Ultrafast fabrication of high-aspect-ratio macropores in P-type silicon: toward the mass production of microdevices

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ABSTRACT
Etching rate is a major concern for the effective mass production of high-aspect-ratio microstructures, especially in p-type silicon. In this work, controlled electrochemical growth of high-aspect-ratio (from 15 to 110) macropores in p-type silicon at ultrafast etching rate (from 16 to 30 µm min$^{-1}$) has been studied. Based on current-burst-model, pore formation was systematically investigated from the nucleation phase to stable pore growth. Good macropores with depth up to 180 µm and aspect ratio beyond 110 was achieved in just 11 min. This sets a new record on state-of-the-art p-type silicon microfabrication and can promote the development of microdevices.

IMPACT STATEMENT
High-aspect-ratio macropores at ultrahigh etching rate were achieved in p-type silicon, which sets a novel record among p-type silicon microfabrication and can promote the effective mass production of microdevices.

Introduction
Porous silicon, produced by electrochemical etching in hydrofluoric acid (HF) containing solution, has been a subject of great attention due to its specific physical and chemical properties. Depending on the substrate type and the etching parameters, numerous different pore morphologies can be obtained, resulting in a wide range of applications over the past few decades. Macroporous silicon, in particular with high aspect ratio (AR), has been used in many technical fields, such as microelectromechanical systems (MEMS) devices [1,2], biosensors [3,4], fuel cells [5,6], microelectronics [7] and photonic crystals [8,9]. All these applications require the development of high-quality pore structures with fast etching speed, which is one of the most important factors in effective mass production.

With mass fabrication in mind, there has been significant interest in the fast pore etching on n-type macroporous silicon in the past few years. The conventional technique [10] of macropore formation on n-type silicon was based on photo-assisted electrochemical etching, where the etching rate was around 1 µm min$^{-1}$. By modulating the HF-containing electrolytes with organic solvents [11,12] or strong oxidizers [13,14], perfect macropores can be produced more rapidly on all kinds of n-type silicon substrates (low-doped [13], moderately-doped [11] and highly-doped [14]) in the dark (without backside illumination). Furthermore, under illumination, fast
macropore formation is realized in aqueous HF electrolytes on low-doped n-type silicon with optimal bias and HF concentration ([HF]) [15]. Recently, Barillaro [16] reported on the controlled electrochemical etching of high-aspect-ratio (from 5 to 100) macropores in n-type silicon at the highest etching rates (from 3 to 10 μm min$^{-1}$). On the other hand, in p-type silicon, it’s much more complicated to achieve macropores with high AR because the hole concentration is much higher than in n-type silicon and hence cannot be controlled in the pore walls [17]. A few studies have been done on high-aspect-ratio macropore formation on p-type silicon [17–21]. However, the etching rates in above works were no more than 2 μm min$^{-1}$. So far few reports have been concentrated on fast macropore etching in p-type silicon.

The purpose of this paper is to obtain fast growing macropores with good quality (straight and smooth pore walls) and high AR on p-type silicon substrates. We demonstrate that macropores with extremely large AR (over 110) and high depth (up to 180 μm) can be achieved in p-type silicon at the highest etching rates (from 16 to 30 μm min$^{-1}$) using a set of optimized parameters, the electrolyte composition, [HF] and current density. The etching rates from the nucleation to stable pore growth are based on a mixture of 48 wt.% aqueous HF and two different organic solvents: dimethylformamide (DMF) and dimethylsulfoxide (DMSO). Mainly four types of electrolytes were prepared in our experiments: (a) HF: DMF, 3:7, (b) HF: DMF, 3:4, (c) HF: DMF, 4:3, and (d) HF: DMSO, 3:4. The [HF] is expressed in terms of volume percentage of HF (but not the pure HF), unless otherwise stated. Galvanostatic current densities increase from 30 to 300 mA cm$^{-2}$, and the etching rates increase from 1.2 to 13.3 μm min$^{-1}$. As can be seen from the enlarged micrograph (Figure 1(h)) and the corresponding top-view image (Figure 1(i)), the macropores were cylindrical and generally uniform with rather straight and smooth pore walls. The average sizes of stable macropores were about 1.4 μm, with the top diameters around 0.8 μm.

Thus the pore morphology and etching rate are very sensitive to the current density. From Figure 1(a–g), the current densities increase from 30 to 300 mA cm$^{-2}$, and the etching rates increase from 1.2 to 13.3 μm min$^{-1}$. However, the pore diameter and opening decrease with increasing the current densities, from 2.1 to 1.4 μm, and 1.5 to 0.8 μm, respectively. In addition, the pore diameters are significantly larger in the middle than at the opening, comparing the cross-section and top-view images of the pores. This observation is attributed to the transition, commonly seen in the electrochemical etching of silicon [23], from the initial to the stable-growth state.

With the aim to gain more insight into the dependence of the macropore etching rates on the applied current densities, two sets of experiments were then carried out at different current densities (10–300 mA cm$^{-2}$) for different HF: DMF ([HF] = 30 vol%, 43 vol%, 57 vol%) at different current densities (10–300 mA cm$^{-2}$) for different HF: DMF ([HF] = 30 vol%, 43 vol%, 57 vol%) at different current densities (10–300 mA cm$^{-2}$) for different HF: DMF ([HF] = 30 vol%, 43 vol%, 57 vol%) at different current densities (10–300 mA cm$^{-2}$) for different HF: DMF ([HF] = 30 vol%, 43 vol%, 57 vol%) at different current densities (10–300 mA cm$^{-2}$) for different HF: DMF ([HF] = 30 vol%, 43 vol%, 57 vol%) at different current densities (10–300 mA cm$^{-2}$) for different HF: DMF ([HF] = 30 vol%, 43 vol%, 57 vol%)
Figure 1. Cross-section and top-view SEM micrographs of pores formed on different current densities: (a, b and c) 30 mA cm$^{-2}$, 15 min; (d, e and f) 150 mA cm$^{-2}$, 5 min; (g, h and i) 300 mA cm$^{-2}$, 1.5 min. All samples were anodized in electrolyte composed of 30 vol% HF (HF: DMF = 3:7).

Electrolytes and different electrolyte compositions (DMF and DMSO). Figure 2(a) shows the experimental data on the etching rate versus current density as a function of [HF] in electrolytes. It is apparent that the macropore growth rate consistently increases with the current density for any [HF]. The curves are in good agreement with the results in Figure 1 and Ref. [20]. Furthermore, the increase of [HF] leads to an enhanced pore etching rate for any current density. By changing the [HF] from 30 to 57 vol%, the average etching rate increase by around 60%. Figure 2(b) shows the dependence of the average pore etching rate with current density for two different electrolyte compositions with 43 vol% [HF]. One consistent trend is that the etching rate in electrolyte using DMF as organic solvent is larger than that in electrolyte containing DMSO, varying the current densities from 10 to 300 mA cm$^{-2}$. Moreover, in agreement with the trend in Figure 2(a), macropore growth rate increases consistently with the current density for any electrolyte composition.

Based on these experimental results, we can infer that at least three prime factors pertain to fast pore etching on p-type silicon, namely [HF], electrolyte composition and current density. According to the CBM [22], two basic dissolution reactions (direct dissolution via HF acid and indirect dissolution by oxidation) take place at the pore tips simultaneously in a current burst during anodization. High [HF] will accelerate the direct removal of silicon and promote the dissolution of the oxides, thus shortening both the time of direct and indirect dissolution in every single current burst, compared with a lower [HF]. Therefore, for a given current density (300 mA cm$^{-2}$), as shown in Figure 2(a), the average etching rate over 5 min increases from 13.3 to 23 μm min$^{-1}$, while the [HF] increases from 30 to 57 vol%.

Secondly, the etching rate is dependent on the electrolyte composition. It has been shown that organic solvents, act as mildly oxidizing reactants, can suppress the oxidation process compared to the pure aqueous electrolyte [24]. This allows for shorter indirect-dissolution time and better macropore growth. Besides, as stressed in CBM, electrolyte compositions determine the velocity of the H-termination, which is regarded as the basic passivation mechanism of the pore walls [25]. The better the passivation of pore walls, the higher is the etching rate at the pore tips. Therefore, the availability of H, i.e. the H donor ability, plays an important role in fast pore etching. In general, the H donor property of DMF is better than that of DMSO [24], resulting in higher dissolution rate of pore tips in DMF-contained electrolyte. Thus, a clear trend can be seen in Figure 2(b), for a given [HF],
Figure 2. Macropore etching rate dependence on the current density in the electrolytes containing: (a) (blue triangle) HF: DMF = 3:7, (red spot) HF: DMF = 3:4, (black square) HF: DMF = 4:3; (b) [HF] = 43 vol% and different organic solvents: (red square) DMF; (black spot) DMSO.

Figure 3. Nucleation process of p-type pore formation with different current densities: (a–c) SEM micrographs of pores formed at 300 mA cm⁻² over (a) 5 s, (b) 7 s, (c) 35 s; (d,e) SEM micrographs of pores formed at 30 mA cm⁻² over (d) 40 s and (e) 60 s; (g) pore depth versus time. All samples were anodized in electrolyte composed of 53 vol% HF (HF: DMF = 4:3).

The etching rate in electrolyte using DMF is much higher than that in electrolyte containing DMSO. The last crucial factor for fast pore etching lies in the applied current density. A larger current density means more available transferred charges, thus enhancing the electronic-hole-intensive reaction [26]. In addition, raising current density leads to a shorter time consumption for H-termination process, and thus optimize the pore nucleation phase [22].

SEM pictures in Figure 3 show the nucleation process of p-type macropore formation for a given 57 vol% [HF] under different current densities (30 and 300 mA cm⁻²). At 300 mA cm⁻², a layer of mesopores were obtained after 5 s anodization (Figure 3(a)). The depth of mesopores was about 400 nm, corresponding to an average etching rate of 4.8 μm min⁻¹. According to the CBM [27], it was in the nucleation phase and the mesoporous layer was the nucleation layer. While the etching time increased to 7 s, the mesoporous nucleation layer grew to a depth of 1 μm and some wavy macropores formed (Figure 3(b)), showing the nucleation was completed and pore formation was transformed to the reorganization
process. The pore depth was about 4.2 μm, with the average etching rate increased to 36 μm min$^{-1}$. By increasing the etching time to 35 s, straight macropores with depth of 22 μm were obtained (Figure 3(c)), and the average etching rate was increased to 37 μm min$^{-1}$, demonstrating the stable pore growth.

For comparison, pore formation at lower current density (30 mA cm$^{-2}$) with the same electrolyte was investigated. A layer of mesopores with thickness of 260 nm (Figure 3(d)) was formed during 40 s anodization, and the reorganization phase appeared when the etching time prolonged to 60 s (Figure 3(e)). Therefore, for a larger applied current density, the time of nucleation phase was optimized from dozens of seconds to no more than 7 s. Figure 3(f) shows the pore growth curves in nucleation phase with two different current densities (30 and 300 mA cm$^{-2}$) in 1 min. From these curves, it is obvious that increasing the current density dramatically shortens the pore nucleation time and thus leads to a great enhancement of the etching rate.

Following these experimental results and analysis, we tried to optimize the etching conditions for stable p-type macropore formation with high AR and high etching rate. Macropore etching in p-type silicon with a number of first optimized parameters (HF: DMF = 4:3, 300 mA cm$^{-2}$) was investigated as a function of the etching time (from 0 to 11 min). The macropore growth curve (pore depth versus etching time) was recorded in Figure 4(a). The pore depth consistently increases with etching time, and macropores with depth of 180 μm were achieved by increasing the etching time to 11 min. This result demonstrates significant enhancement of macropore etching rate with respect to the literatures [17–20], in which it takes about 2 h to produce p-type macropores with the same depth.

Figure 4(b) shows the average etching rate as a function of the etching depth. The etching rate was relatively small (4.8 μm min$^{-1}$) in the nucleation phase, followed by largely varying etching rates in the reorganization phase and relatively stable etching rates (above 15 μm min$^{-1}$) in the stable growth phase. This indicates that the optimized process can dramatically enhance the etching rate at any depth. The average etching rate was reduced from 30 μm min$^{-1}$ at the depth of 30 μm to 16 μm min$^{-1}$ at the depth of 180 μm, probably due to the reactant diffusion limit over deep depth.

Figure 4. Macropore formation with optimized electrolyte and current density: (a) pore depth versus time; (b) etching rate versus depth; (c,d) cross-section SEM micrographs of macropore obtained after 11 min anodization with depth up to 180 μm and diameter of 1.6 μm. All samples were anodized in 57 vol % HF (HF: DMF = 4:3) at 300 mA cm$^{-2}$. 
Figure 4(c,d) show the SEM micrographs of the obtained macropore structure after electrochemical etching of 11 min. The pore walls were very straight and smooth (Figure 4(d)) with the depth up to 180 μm and diameters of 1.6 μm, corresponding to the AR above 110 and the average etching rate of 16 μm min⁻¹. Therefore, ultrafast macropore fabrication can be obtained with ultrahigh AR at higher depth without loss of pore quality.

Conclusions
In summary, we demonstrate that p-type macropores with ultrahigh AR can be fabricated at ultrafast etching rate. Under the conditions of high current density, high [HF] and DMF-containing electrolyte, the time of nucleation phase was greatly shortened, and the etching rate was dramatically enhanced (16–30 μm min⁻¹) both at smaller and higher depths (up to 180 μm) without any significant loss of good ‘quality’, which was at least ten times larger than that with state-of-the-art micro-fabrication processes. The experiment results verify the judgment inferred from the CBM and three prime factors are responsible for the great rate enhancement.

Disclosure statement
No potential conflict of interest was reported by the authors.

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References
[1] Lammel G, Schweizer S, Schiesser S, et al. Tunable optical filter of porous silicon as key component for a MEMS spectrometer. J Microelectromech. S. 2002;11(6):815–828.
[2] Rodriguez A, Molinero D, Valera E, et al. Fabrication of silicon oxide microneedles from macroporous silicon. Sensor Actuat B. 2005;109(1):135–140.
[3] Anglin EJ, Cheng L, Freeman WR, et al. Porous silicon in drug delivery devices and materials. Adv Drug Deliver Rev. 2008;60(11):1266–1277.
[4] Zhao Y, Gaur G, Retterer ST, et al. Flow-through porous silicon membranes for real-time label-free biosensing. Anal Chem. 2016;88(22):10940–10948.
[5] Kouassi S, Gautier G, Therj J, et al. Poron exchange membrane micro fuel cells on 3D porous silicon gas diffusion layers. J Power Sources. 2012;216:15–21.
[6] Desplombain S, Gautier G, Ventura L, et al. Macroporous silicon hydrogen diffusion layers for micro-fuel cells. Phys Stat Sol (a). 2009;206(6):1282–1285.
[7] Gautier G, Leduc P. Porous silicon for electrical isolation in radio frequency devices: A review. Appl Phys Rev. 2014;1(1):011101.
[8] Pacholski C. Photonic crystal sensors based on porous silicon. Sensors. 2013;13(4):4694–4713.
[9] Ge DH, Lu L, Zhang JH, et al. Electrochemical fabrication of silicon-based micro-nano-hybrid porous arrays for hybrid-lattice photonic crystal. ECS J Solid State Sci. 2017;6(12):P893–P897.
[10] Lehmann V. The physics of macropore formation in Low doped n-type silicon. J Electrochem Soc. 1993;140(10):2836–2843.
[11] Frey S, Kemell M, Carstensen J, et al. Fast pore etching. Phys Stat Sol (a). 2005;202(8):1369–1373.
[12] Föll H, Carstensen J, Frey S. Porous and nanoporous semiconductors and emerging applications. J Nanomater. 2006;2006:1–10.
[13] Bao XQ, Jiao JW, Zhou J, et al. Fast speed pore formation via strong oxidizers. Electrochim Acta. 2007;52(24):6728–6733.
[14] Ge DH, Jiao JW, Zhang S, et al. Fast speed nanosized macropore formation on highly-doped n-type silicon via strong oxidizers. Electrochem Commun. 2010;12(4):603–606.
[15] Bao XQ, Ge DH, Zhang S, et al. Fast pore etching on high resistivity n-type silicon via photoelectrochemistry. Chinese Phys B. 2009;18(2):664–670.
[16] Cozzi C, Polito G, Kolasinski K, et al. Controlled micro-fabrication of high-aspect-ratio structures in silicon at the highest etching rates: the role of H2O2 in the anodic dissolution of silicon in acidic electrolytes. Adv Funct Mater. 2017;27(6):1604310.
[17] Lehmann V, Ronnebeck S. The physics of macropore formation in low-doped p-type silicon. J Electrochem Soc. 1999;146(8):2968–2975.
[18] Zheng J, Christophersen M, Bergstrom PL. Thick macroporous membranes made of p-type silicon. Phys Status Solidi (a). 2005;202(8):1402–1406.
[19] Quiroga-Gonzalez E, Carstensen J, Glynn C, et al. Pore size modulation in electrochemically etched macroporous p-type silicon monitored by FFT impedance spectroscopy and Raman scattering. Phys Chem Chem Phys. 2014;16:255–263.
[20] Vyatkin A, Starkov V, Tzeitlin V, et al. Random and ordered macropore formation in p-type silicon. J Electrochem Soc. 2002;149(1):G70–G76.
[21] Park J, Yanagida Y, Hatsuzawa T. Fabrication of p-type porous silicon using double tank electrochemical cell with halogen and LED light sources. Sensor Actuat B. 2014;233:136–143.
[22] Carstensen J, Christophersen M, Föll H. Pore formation mechanisms for the Si-HF system. Mater Sci Eng B. 2000;69-70:23–28.
[23] Lehmann V, Stengl R, Luigart A. On the morphology and the electrochemical formation mechanism of mesoporous silicon. Mater Sci Eng B. 2000;69-70:11–22.
[24] Christophersen M, Carstensen J, Voigt K, et al. Organic and aqueous electrolytes used for etching macro- and mesoporous silicon. Phys Stat Sol (a). 2003;197(1):34–38.
[25] Allongue P, Villeneuve CH, Pinsard L, et al. Evidence for hydrogen incorporation during porous silicon formation. Appl Phys Lett. 1995;67(7):941–943.

[26] Christophersen M, Carstensen J, Feuerhake A, et al. Crystal orientation and electrolyte dependence for macropore nucleation and stable growth on p-type Si. Mater Sci Eng B. 2000;69-70:194–198.

[27] Christophersen M, Carstensen J, Feuerhake A, et al. Crystal orientation and electrolyte dependence for macropore nucleation and stable growth on p-type Si. Mater Sci Eng B. 2000;69-70:194–198.