Formation of High Aspect Ratio Macropore Array on p-Type Silicon

K. J. Chao, S. C. Kao, C. M. Yang, M. S. Hseu, and T. G. Tsai

Department of Chemistry, National Tsinghua University, Hsinchu, Taiwan

The fabrication of high aspect ratio macropore arrays on p-type silicon under optimum anodization conditions is demonstrated. The depth of the macropore can reach 400 μm with an aspect ratio of 100. The thickness of the pore wall is 1-2 μm. Presence of cationic surfactant in the electrolyte protects the pore walls and promotes the growth of the unidirectional macropores. The shape of pre-etched pits is critical for the formation of high aspect ratio macropores on p-type silicon. A self-supported silicon membrane of straight-through macroporous channels has also been obtained.

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A porous silicon layer on silicon substrate can be prepared by chemical or electrochemical etching in hydrofluoric acid (HF) solution. The average pore diameter is used to classify the materials as microporous (<2 nm), mesoporous (2-50 nm), or macroporous (>50 nm) silicon. Among these, porous silicon of ordered arrays of macropores with high aspect ratios is interesting and promising materials for micromechanical and biosensing applications.

Because the electrochemical dissolution of silicon, an anodization process, is controlled by the number of holes available at the electrode surface and by the diffusion of fluoride ions to the electrode surface, the electric field enhancement at the pore tips as well as the passivation on the pore walls are considered critical for the fabrication of macropores with high aspect ratio. For n-type silicon, macropore formation was observed by photochemical anodization in aqueous HF solution. During the anodization process, the pore tips can efficiently collect the minority charge carriers (i.e., the holes) generated by illumination that, in turn, initiate the dissolution process and promote the formation of straight-channel-type macropores on n-type silicon. Due to the depletion of holes, the pore wall is spontaneously passivated against dissolution. High aspect ratio macropore array fabricated on prepatterned n-type silicon has been demonstrated before. However, for p-type silicon, the electrochemical oxidation of silicon and subsequent dissolution occur on etching without illumination, and the extended space-charge region is not expected in the anodic regime. Hence, it is difficult both to control the collection of the charge carriers at the pore tips for the anisotropic dissolution of silicon and to passivate the pore walls against dissolution during anodization. The fabrication of high aspect ratio macropores on p-type silicon is thus rather limited.

Recently, macropore formation on p-type silicon electrodes in a water-free mixture of pure HF and organic solvents was reported by Kohl and co-workers. Ponomarev and Lévy-Clement proposed a model in which the adsorption of organic solvent molecules on the silicon surface changes the local dissolution rate of p-type silicon during anodization in a nonaqueous HF solution. In 1998, Wehrspohn et al. reported that macropore formation could be observed only for p-type silicon substrates with resistivities higher than or equal to the electrolyte resistivity, and they claimed that was the first time for such observation in aqueous HF solution. However, Lehmann and Rönnebeck demonstrated that both models could explain only part of the results under certain experimental conditions, and these models were in contradiction with some experimental observations. Lehmann and Rönnebeck suggested that the macropore formation on p-type silicon is a consequence of charge-transfer in a Schottky diode applied to a non-planar interface. In their work, patterned n- and p-type silicon substrates were used for the fabrication of macropore array. They also found that further growth of macropores on p-type substrates was unstable as far as pore depth and growth direction were concerned, and this was not the case for the n-type substrates. Christophersen et al. considered that the role of organic electrolyte is to optimize the H-termination of the surface and, in turn, the passivation of macropore sidewalls.

In this report, an attempt was made to fabricate stable macropore array with high aspect ratio by anodization of the patterned and pre-etched p-type silicon in surfactant-containing electrolytes. In the current study the holes for oxidation in the p-type silicon substrate are not generated by illumination. To collect holes at the pore tips efficiently, pre-etched pits had initiated macropore growth. Other reaction parameters, such as composition of the electrolyte, anodization time, and current density, were also investigated and optimized. Note that after prolonged anodization the macroporous layer could be depleted from the silicon electrode and formed a self-supported silicon membrane.

Experimental

p-Type, boron-doped (100) oriented silicon substrates with resistivity of 13 Ω cm were used. The substrates with patterned silicon nitride layer were produced by standard photolithographic process. The pattern consisted of hexagonally arranged 2 x 2 μm square holes spaced at a distance of 5 μm. The cleaned substrate was pre-etched in 15 wt % KOH at 60°C to generate pyramid-shaped pits, and a back contact was formed by depositing a Pt/Pd layer. The electrochemical oxidation of p-type silicon electrode was performed under a constant current condition in a Teflon cell using a two-electrode setup, and a Pt foil served as the counter electrode. Current density was controlled in the range of 7 to 53 mA/cm². Electrolytes were prepared by mixing HF (48% aqueous solution, Merck), ethanol (99.5%), and deionized water at different weight ratios. The electrolyte composition for a typical anodization was set at a weight ratio 1:2:3 of HF:ethanol:H₂O, and the current density was 27 mA/cm². For comparison, certain amounts of surfactant were added to a premixed electrolyte solution before the anodization process. Surfactants used in this study were cetyltrimethylammonium chloride (CTAC), sodium n-dodecyl sulfate (SDS), and Triton X-100. Scanning electron microscopy (SEM) was used to study the macropore morphology after anodization.

Results and Discussion

The effects of addition of surfactants.—Three different types of surfactants were added to the electrolyte solution to investigate their effects...
on the morphology of macropore array formed by anodization. The concentration of surfactants was kept at $10^{-3}$ M. Figure 1 shows the cross-sectional micrographs of the resulting porous structures after anodization for 30 min in the electrolytes containing either SDS or CTAC. In the presence of CTAC, the resulting macropores were deep with thick pore walls and showed a tendency to form straight channels. In the absence of surfactant or in the presence of either SDS or Triton X-100, the macropores were relatively random-directed with thin pore walls.

During the anodization process, amphiphilic surfactants were adsorbed on the surface of the electrode, with their nonpolar tails attached on the hydrophobic silicon surface. The density of adsorbed surfactant on the sidewall of macropores could be higher than that at the tip region due to geometric constraint. This may modify wetting properties of silicon surface as well as the electric field at the interface, which may, in turn, protect the sidewalls against dissolution. The polarity of the surfactant head group may also affect the electrochemical dissolution process. In an anodization process, anionic surfactant molecules may hinder the diffusion of anionic fluoride ions/silicon fluoride complexes at the interface. The equilibrium charge distribution could also be altered under the existence of anionic surfactant molecules. On the contrary, the head group of CTAC carries positive charge, and may be repulsive from the anode during anodization. Such charge-electric field interaction described above probably explains why different types of surfactants have different effects on the anodization process of p-type silicon electrodes.

The depth of macropores grown in electrolytes with or without CTAC increased linearly with time, and the growth rates were approximately 0.8 and 0.6 $\mu$m/min, respectively, as shown in Fig. 1d. Although macropores can be formed without the presence of surfactants in the electrolyte, the pore walls are relatively thin, and the resulting macropore arrays are not suitable for either further fabrications or various applications.

The effect of the shape of pre-etched pits.—Silicon substrates were pre-etched in aqueous KOH solution prior to the anodization process. On silicon(100), an alkaline, anisotropic etching generates pyramid-shaped pits (Fig. 2a), which were able to sufficiently collect charge carriers at the tip and induce unidirectional macropore formation. The shape of the pre-etched pits was critical for the formation of ordered macropore array by anodization on p-type silicon. Figures 2b and c show the macropore array fabricated from pre-etched pits obtained by immersing in aqueous KOH solution for 4 and 5.5 min, respectively. If the pre-etched pits were in perfect pyramid shape, the resulting channels (Fig. 2c) were uniform and straight with the average thickness of the pore walls of 2 $\mu$m, and the tips of the macropores retained their pyramid shape. In contrast, if the shape of the pre-etched pits was not pyramid, due to the conditions such as insufficient pre-etching time, the subsequent electrochemical reaction would result in macropores with very thin and fragile walls, as shown in Fig. 2b.

In the anodization on n-type silicon, holes in the substrate are generated by illumination, and the formation of macropores with high...
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aspect ratio was thus observed on unpre-etched and patterned n-type silicon substrate. In contrast, pre-etching seems to play an important role in the macropore formation on the p-type silicon system. Macropore formation by anodization on p-type silicon is controlled mainly by the enhanced diffusion currents through the tip compared with those through the walls. Due to the geometric field enhancement around perfectly pre-etched pits, macropores of straight channel pattern with thick pore walls as well as pyramid-shaped tips can thus be obtained after a prolonged unidirectional etching process.

Compositions of the electrolytes.—Effects of the weight ratio of HF, ethanol, and water as well as concentration of CTAC on the morphology of macropores were examined and shown in Table I. In this part of the work, the current density was kept at 27 mA/cm$^2$, and the anodization time was 30 min. From samples with a fixed weight ratio of ethanol and water, the lower limit of weight percent of HF was 17% for a stable macropore formation. If the weight percent of HF was below the limit, the anodization process resulted only in polished samples. The growth rate was insensitive to CTAC concentration at equal or greater than 10$^{-3}$ M. However, the growth rate decreased slightly with CTAC concentration at ~10$^{-4}$ M, and pore walls also became thinner. It was found that for electrolytes with concentration of CTAC on the order of 10$^{-2}$ to 10$^{-3}$ M, it effectively promoted the unidirectional growth of macropores.

The effects of current density.—Finally, the effect of current density on macropore formation was investigated. Under galvanostatic anodization, if the current density was less than 14 mA/cm$^2$, the resulting macropores appeared to be slightly branched. As current densities were greater than 14 mA/cm$^2$, only straight macropores were observed. Furthermore, pore depth and wall thickness decrease with the increase of current density. In the present study, the current density should be controlled at 14-18 mA/cm$^2$ for the formation of branchless macropores. Figure 3b further shows the relationship between pore depth and current density over the same anodization time of 670 min. The pore depth reached a maximum value at the current density of 14 mA/cm$^2$, and it decreased with higher current density.

Anodization on bare and patterned p-type silicon.—The anodization for 30 min on bare p-type substrate was compared with that on patterned substrate in Fig. 4. The anodization was performed in electrolyte containing HF, ethanol, and water with weight ratio of 1:2:3, Table I. Influence of electrolyte composition on the depth of macroporous layer.

<table>
<thead>
<tr>
<th>Weight ratio of electrolyte mixture</th>
<th>CTAC (mM)</th>
<th>Pore depth (μm)$^b$</th>
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<tr>
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<td>25</td>
</tr>
<tr>
<td>1 2 3 1</td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>1 2 3 100</td>
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<tr>
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<tr>
<td>1 2 1 100</td>
<td>100</td>
<td>29</td>
</tr>
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$^a$ Patterned p-Si(100) 13 Ω cm anodized for 30 min under 27 mA/cm$^2$ current density.

$^b$ The deviation is ±1 μm.

Figure 3. The effect of current density on macropore growth rate. Patterned layers of p-Si(100) 13 Ω cm were anodized in 8% HF and 10 mM CTAC with constant total electrical charge of (a) 115 C and (b) constant anodization time of 670 min. In region A, pore branching occurred, and in region B, straight channels with high aspect ratio were observed.

Figure 4. (a-d) SEM images of (a,c) electrochemically etched patterned and (b,d) nonpatterned p-Si(100) 13 Ω cm in 8% HF and 10 mM CTAC, under current density of 27 mA/cm$^2$ for (a,b) 30 min and (c,d) 5 h. (e) Comparison of macropore growth rates on patterned and bare p-Si. p-Si(100) 13 Ω cm (electrochemically anodized in 8% HF and 10 mM CTAC under current density of 27 mA/cm$^2$). △ indicates that the bare p-Si sample was electrochemically polished.
and a current density of 27 mA/cm². The resulting macropores on bare silicon were randomly distributed on the silicon surface, and pore depths varied greatly (Fig. 4b). Pore diameter was somehow larger at the pore tip, similar to that obtained by Lehmann and Rönnebeck. After anodization for 300 min, the macroporous layer was polished from the bare substrate, and the depth of the macropores was ca. 105 μm (Fig. 4d), about half the depth of the macropores obtained on a patterned substrate for the same anodization duration (Fig. 4c). Pore walls of the polished macroporous layer were thin, and hence were too fragile to handle. A comparison of the growth rate of macropores on bare and patterned p-type silicon substrates is shown in Fig. 4e. This demonstrates that the macroporous layer on bare p-type silicon exhibits shorter and more diverse pore depth with thinner pore walls than that derived from patterned p-type silicon under the same anodization condition.

Fabrication of the high aspect ratio macropore array.—Pre-etched p-type silicon substrate with pyramid-shaped pits was anodized in a CTAC-containing electrolyte, and current density was controlled within the optimum range. Figure 5 shows a representative high aspect ratio macropore array on p-type silicon substrate with pore depth of 213 μm. The maximum pore depth achieved in the current study is ca. 400 μm and an aspect ratio of 100. Pore walls under optimum conditions were 1.5-2 μm thick, and this may provide sufficient mechanical strength for further processing. Note that after prolonged anodization under controlled anodization condition the entire macroporous silicon layer with uniform straight pores was able to be electrochemically polished, and resulted in a self-supported macroporous silicon membrane (Fig. 5c). Such macroporous silicon membrane may offer some interesting applications, and further studies are in progress.

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References

Figure 5. SEM images of the macropore array on (a,b) p-Si(100) and (c) a macroporous silicon membrane. The inset in (a) shows the magnification of the tips of the macropores, and the inset in (c) shows the magnification of bottom structure of an anodic silicon membrane.