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p-Type macroporous silicon having three-dimensional structure†

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Macroporous silicon with three-dimensional structure was fabricated using organic-based electrolyte, dimethylformamide (DMF), in the p-type silicon. The obtained three-dimensional macroporous structures grew wholly along the $<100>$ orientation of the p-type silicon wafer.

Since the discovery in 1956 of porous structure silicon wafers,[1] research has been associated with emerging technologies, *e.g.* applications as photonic crystals for optical band pass filters and micro chemical reaction applications in micro chemical reactors and micro fuel cells.[2] Their importance is due to their very high surface area for reaction, photonic properties and process compatibility to semiconductor technology.

The preparation of a macroporous structure with over 50 nm pore size according to the IUPAC standard has been a target of interest in recent years. Especially, macroporous structure formation using the silicon wafer has been of interest in the fields of bio, micro chemical reactor systems, microelectromechanical systems(MEMS), and photonics owing to the extremely high aspect ratios, large porosities, and high surface to volume ratios associated with macroporous silicon structures.[3–7] These structures have been grown by electrochemical etching methods using organic electrolytes such as acetonitrile (MeCN), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and hydrofluoric acid mixed with water. The first research on macroporous silicon structure was performed during the past decade on n-type silicon using hydrofluoric acid and on p-type silicon using organic electrolytes containing hydrofluoric acid.[8–10]

Two-dimensional and three-dimensional macroporous silicon structures have recently attracted much attention for use in photonic applications .[11–13] Two- and three-dimensional spatially periodic pores in silicon wafer can be obtained by etching pit patterns on the silicon wafer using semiconductor photolithography. These pores have ordered pore arrays with pore sizes in the range of a few nanometers to a tens of micrometers and have high aspect ratios of more than a hundred. Usually, two- and three-dimensional macroporous silicon structures have been obtained with n-macroporous structures grown by aqueous electrolyte or p-macroporous silicon structure formed by organic electrolyte. It had been considered that a three-dimensional macroporous structure could not be obtained as easily as the two-dimensional macro structure, even though many researchers had worked to get the three-dimensional macro structure. Moreover, real three-dimensional macroporous structures using organic-based electrolyte had not yet been obtained in p-type silicon.

This communication reports a novel three-dimensional macroporous silicon structure that we have obtained in p-type silicon with medium resistivity using the organic-based electrolyte dimethylformamide (DMF, 99.5% Wako Chemicals). The macroporous structures grew along the $<100>$ direction of the p-type silicon wafer. Moreover, the macroporous structures formed at the bottom as well on the walls of the silicon microchannels.

In the electrochemical etching system, the organic-based electrolyte was composed of mixtures of dimethylformamide (DMF) + HF + H_2O. p-Type silicon sample preparation composed of silicon microchannels was performed by a standard semiconductor process and deep reactive ion etching. Cleaned silicon wafer was oxidized in the oxidation furnace to obtain a silicon oxide layer of 1 μm thickness to be used as mask in electrochemical etching. We spin-coated the photoresist on the silicon oxide and patterned it by a standard photolithography process. After photolithography, we etched the silicon oxide using hydrofluoric acid and deep-etched using deep reactive ion etching to make the silicon microchannel of 500 μm width, 72 μm depth composed of rectangle-shaped silicon micropillars. Finally, we made the silicon microchannel structure with micropillars of top area 35 μm × 50 μm and height of 72 μm to form the three-dimensional macroporous structure as shown in Fig. 1. Silicon micropillars were situated in different positions of the silicon microchannels—near the wall and far from the wall as shown respectively in (a) and (b) of Fig. 1. To provide a constant adjustable current to silicon microchannel of Fig. 1 for electrochemical etching, a controllable power source (Takasago EX-750 H) was used. An output current of 0–12.5 A was used controlled by an analogue input signal between 0–10 V. This input signal was provided by a Digital-Analogue-Converter (DAC – National Instruments DAQ 1200) connected to a notebook computer. The DAC itself was driven by LabVIEW software (National Instruments). The program basically controlled current density gradients at the beginning and at the end of each etching process and etching cycles allowing the etching of layer stacks with alternating porosities.

p-Type silicon having the (100) orientation and resistivity of 8–12 ohm-cm was selected for macroporous formation. Platinum wire for cathode electrode and gold/chromium films for ohmic contact of silicon were used in the electrochemical etching system. Organic-based electrolyte was composed of mixtures of dimethylformamide (DMF) 92% + HF 4% + H_2O 4%. Electrochemical silicon etching was performed under conditions of anodic current density of 6.2 mA cm^{-2} for 30 min.

Fig. 2(a) shows the scanning electron microscopy (SEM) results of silicon micropillar of Fig. 1 (a) positioned near the wall of silicon microchannel. It shows a rectangular shaped three-dimensional macroporous silicon structure of 67.6 μm height. All macroporous silicon grew along the $<100>$ orientation of the silicon wafer. Grown macroporous silicon and boundaries of inter-planes are shown magnified in Fig. 2(b).

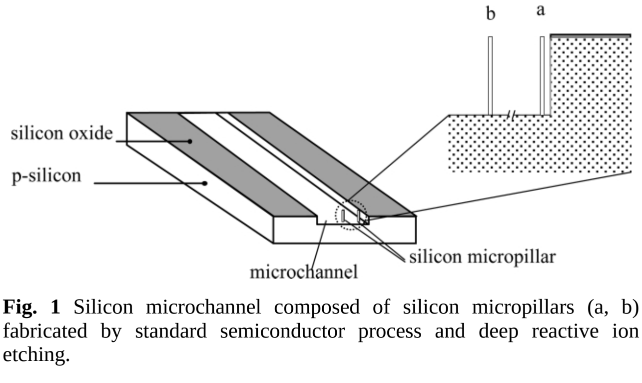

Fig. 1 Silicon microchannel composed of silicon micropillars (a, b) fabricated by standard semiconductor process and deep reactive ion etching.

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The silicon micropillar of Fig. 1 (b) positioned far from the wall of the silicon microchannel showed a rod-shaped three-dimensional macroporous silicon structure of 35.4 μm height as shown in Fig. 3(a). We confirmed that the macroporous silicon structure grew along the < 100 > crystal orientation from the magnified scanning electron microscopy (SEM) image Fig. 3(b). As a result of its position far from the wall, this rod-shaped porous structure was exposed to more anodic current than the rectangular shaped porous structure of Fig. 2. The authors consider that this result requires further work.

We obtained the novel three-dimensional macroporous silicon structures with a very high variety in orientation. Electrochemical etching was performed under conditions of organic-based electrolyte of dimethylformamide (DMF) 92% + HF 4% + H_2O 4%, anodic current density of 6.2 mA cm^{-2} for 30 min on the p-type silicon wafer with 8–12 ohm-cm resistivity. Macroporous structures grew wholly along the < 100 > orientation in the p-type silicon wafer without etch pits for nucleation centers for macropores.

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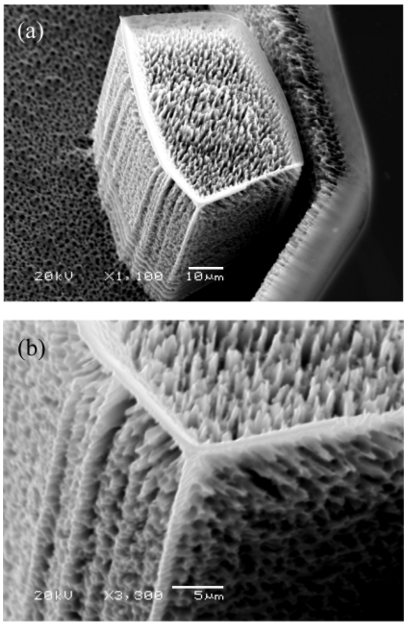

Fig. 2 SEM pictures of rectangular shaped three-dimensional macroporous silicon structure. Electrochemical silicon etching was performed under conditions of 6.2 mA cm^{-2} for 30 min.

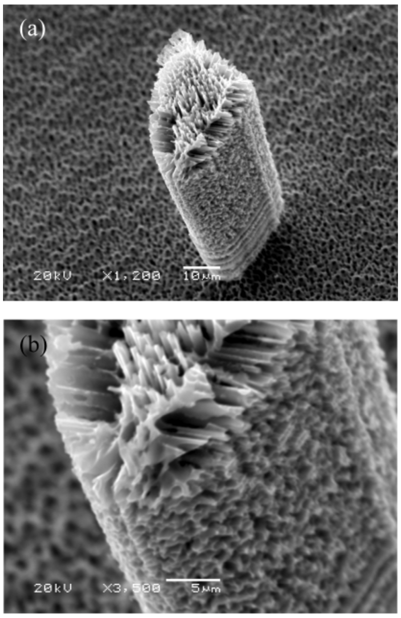

Fig. 3 Macroporous silicon of rod-shaped three-dimensional structure obtained under conditions of 6.2 mA cm^{-2} for 30 min.

Notes and references

1 A. Uhlir, *Bell System Tech. J.*, 1956, **35**, 333.
2 V. Lehmann, *Electrochemistry of Silicon*, Wiley-VCH, 2002.
3 A. Birner, R. B. Wehrspohn, U. M. Gösele and K. Busch, *Adv. Mater.*, 2001, **13**, 377.
4 W. Ehrfled, V. Hessel and H. Löwe, *Microreactors: New Technology for Modern Chemistry*, Wiley-VCH, Weinheim, 2000.
5 H. Ohji, P. J. French and K. Tsuksumi, *The 10th Intenational Conference on Solid-State Sensors and Actuators*, 1999, 1086.
6 V. Lehmann, *The Ninth Annual International Workshop on Micro Electro Mechanical Systems*, 1996, 1.
7 J. Drott, K. Lindström, L. Rosengren and T. Laurell, *J. Micromech. Microeng.*, 1997, **7**, 14.
8 V. Lehmann and H. Föll, *J. Electrochem. Soc.*, 1990, **137**, 653.
9 E. K. Propst and Paul A. Kohl, *J. Electrochem. Soc.*, 1994, **14**, 1006.
10 E. A. Ponomarev and C. Lévy-Clément, *Electrochem. Solid-State Lett.*, 1998, **1**, 42.
11 J. Schilling, R. B. Wehrspohn, A. Birner, F. Müller, R. Hillebrand, U. Gösele, S. W. Leonard, J. P. Mondia, F. Genereux, H. M. van Driel, P. Kramper, V. Sandoghdar and K. Busch, *J. Opt., A: Pure and Appl. Opt.*, 2001, **3**, S121.
12 S. Ottow, V. Lehmann and H. Föll, *J. Electrochem. Soc.*, 1996, **143**, 385.
13 E. Yablonovitch and T. J. Gmitter, *Phys. Rev. Lett.*, 1991, **67**, 2295.