of a polished n-type silicon wafer was presented in aqueous HF using back-side illumination. The critical current density J_{PS} was discussed and the basic condition of etching current density for steady MSA growth was proposed. An indirect method was presented to measure the relation of J_{PS} at the pore tip and etching time. MSA growth was realized with the pore diameter constant by changing the etching current density according to the measuring result of J_{PS} . MSA with 295 μm of depth and 98 of aspect ratio was obtained.

Key words: current density; macroporous silicon arrays; photo-electrochemical etching; initial pits

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1. Introduction

The electrochemical etching of porous silicon (PS) on silicon wafer during anodization in HF solutions has been known for five decades^[1,2]. PS is classified according to size as micropore if < 2 nm wide, as mesopore if 2 to 50 nm wide, and as macropore if > 50 nm wide^[3]. Macropore formation on n-type substrates in aqueous HF was first observed in 1972^[4]. Early in 1990s, Lehmann and Föll^[5,6] reported the formation of straight, smooth and well spaced macroporous silicon arrays (MSA) using an n-type silicon wafer having initial pits array on front side and illuminated on backside. The first report of the formation of MSA on p-type silicon wafer was published in 1994^[7].

Generally, there are two kinds of methods for the preparation of MSA. These are: fluorine based inductively coupled plasma (ICP) and electrochemical etching process. Compared with ICP, the remarkable feature of the electrochemical etching technique is that it can prepare the MSA with extremely high aspect ratio at a low cost.

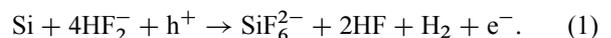
In the 1990s, the potential for making macroporous silicon devices was convinced and electrochemical etching technique of MSA was studied extensively for the fabrication of silicon structures. The application fields of macroporous silicon have increased considerably, for example, MEMS devices (accelerometers, biochemical devices etc.)^[8], inter-connection of electrical signal in multi-layer semiconductor devices^[9], heat sink devices^[10], microchannel plates^[11,12], photonic crystals in the IR regime and so on^[13].

To fabricate MSA with straight pore or the diameter of pore periodically changing along the growing direction, the etching current density should be adjusted because the etching current density effects on the morphology of macropore in the

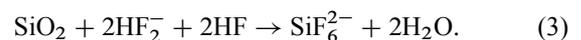
electrochemical etching. However, little information was reported about these effects. In this paper, the mechanism and experiments of macropore formation in n-type silicon by photo-electrochemical (PEC) etching were introduced. The relation of the local current density J_{tip} around macropore tip and the critical current density J_{PS} was discussed. An indirectly method was presented for measuring the J_{PS} at the pore tip.

2. Macropore formation mechanisms in n-type silicon

In acidic electrolytes with fluoride, electrochemical dissolution of a silicon wafer takes place at anodic potentials. PS is formed when anodic current density is lower than the critical current density J_{PS} , which is the symbol of the reaction transforming from the charge-supply-limited to the mass-transport-limited case. The active particles in the dissolution process are HF, $(\text{HF})_2$ and HF_2^- . A dissolution reaction for this regime is^[14]:



When the current density becomes larger than J_{PS} , dissolution occurs via an intermediate anodic oxide film. Hence the reaction can be separated into electrochemical oxide formation according to Eq. (2) and chemical dissolution of the oxide due to HF, $(\text{HF})_2$ and HF_2^- according to Eq. (3):



According to the reactions above, holes must be presented for dissolution of a silicon wafer. At room temperature, the number of thermal generated holes is little, so the silicon wafer must be illuminated or the applied bias reached the

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[†] Corresponding author. Email: dmqd@163.com

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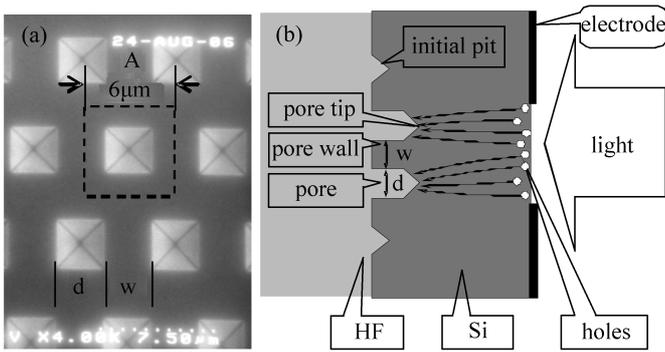


Fig. 1. (a) Initial pits array and (b) macropore formation mechanisms in n-type silicon with PEC etching.

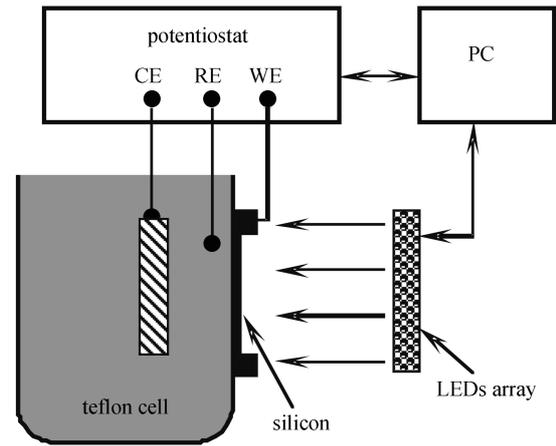


Fig. 3. PEC etching set-up.

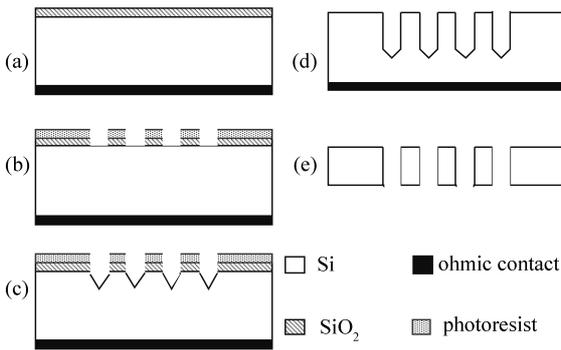


Fig. 2. Flow diagram of electrochemical etching process for MSA.

breakdown field strength for dissolution of an n-type silicon wafer.

Two requirements must be satisfied for MSA by electrochemical etching: (1) the pore walls must be passivated against dissolution; and (2) the pore tips must be in a condition that promotes dissolution. That means holes must be depleted at the pore walls and be accumulated at the pore tips. In order to produce periodically arranged macropore arrays, the initial pits array must be formed on the front side of silicon wafer prior to the etching to determine the nucleation sites. As shown in Fig. 1, the initial pits array having sharp tips can collect the holes effectively. When a flow of photo generated holes is provided from the back side of silicon wafer, holes are collected by the pit tips and dissolution of silicon takes place there. If all holes are consumed in the dissolution reaction at the pore tips and no holes are left to penetrate into the walls between the pores, the walls become passivated, and then macropores were formed^[6].

3. Experiment

Figure 2 shows the process flow of MSA by PEC etching. Taking the effect of crystal orientation into account, a (100) silicon wafer was selected for a perpendicular macropore.

First, ion implantation was performed on the back surface of silicon wafer to achieve good ohmic contact. To activate the implanted ions and form silicon dioxide (SiO₂), the sample was annealed at 1000 °C in oxygen for one hour. Above process steps is shown in Fig. 2(a).

After coating the front surface of silicon wafer with a photoresist, a periodic pattern was transferred to the photoresist

film by photolithography. Then the patterned SiO₂ were etched using reactive ion etching. Above process steps is shown in Fig. 2(b).

The silicon substrate was etched through the remaining SiO₂ mask by tetramethylammonium hydroxide (TMAH) etching, and then the initial pits array was made as shown in Fig. 2(c). The initial pits were inverted-pyramid-shaped as shown in Fig. 1(a).

The silicon wafer was then placed into an electrochemical cell. After PEC etching for several hours, MSA formed as shown in Fig. 2(d).

Finally, the backside of silicon wafer was etched using a KOH solution to make the through pore as shown in Fig. 2(e).

The PEC etching set-up is shown in Fig. 3. A window in the teflon electrochemical cell was made to place the silicon wafer. An array of LEDs with a peak emission wavelength of 850 nm was used to illuminate the silicon wafer back surface for exciting electron-hole pairs. A PARSTAT 2273 potentiostat was used to control the three electrodes. The counter electrode was a 25 cm² platinum grid. The etching current was adjusted by changing the light intensity of the LEDs array. The electrolyte was 3.5 wt% hydrofluoric acid with 0.005 mol/L non-ionic surface active agent (Triton X-100). To remove hydrogen bubbles from the sample front surface, the electrolyte was stirred slightly. The electrolyte was kept at 300 K by a temperature controller.

4. Results and discussion

4.1. Basic condition of macropore growth

The current-voltage curve of a polished n-type silicon wafer in 3.5 wt% aqueous HF using back-side illumination is shown in Fig. 4. The critical current density J_{PS} is easily identified by the peak in the current-voltage curve. J_{PS} is dependent on the mass transport, the HF concentration c , the absolute temperature T , diffusion coefficients and activation energy E_a . J_{PS} (in mA/cm²) can be described by^[6]

$$J_{PS} = Bc^{3/2} \exp(-E_a/K_0T), \quad (4)$$

where $B = 3.3 \times 10^9$ mA/cm², $E_a = 0.345$ eV, $K_0 = 1.38 \times 10^{-23}$ J/K, c (in wt%), T (in K).

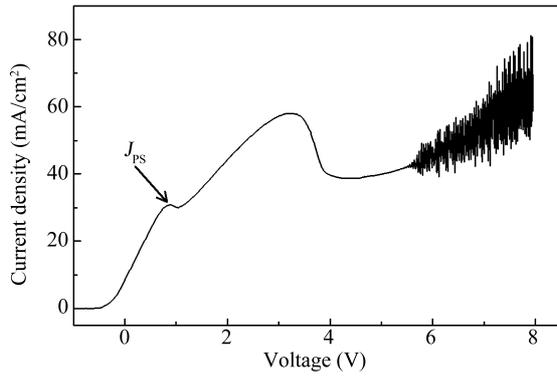


Fig. 4. Current–voltage curve for n-type silicon in an electrolyte of hydrofluoric acid.

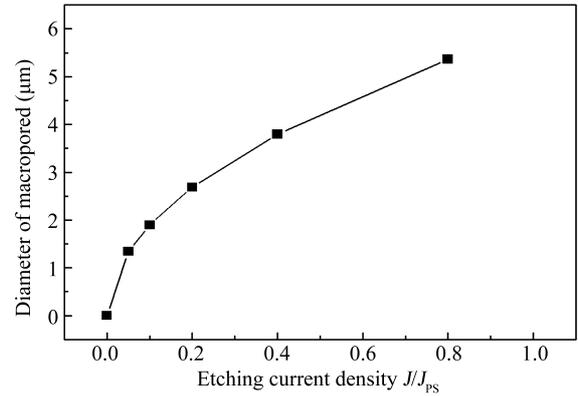


Fig. 5. Curve of diameter d of macropore versus the etching current density J .

The basic condition for stable macropore growth in a silicon wafer is that the local current density J_{tip} around macropore tip equals J_{PS} . J_{tip} equals the etching current via a pore divided by the cross section areas of a pore. If current density $J_{tip} < J_{PS}$, the reaction is limited by charge supply, holes are insufficient around the macropore tip, and HF is enough to consume these holes. Therefore, only a small area around the pore tip can initiate pore growth because the sharp tip can collect the holes effectively. The pore diameter d decreases and the pore wall thickness w increases. The local current density J_{tip} is enhanced and reaches J_{PS} . If $J_{tip} > J_{PS}$, holes are enough to consume the HF around macropore tip, and HF is insufficient. For the number of the offered holes is more than that of the consumed holes at the tip, they start to penetrate into the pore walls and dissolution takes place on the surface of the pore walls. The pore diameter d increases and the pore wall thickness w reduces. Therefore, the local current density J_{tip} was restrained and remained J_{PS} .

4.2. Relation of the diameter of pore and etching current density

Silicon wafers with initial pits array as shown in Fig. 1(a) were etched to form macropore arrays at different etching current density J , which equals the total etching current divided by the area of front surface of silicon wafer, with an applied bias of 1.5 V. The higher the etching current density is, the greater the diameter of pore is. The curve of macropore diameter d versus J is shown in Fig. 5. The diameter d is a function of square root of J and can be described approximatively by

$$d = A(J/J_{PS})^{1/2}, \tag{5}$$

where A is the length of side of the repeat unit of the pattern, as shown in Fig. 1(a). Equation (5) further indicates the basic condition that the local current density J_{tip} around macropore tip should equals J_{PS} for steady macropore growth in a silicon wafer is validity.

Along with the pore growth, the rate of mass transport reduces in the pores. This results in the concentration of HF at the pore tip decreases and the J_{PS} reduces accordingly. According to Eq. (5), if the etching current is constant in the etching process, the diameter of pores should increase gradually, which was proved by experiments.

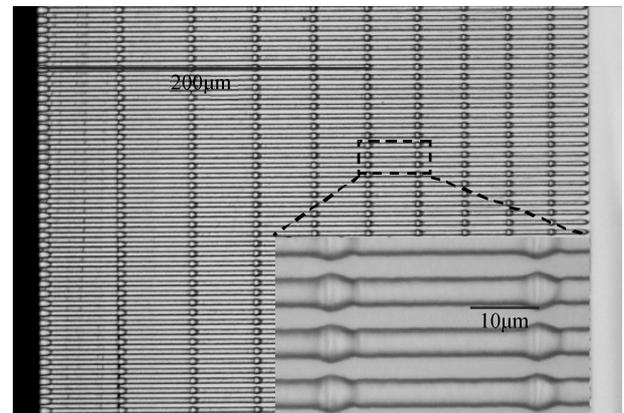


Fig. 6. Metalloscope photograph of macropore array with the diameter changed periodically.

4.3. Relation of J_{PS} and etching time

In order to keep the diameter constant, the etching current density J should be adjusted according to the relation of J_{PS} at the pore tip and etching time. It is difficult to calculate the relation between J_{PS} and t directly because the influencing factors of mass transport in the pore comprise convection, diffusion, electrical field, interfacial tension and so on. Therefore, the relation was calculated indirectly as is discussed later.

The J_{tip} is a measure of the growth rate V of the pore. As explained above, J_{tip} equals J_{PS} for a stable pore growth. So V (in cm/s) can be described by

$$V = \frac{J_{PS}}{n(-e)N_{Si}}, \tag{6}$$

where e is the elementary charge (1.602×10^{-19} C), N_{Si} is the atomic density of silicon wafer (5×10^{22} cm⁻³), and n is the dissolution valence (number of charge carriers per dissolved silicon atom) and equals approximatively 2.65.

Equation (5) offers a way of tuning the pore diameters during pore growth by a variation of J . As shown in Fig. 6, the observed markers along the pore length are created by suddenly increasing the etching current for 2 min every 58 min. By measuring the length from the markers to the front surface, the dot line of pore length L versus etching time was obtained as shown in Fig. 7.

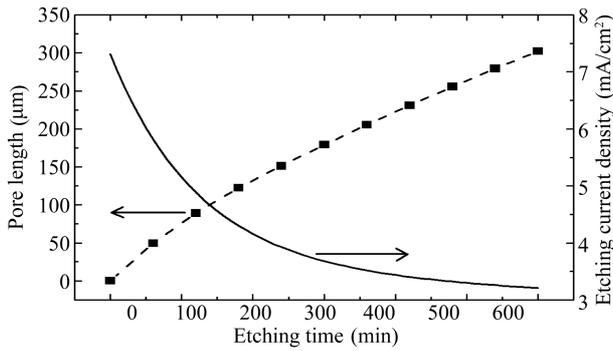


Fig. 7. Curves of pore length and etching current density versus etching time.

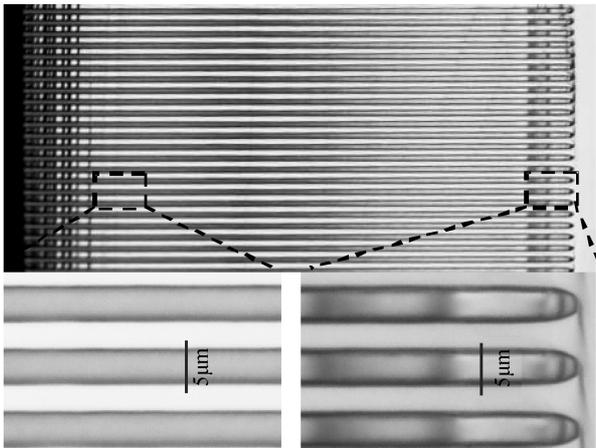


Fig. 8. Metalloscope photograph of the MSA cross section.

By curve fitting of the dot line in Fig. 7, the relation of L (in μm) and t (in min) was obtained and described by

$$L = 225 + 0.3t - 55 \exp(-t/123) - 170 \exp(-t/1342). \quad (7)$$

After differentiating of Eq. (7), the relation of V and t was obtained and described by

$$V = 0.3 + 0.45 \exp(-t/123) + 0.13 \exp(-t/1342). \quad (8)$$

Then the relation of critical current density J_{PS} at the pore tip and etching time t can be calculated from Eq. (4) and described by t :

$$J_{PS} = 10.6 + 15.8 \exp(-t/123) + 4.5 \exp(-t/1342). \quad (9)$$

The calculated results suggest that both J_{PS} and V are exponential damping and the etching current density must be changed during the electrochemical etching process. According to Eqs. (5) and (9), the etching current density J can be calculated to control the diameter of macropore in the etching process. MAS was etched by PEC using a programmed J as shown in Fig. 7 (line). The macropore growth was realized with the pore diameter constant as shown in Fig. 8. The depth

of pores is up to $295 \mu\text{m}$, the diameter of pore is $3 \mu\text{m}$, and the aspect ratios are more than 98. By a similar changing of etching current density, the pore diameter can be periodically adjusted along the growing direction, which is a remarkable feature of PEC etching. The periodically adjusted of macropores can enables the realization of 3D structures of silicon.

5. Conclusion

This paper asserts that the local current density J_{tip} around the macropore tip must equal J_{PS} for steady macropore growth in a silicon wafer. Experimental results indicate that the diameter d of pore is a function of the square root of etching current density J . An indirect method to measure the relation of J_{PS} at the pore tip and etching time was proposed and proved available. According to the calculated result of J_{PS} , The macropore growth was realized with the pore diameter constant by adjusting the etching current density J . MSA of depth up to $295 \mu\text{m}$ and aspect ratios of more than 98 was obtained.

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