Processing of Macroporous Silicon

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Abstract

Macroporous silicon layers, with micron diameter pores, can be subjected to many standard processes developed by the microelectronics industry for silicon wafers, but these processes require tuning and optimization. A variety of processing techniques to manipulate macropore morphology, chemical composition, and patterning are reviewed.

Introduction

Methods for electrochemical, catalytic (metal assisted), and deep reactive ion etching (DRIE) of silicon have been developed, which enable fabrication of arrays of deep cylindrical or modulated pores, walls, tubes, combinations of these, and other forms with vertical walls (Wu et al. 2010). As a rule, the regular arrays produced by electrochemical etching are characterized by constant porosity and pore depths (up to 500 μm) and form a planar front propagating into the substrate. Various devices and functional elements for micromechanics, photonics, chemical power sources, microfluidics, photovoltaics, etc. (see "▶ Porous Silicon Application Survey" chapter), are commonly fabricated on the basis of these arrays by

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post-anodization treatment intended to modify the structure and properties of macroporous silicon: to raise or reduce its porosity, change the shape of pores, transform the pore array into a column array, change the properties of the inner surface of pores, coat it with the film of a metal or insulator, open up pores, fill pores with various fillers, dope the silicon walls, etc. Some procedures can be performed locally, which requires formation of a pattern and subsequent structuring.

Compared with micro- and mesoporous silicon, macroporous silicon is the closest in its properties to the starting single-crystal material, and, therefore, it can be subjected to standard technological procedures of microelectronics: thermal oxidation, high-temperature annealing, introduction of impurities by diffusion, thin-film deposition, photolithography, etc. However, the processing of macroporous silicon has its own specific features. For example, ordinary thermal oxidation gives rise to mechanical stresses, which may lead to deformation of a sample and can cause destruction or appearance of dislocations. Treatment in liquid reagents requires that the solution should penetrate into pores, for which a good surface wettability and prolonged keeping in solution (or forced pumping of the solution via through pores) are necessary. To perform photolithography, it is necessary to preliminarily planarize the surface by pore cupping or filling or to form a pattern on the backside of the substrate. Samples of macroporous silicon have a reduced mechanical strength and, because of the developed surface, possess a higher reactivity, compared with ordinary silicon wafers. However, the problems with drying and storage-induced "aging" characteristic for mesoporous silicon are much less severe.

Global Processing

Let us consider in more detail various processes for posttreatment of macroporous silicon, listed in Table 1.

1. The simplest way to open up pores is by mechanical removal of the substrate by grinding and polishing. A disadvantage of this method is that a sample is contaminated with wax used to glue a sample (its removal is no difficulty), and abrasive particles and silicon fines are introduced (can hardly be removed). A widely used way to fabricate membranes is by chemical dissolution of the substrate in hot alkaline etchants. For this purpose, the inner surface of macropores is preliminarily protected by thermal silicon oxide or by silicon nitride, which is stable in alkalis and prevents dissolution of porous silicon. The rate of SiO_2 etching is approximately three orders of magnitude lower than that of silicon (Kendall 1979). Also, the porous layer is frequently separated from the substrate in the final stage of anodization, which is, strictly speaking, not related to posttreatment. However, a combined variant is possible, in which rather thin silicon walls are obtained at the end of the electrochemical etching due to the increase in the pore diameter in the lower part of the porous layer. These walls are oxidized across their entire thickness in the course of the subsequent thermal

Table 1 Post-anodization treatment of macroporous silicon (global)

N	Purpose of posttreatment	Basis of technique	Technique	References
1	Through pores (membrane)	Substrate removal	Mechanical grinding	Astrova et al. (2003)
			Thermal oxidation + substrate etching (alkaline or reactive ion)	Langner et al. (2011)
2	Pore coalescence and closing	Surface diffusion of Si	Annealing in H_2	Sato et al. (2000), Mizushima et al. (2000)
3	Porosity increase, formation of pillars and wires, change of pore shape	Isotropic treatment	Sacrificial thermal oxidation	Lauet al. (1996), Matthias et al. (2004, 2005a), Trifonov et al. (2008), Muller et al. (2000)
			Chemical etching	Ossei-Wusu et al. (2011)
		Anisotropic treatment	Chemical etching in alkaline solutions	Lehmann (2007), Matthias et al. (2005b), Chernienko et al. (2013), Zharova et al. (2011)
			Anisotropic sacrificial thermal oxidation	Trifonov et al. (2007)
4	Conformal treatment	Smoothing	Sacrificial SiO_2	Langner et al. (2011), Kalem et al. (2009)
			Wet etching	Astrova et al. (2011b)
		p-n or heterojunction formation	Shallow diffusion doping	Grigoras et al. (2000), Badel et al. (2005), Sun et al. (2005), Xianyu Ao et al. (2012), Kui-Qing Peng et al. (2010)
			Thin film spraying	Cachet et al. (1997)
		Coating	Galvanic or chemical deposition	Fang et al. (2007), Zacharatos and Nassiopoulou (2008), Gutman et al. (2008), Steinhauer et al. (2005)
			CVD, ALD	Lehmann et al. (1996), Langner et al. (2008)
		Altering of surface functionality	Chemical liquid or vapor treatment	Gun'ko et al. (2003), Kalem and Yavuzcetin (2000), Hayden et al. (2009)

(*continued*)

Table 1 (continued)

N	Purpose of posttreatment	Basis of technique	Technique	References
5	Thick modified layer	Through doping of Si walls	Gas phase diffusion	Astrova et al. (2000)
		Through oxidation of Si walls	High-temperature heat treatment in oxidizing atmosphere	Kan and Finstad (2005), Barillaro et al. (2003)
6	Pore filling	Fluidity of filler + wettability of Si	Liquid or melt infiltration	Kitzerow et al. (2007), Astrova et al. (2010a, 2011a), Lehmann and Rönnebeck (2001), Badel et al. (2004)
		Electrical conductivity	Galvanic deposition	Fang et al. (2007), Zacharatos and Nassiopoulou (2008)
		Catalyst pretreatment	Chemical deposition	Matthias et al. (2002)
7	Inverted structures	Macroporous Si as a template	Pore filling or covering + removal of Si mold	Lehmann and Rönnebeck (2001), Matthias et al. (2002), Palacios et al. (2008), Chen et al. (2006), Langner et al. (2008), Trifonov et al. (2005), Astrova et al. (2005a), Schilling et al. (2004), Rodriguez et al. (2005), Zhao et al. (2005), Bharadwaja et al. (2006)
8	Silicon particulates	Fracture of macroporous Si	Sonication	Thakur et al. (2012)

oxidation, and the substrate is removed under dissolution of SiO_2 in HF. For a general review of both mesoporous and macroporous membranes, see "▶ Porous Silicon Membranes" chapter in this handbook.

2. The macroporous structure is radically transformed in high-temperature annealing in hydrogen, when porous channels are converted to closed spherical voids capable of merging under proper conditions to give, at a certain depth in the sample, a plate-shaped empty space parallel to the surface, the so-called "silicon-on-nothing" structures (Sato et al. 2000; Mizushima et al. 2000) (for more detail, see "▶ Sintering of Porous Silicon" chapter in this handbook).
3. The porosity can be made more pronounced, and a columnar structure can be formed via repeated thermal oxidation, followed by dissolution of the oxide in HF (Lau et al. 1996; Matthias et al. 2004, 2005a; Trifonov et al. 2008)

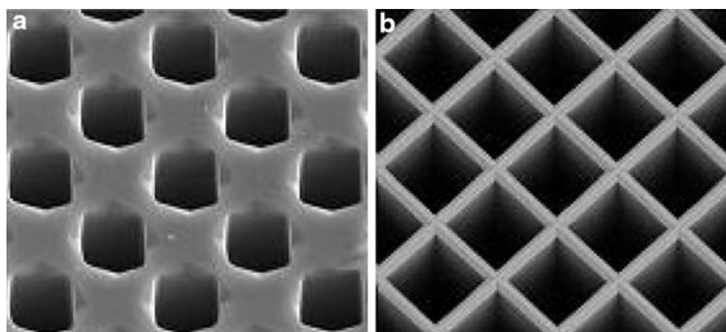

Fig. 1 Alkaline anisotropic posttreatment of cylindrical macropores organized in a square lattice after subsequent etching in (**a**) 50 % KOH, 105 °C for 10 sec, (**b**) 2 % KOH + 10 % propanol, 14 °C for 10 h (Lehmann 2007)

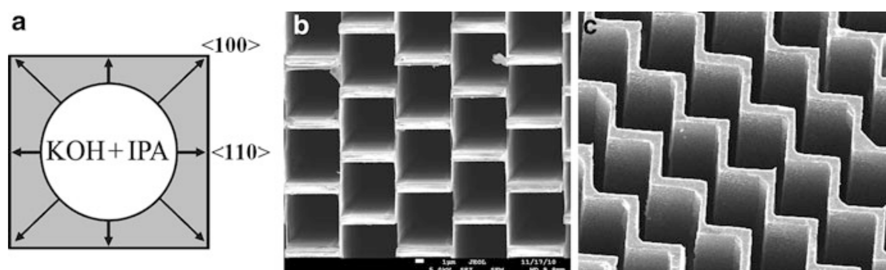

Fig. 2 Shaping of macropores at room temperature (Chernienko et al. 2013) (With kind permission from Springer Science + Business Media B.V): (**a**) schematic of anisotropic transformation of an initially round macropore when etch rate for <100> exceeds rate for <110> crystallographic direction. Structures obtained from macroporous Si organized in a triangular lattice upon chemical shaping in 12 % aq. KOH + IPA (2:3): (**b**) squares when the initial pore rows are aligned along <110> direction, (**c**) zigzag Si walls when the pore rows are aligned along <100> axis

(see "▶ Oxidation of Macroporous Silicon" chapter in this handbook). The same goal can be achieved through pore expansion under isotropic etching in acid etchants (based on HF + HNO_3) (Ossei-Wusu et al. 2011). Anisotropic posttreatment in various alkaline solutions makes it possible to change the cross-sectional shape of cylindrical macropores from circular to squared. In alkaline solutions, the etching rate of the (111) plane is 2 orders of magnitude lower than that of other planes. The ratio of the etching rates of the (100) and (110) planes may be inverted, depending on the etchant composition and treatment conditions (Zubel and Kramkowska 2002). This property was used to obtain square pores oriented in a particular way relative to the crystallographic directions (Fig. 1). Figure 2 shows macropores, produced by anisotropic posttreatment at room temperature of the initially round pores in mixture of KOH and isopropyl alcohol (IPA). Figure 3 presents a scaffold-like structure of a cubic three-dimensional photonic crystal obtained by alkaline anisotropic etching.

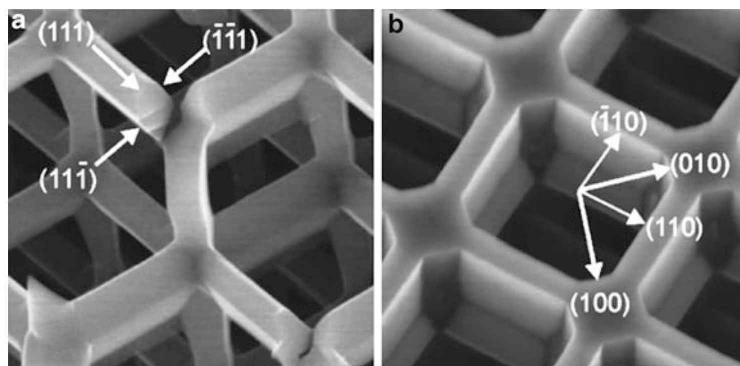

Fig. 3 Scaffold-like structure obtained by anisotropic etching of modulated macropores. SEM pictures of (**a**) side view, (**b**) top view (Reprinted with permission from (Matthias et al. 2005b). Copyright 2005, AIP Publishing LLC)

4. Conformal treatment presumes that surface characteristics (roughness, wettability, thin-film coating, etc.) are changed. Upon anodization, pore walls may be covered with a mesoporous layer. This layer can be removed with a weak alkaline solution. The hydrogen-terminated hydrophobic surface is converted to hydrophilic via chemical oxidation or formation of hydroxy (OH) groups on the surface. The surface of macropores can be coated with thin films of metals, insulators, and semiconductors and be functionalized by various methods, such as oxidation, electroplating, chemical vapor deposition (CVD), and atomic layer deposition (ALD). These may be chemical processes, both involving silicon and not. The coating of macropore inner surface can serve as a mask for subsequent treatment or to prevent denaturation of protein-based probes on silicon microarrays (Steinhauer et al. 2005). The main difficulty is in obtaining a uniform coating of the 3D surface. The deposition of thin doped films and formation of p-n junctions can be attributed to a separate group. These junctions are formed as a result of high-temperature diffusion from the gas phase.
5. If the walls of a porous structure are subjected to a through diffusion saturation, thick (tens and hundreds of micrometers) quasi-homogeneous diffusion layers are obtained, and this method can replace epitaxy (Astrova et al. 2000). Similarly, full thermal oxidation of silicon walls makes it possible to obtain thick oxide layers, which are used, e.g., for thermal insulation purposes (Kan and Finstad 2005; Barillaro et al. 2003). The increasing volume of the oxide leads to filling of pores, which enables, at a correct choice of the porosity ($\leq$56 %), formation of a thick monolithic SiO_2 layer. For more details, see "▶ Thermal Isolation with Porous Silicon" chapter in this handbook.
6. The chemical inertness of silicon and its high thermal stability enable filling of macropores with various fillers in the liquid state, including those in the form of melts and gels. The rather high electrical conductivity of macroporous silicon enables electroplating (see "▶ Porous Silicon and Electrochemical Deposition"

chapter in this handbook). The infiltration of macropores with lead (Lehmann and Rönnebeck 2001), cesium iodide (Badel et al. 2004), copper (Fang et al. 2007; Zacharatos and Nassiopoulou 2008), gold (Matthias et al. 2002), liquid crystals (Kitzerow et al. 2007; Astrova et al. 2010a, 2011a), conducting polymers (Palacios et al. 2008), mesoporous silica (Chen et al. 2006), etc., has been reported.

7. To the preceding processes of conformal coating and total infiltration of macropores are closely related methods for fabrication of inverted structures, in which the macroporous matrix is used as a sacrificial template and is removed in the final stage. This can be done either by selective dissolution of Si (as a rule, in alkaline solutions) or by pulling out the resulting structure (Chen et al. 2006). In the former case, it is necessary that the filler should be resistant to a hot alkali. Silica tubes and needles formed by thermal oxidation (Trifonov et al. 2005; Astrova et al. 2005a; Schilling et al. 2004; Rodriguez et al. 2005), lithium niobate (Zhao et al. 2005), ferroelectric (Bharadwaja et al. 2006) tubes, and 3D TiO_2 microstructures (Langner et al. 2008) also belong to inverted structures.
8. Some applications require cheap electroconductive material based on small silicon particulates of high surface area. Authors of paper (Thakur et al. 2012) report on ultrasonically fractured macroporous membranes, mixing silicon particulates (size range 10–50 μm) with pyrolyzed polyacrylonitrile and application of the mixture for producing long life anodes of lithium ion batteries.

Local Processing

In the procedures considered above, the structure is subjected to a global treatment. A local transformation of the macroporous structure requires that a pattern should be created in it. The simplest operation is local pore opening. For this purpose, a mask is created on the backside of an oxidized (or Si_3N_4-coated) structure by photolithography, the silicon substrate is anisotropically etched to a depth required for reaching the pore tips, and the oxide protecting the macropore walls is removed (Langner et al. 2011; Trifonov et al. 2005). A general review on "▶ Photolithography on Porous Silicon" is available elsewhere in this handbook. The thus opened-up pores have been used to create anodes with a reinforcing skeleton for fuel cells (Astrova et al. 2007) and to perform a local infiltration of macropores in fabrication of heterojunctions and defects in a photonic crystal (Fig. 4).

Other methods for local infiltration of macropores have also been reported (Intonti et al. 2006; Nolte et al. 2009), e.g., global closure of pores, followed by their opening up by direct writing with a focused ion beam (FIB).

The flow of the latter of these is shown in Fig. 5: (a) macroporous silicon with edges inclined in the process of etching, (b) global infiltration of the pores with wax for their stabilization in the subsequent polishing step, (c) polishing of the samples, (d) deposition of a seed layer of gold by sputtering, (e) removal of the previously introduced wax and of the seed layer deposited over the pores, (f) selective removal of the seed layer by FIB, (g) electrochemical extension of the gold layer by

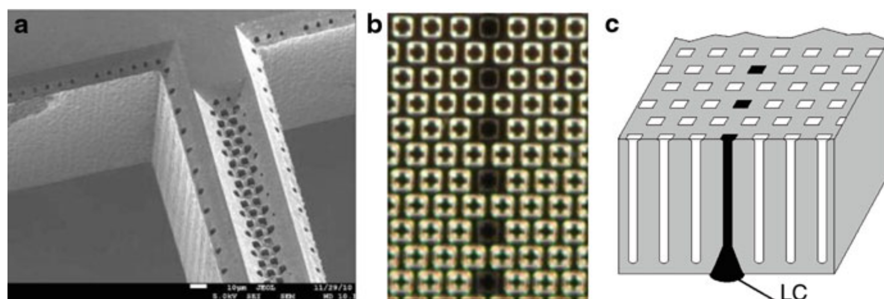

Fig. 4 Local opening and infiltration of pores: (**a**) example of a structure with locally opened pores (back side view), (**b**) front view with a pore row infiltrated with a liquid crystal (*LC*) from the back side (Zharova et al. 2011) (With kind permission from Springer Science + Business Media B.V); (**c**) scheme of the infiltration

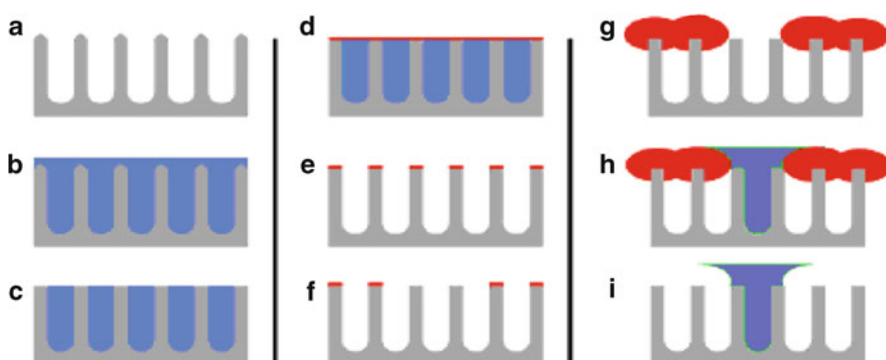

Fig. 5 Process steps during the local infiltration (Nolte et al. 2009) (Permission granted by SPIE)

electrochemical deposition from a $KAu(CN)_2$ solution, (h) local infiltration with either a solution or a melt, and (i) removal of the metal layer with a KI/I_2 solution.

A local processing of the porous structure is used as well to fabricate structures with vertical walls. The micromachining of structures with steplike high-aspect features assumes that a long route is to be used, including various procedures for posttreatment of macroporous silicon. This is done on the basis of a regular macropore array. The macroporous matrix is used as a quasi-homogeneous substrate in which larger structures are created by photolithography and other technological processes (Ottow et al. 1996a, b). The photolithography in samples of macroporous silicon meets severe difficulties because a positive photoresist flows into pores, is not exposed there, and, accordingly, cannot be dissolved in the development stage. A negative photoresist cannot solve the problem, either, and therefore, a preliminary planarization of the surface via pore capping or filling is necessary for performing photolithography. Figure 6 shows the Ottow process flow, in which an aluminum layer was used for planarization purposes. First, the inner surface of pores is covered by a protection layer. Then, aluminum is deposited by

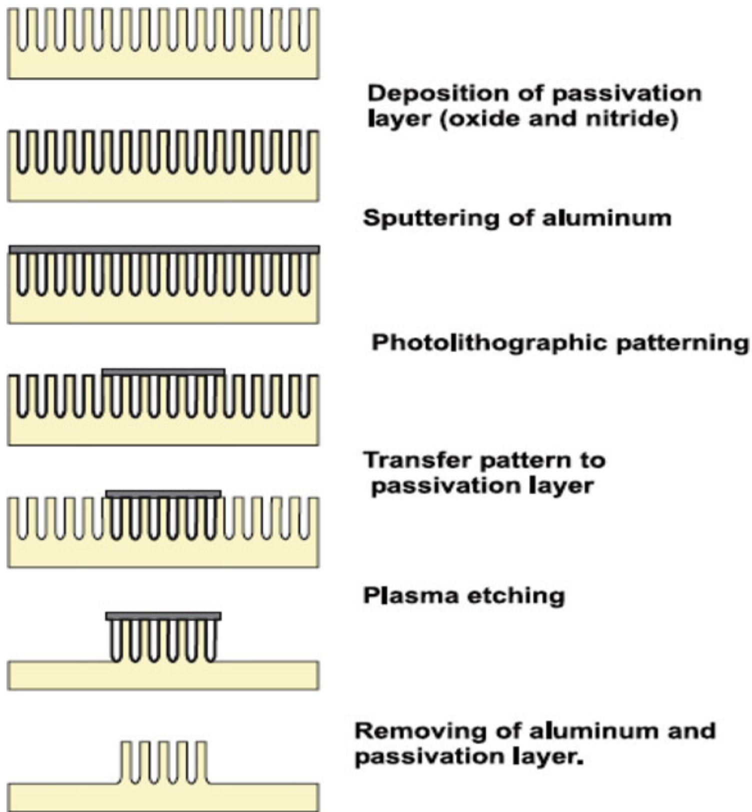

Fig. 6 Scheme of the Ottow microstructuring process (Muller et al. 2002) (With kind permission from Springer Science + Business Media B.V)

sputtering and patterned by the conventional photolithography. Subsequently, the protection layer is removed by chemical etching. The following isotropic plasma process removes porous silicon in the already unpassivated areas. To get complete, compact microstructures, the pores can be filled with polysilicon (Fig. 7).

The Ottow technique was used to fabricate 2D photonic crystal bars of macroporous Si with a precision of less than one pore lattice constant (Muller et al. 2000; see Fig. 8a).

A variation of the method, which does not require any surface planarization and plasma etching, is by photolithography on the substrate backside (Astrova et al. 2004, 2005b; Chernienko et al. 2013; Zharova et al. 2011). Example of such a structure is shown in Fig. 8b.

Another approach to fabrication of structures with vertical walls is by simultaneous electrochemical etching of pores and trenches first introduced by Geppert et al. (2006). Forming a closed contour, the trenches define the sacrificial parts of the structure, which fall out from a sample after the substrate is removed.

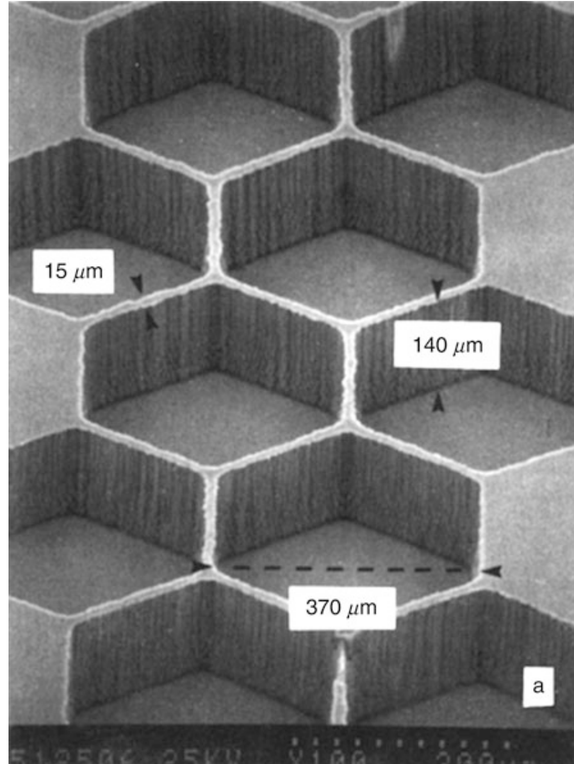

Fig. 7 Microstructures obtained after pore filling with polysilicon (Ottow et al. 1996b) (With kind permission from Springer Science + Business Media B.V)

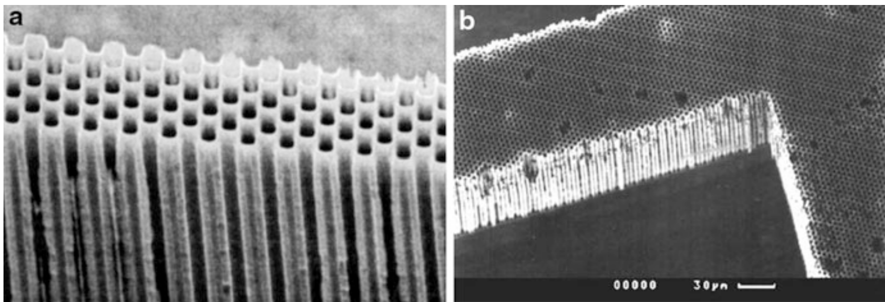

Fig. 8 SEM images of macroporous silicon bars with vertical walls: (**a**) a bar of about 3.5 pore layers or 5 μm, obtained by Ottow process (Muller et al. 2000) (With kind permission from Springer Science + Business Media B.V); (**b**) stripes fabricated by photolithography on the back side of the substrate (Astrova et al. 2005b) (With permission from Elsevier, 2005)

Figure 9 shows a schematic of the method and a bar of a 2D photonic crystal, produced by removal of sacrificial parts of the sample.

3D photonic crystals can be fabricated by means of focused-ion-beam drilling of macroporous silicon. Yablonovite-like structure was formed by three sets of drilled

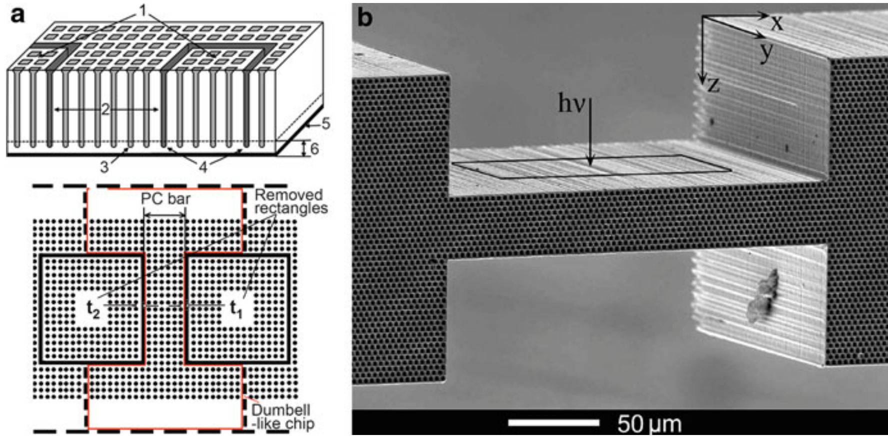

Fig. 9 Schematic for patterning of 2D structure: (*1*) removed square area, (*2*) bar of a 2D structure constituted by six rows of macropores, (*3*) macropores, (*4*) trenches, (*5*) n^+-layer, and (*6*) substrate removed in opening of trenches and pores (Astrova et al. 2010b) (With kind permission from Springer Science + Business Media B.V); (**b**) Scanning electron microscope (SEM) image of a two-dimensional photonic crystal bar obtained by this technique (Reprinted figure with permission from (Dyakov et al. 2012). Copyright 2012 by the American Physical Society)

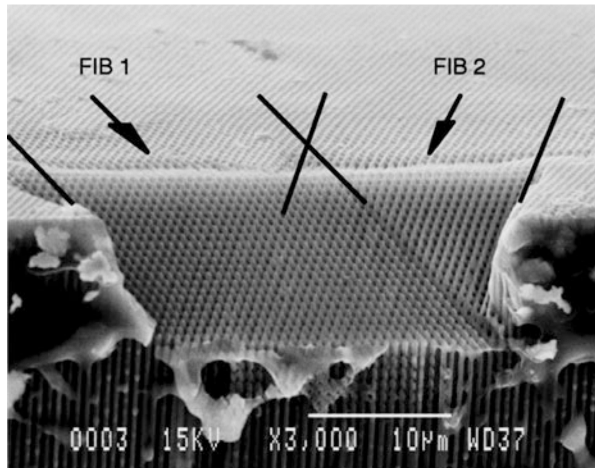

Fig. 10 Scanning electron microscope image of the fabricated 3D Yablonovite-like crystal showing the oblique interface obtained by FIB milling (Reprinted with permission from (Chelnokov et al. 2000). Copyright 2000, AIP Publishing LLC)

holes (Wang et al. 2000, 2003; Chelnokov et al. 2000; Fig. 10). Authors of paper (Schilling et al. 2005) obtained 3D photonic crystal of orthorhombic structure with large photonic band gap by utilization of only one orthogonal set of FIB-drilled holes interpenetrating with photoelectrochemically etched macropores.

Methods suggested in Kleimann et al. (2001, 2005) and Bassu et al. (2012) enable fabrication of high-aspect-ratio microstructures directly in the course of electrochemical etching without any additional posttreatment. In the Kleimann's method (Kleimann et al. 2001, 2005), n-Si is first etched through a mask in the

isotropic mode, and then the etching is continued in the anisotropic mode. In contrast, the Barillaro's technique (Bassu et al. 2012) involves deep anisotropic etching in the first phase and isotropic etching in the second, so that the diameter of the pores grows in the lower part of the structure and they, being connected with the neighboring pores, merge into a single void. In the isotropic-etching phase, free-standing and sacrificial parts of the wafer are detached from the substrate. Similar approach was used in Bobo et al. (2012) for separating macroporous arrays from p-type silicon substrate. Other micromachining methods have also been suggested. For example, selective photoelectrochemical etching of macropores in high-resistivity n-Si was performed in Tao and Esashi (2005), with a mask on the electrolyte side and a mask on the side opposite to the illuminated surface. Then, porous regions were dissolved in KOH to leave prescribed figures with vertical walls. The walls are not very even because of the underetching and pore branching at the mask edge.

Thus, various high-aspect-ratio structures can be fabricated by combination of deep anodization with subsequent processing of macroporous silicon.

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