

## Metal-assisted chemical etching in HF/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> OR HF/KMnO<sub>4</sub> produces porous silicon

T. Hadjersi<sup>a,\*</sup>, N. Gabouze<sup>a</sup>, E.S. Kooij<sup>b</sup>, A. Zinine<sup>b</sup>, A. Ababou<sup>a</sup>, W. Chergui<sup>a</sup>, H. Cheraga<sup>a</sup>, S. Belhousse<sup>a</sup>, A. Djeghri<sup>a</sup>

<sup>a</sup>Unité de Développement de la Technologie du Silicium (UDTS), 2, Bd. Frantz Fanon, B.P. 399 Alger-Gare, Alger, Algeria

<sup>b</sup>Solid State Physics MESA + Research Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Available Online March 5 2004

### Abstract

A new metal-assisted chemical etching method using Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> or KMnO<sub>4</sub> as an oxidizing agent was proposed to form a porous silicon layer on a highly resistive p-type silicon. A thin layer of Ag or Pd is deposited on the Si(100) surface prior to immersion in a solution of HF and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> or HF and KMnO<sub>4</sub>. The properties of porous silicon layer formed by this method as a function of etching time were investigated by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray (EDX) and reflectance spectrometry. It shows that the surface is porous and the layer thickness is not limited by an instability as observed with electrochemical methods. In addition, reflectance measurements made with a variety of etching conditions show a lowering of the reflectance from 38 to 6%, measured with respect to the bare polished substrate. However, this result can be improved by changing the experimental conditions (concentration, time, temperature, etc.).

© 2003 Elsevier B.V. All rights reserved.

PACS: 81.05.Rm; 78.55.Mb; 68.37.Hk

Keywords: Porous silicon; Optical behavior; Structure; Metal-assisted chemical etching

### 1. Introduction

The interest in porous silicon (PS) has increased greatly over the last decade, mainly due to its photoluminescence (PL) and the potential applications which arise from these [1]. Porous silicon is normally produced by anodic etching of silicon in aqueous hydrogen fluoride (HF) [2,3]. However, for highly resistive crystalline and amorphous p-type silicon an instability of the electric field at the electrolyte/silicon interface, which limits the maximum thickness of the nanoporous film, is observed [4]. Several strategies may be considered to increase the maximum thickness of PS [4–6]. Chemical etching is an attractive method since it is simple and it requires no external bias [1,6,7]. Unfortunately, it is slow and is not uniform in producing porous silicon layers. Recently, a new method, termed metal-assisted chemical etching, has been developed, which does not

need an external bias and enables formation of uniform porous silicon layers, more rapidly than the conventional stain etching method [8–10]. In this method, a thin metallic film (Pd, Pt, Al ...) is deposited directly on a silicon substrate prior to immersing in an etchant composed of HF and oxidizing agent. The thin metallic film facilitates the etching in the etching solution. For this method, only hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and nitric acid (HNO<sub>3</sub>) have been used up to now [8,11].

In this paper, a new metal-assisted chemical etching method using Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> or KMnO<sub>4</sub> as an oxidizing agent is proposed to form a porous silicon layer on highly resistive p-type silicon. We study the etching time dependence of morphology of porous silicon layers and of reflectance of etched silicon obtained by this way. The elemental analysis of the porous silicon layers is performed using the energy-dispersive X-ray (EDX) technique. The chemical composition of the etched silicon films is determined by X-ray photoelectron spectroscopy (XPS). The changes in the reflectance spectrum

\*Corresponding author. Tel.: +213-21-43-35-11; fax: +213-21-43-35-11.

E-mail address: [hadjersi@yahoo.com](mailto:hadjersi@yahoo.com) (T. Hadjersi).

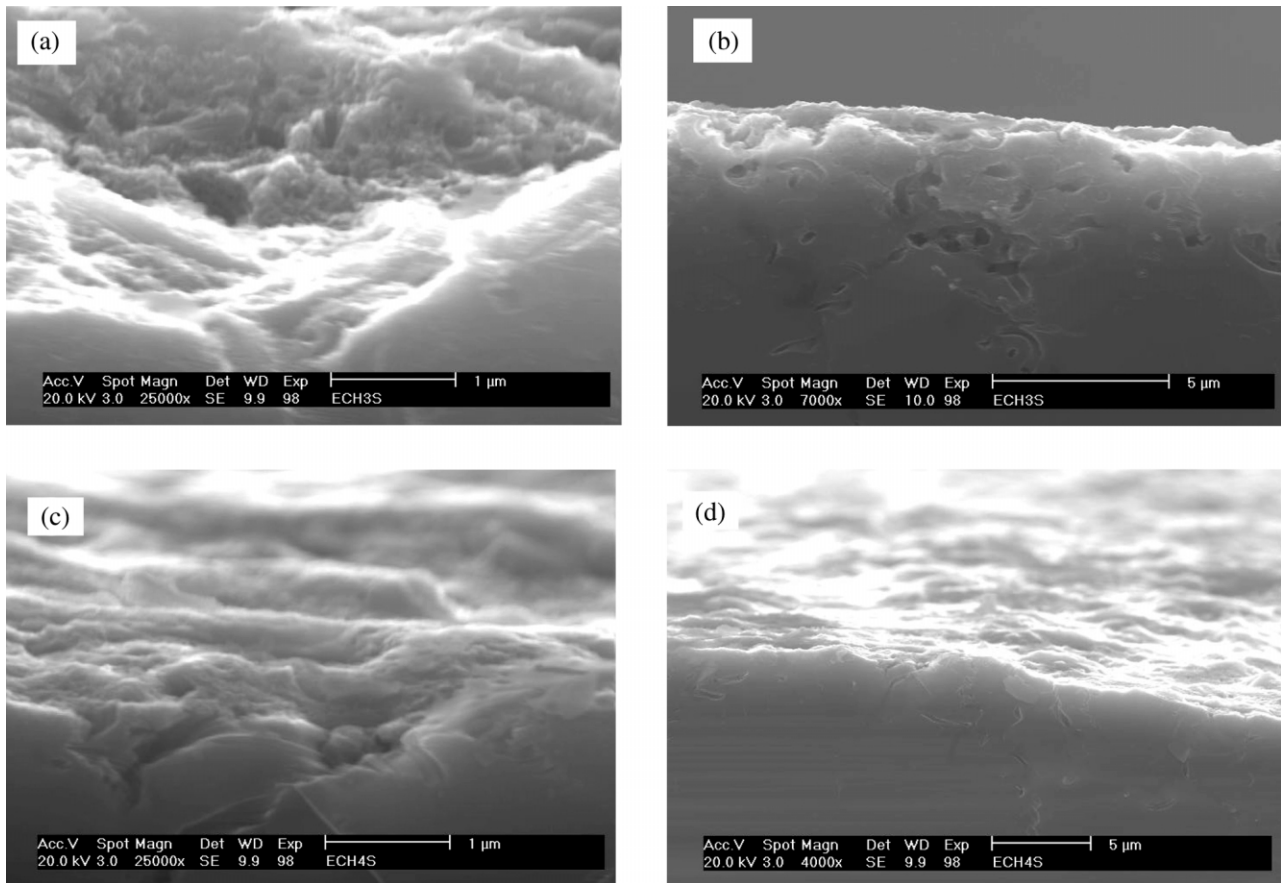


Fig. 1. Plan (a and c) and cross-sectional (b and d) view SEM images of Si(100) with a resistivity of  $100 \Omega \text{ cm}$  after etching in 22.5 M HF–0.05 M  $\text{Na}_2\text{S}_2\text{O}_8\text{--H}_2\text{O}$  solution. (a) and (b) for 30 min, (c) and (d) for 60 min. A thin film of Pd was deposited before etching.

are attributed to the structural modifications of porous silicon layers due to the etching procedure.

## 2. Experiments

In our experiments p-Si(111) ( $1\text{--}2 \text{ k}\Omega \text{ cm}$ ) and p-Si(100) ( $100 \Omega \text{ cm}$ ) single crystal wafers are used. Thin metallic films of approximately  $200 \text{ \AA}$  are evaporated under vacuum ( $\sim 10^{-5}$  torr) conditions onto the silicon samples. Two types of metal have been deposited: palladium and silver. The etchant solutions used are 22.5 M HF–0.05 M  $\text{KMnO}_4\text{--H}_2\text{O}$  and 22.5 M HF–0.05 M  $\text{Na}_2\text{S}_2\text{O}_8\text{--H}_2\text{O}$ . After etching the samples are rinsed with deionised water. The etching is performed at room temperature. The time of etching is varied between 30 s and 1 h.

For the SEM measurements, a Philips XL 30 microscope is used which is equipped with a Energy-dispersive X-ray analyzer (EDX). Chemical analyses are performed by EDX and X-ray photoelectron spectroscopy (XPS). The XPS spectra are acquired on a Kratos XSAM 800 (Manchester, UK) with a spot size of 1.5 mm of diameter. Integrated reflectance of porous films is measured using a Varian Cary 500 spectrophotometer

equipped with an integrating sphere. Measurements are taken at 1 nm intervals with a scan rate of  $600 \text{ nm/min}$ .

## 3. Results and discussion

### 3.1. Morphology and chemical composition of porous silicon layers

Fig. 1a displays a plan view SEM image of a p-Si(100) sample ( $100 \Omega \text{ cm}$ ) which was subjected to Pd-assisted chemical etching in 22.5 M HF–0.05 M  $\text{Na}_2\text{S}_2\text{O}_8\text{--H}_2\text{O}$  solution for 30 min. It shows that the surface is porous and has a sponge-like structure. The cross-sectional SEM view of the same sample shows the presence of large pores propagating into the bulk from the surface in a random manner (Fig. 1b). The thickness of porous silicon layer formed is approximately  $7 \mu\text{m}$  (Fig. 1b). We can observe from Fig. 1d that the increase of the etching time to 60 min leads to increase of porous silicon layer thickness to approximately  $12 \mu\text{m}$ . However, from Fig. 1b and d, there is not a clear interface between the porous silicon film and substrate. The morphology of the porous Si layer

obtained by the metal-assisted chemical etching method is quite different from that observed on anodically etched PS obtained on low resistivity silicon. Indeed, in the latter case, macropores propagate anisotropically, perpendicular to the surface and the interface between the porous silicon layer and substrate is reasonably well-defined [4]. Li et al. [8] show that large ( $\sim 30$  nm) interconnected pores propagating anisotropically perpendicular to the surface were formed when a Au-coated  $p^+$  Si was subjected to etching in the solution EtOH:HF(49%):H<sub>2</sub>O<sub>2</sub>(30%) (1:1:1 by vol.). This confirms that different morphologies can be produced by varying either the type of metal, the dopant level, the dopant type, or the type of etchant solution.

Fig. 2 shows a plan view SEM image of p-Si(111) sample (2–10 k $\Omega$  cm) which was etched in 22.5 M HF–0.05 M KMnO<sub>4</sub>–H<sub>2</sub>O solution for 1 min. Pore diameters of few tens of nanometers size can be observed. This result is very interesting, since it is difficult to form nanopores on highly resistive silicon by the electrochemical method. As mentioned in the introduction an instability is generally observed, which limits the maximum thickness of the nanoporous layer to a few nanometers. The metal Pd-assisted chemical etching method enables formation of a porous silicon layer on high resistivity silicon. It is important to note also that, for the solutions quoted above, porous silicon layers are only formed in the regions where the metal was deposited.

To obtain information about the chemical composition of porous silicon layers produced by this method, XPS

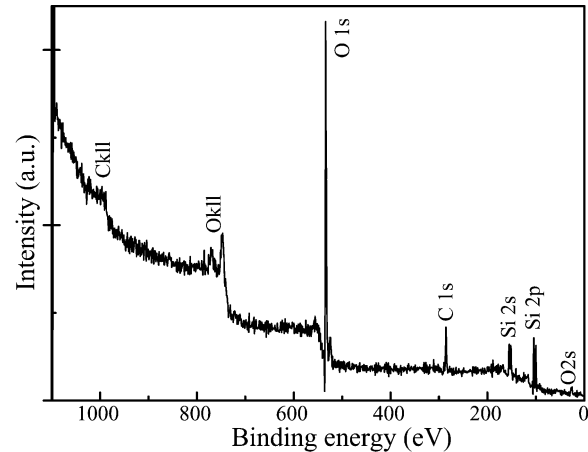


Fig. 3. XPS spectrum of a porous silicon layer formed on highly resistive silicon (2–10 k $\Omega$  cm) by treatment in the 22.5 M HF–0.05 M KMnO<sub>4</sub>–H<sub>2</sub>O solution for 5 min. A thin film of Pd was deposited before etching.

and EDX measurements were performed. The XPS spectrum shown in Fig. 3 suggests that the deposited metal does not remain on the porous silicon surface after etching. This result is confirmed by EDX analysis where only Si is detected as observed in Fig. 4a. However, for non-etched sample the Pd-peak is present in EDX spectrum as shown in Fig. 4b. This result means that the thin film of Pd deposited has been completely dissolved in the solution. Thus, we can deduce that the deposited metal initiates the etching. In the subsequent etching procedure, the metal does not play a role. These

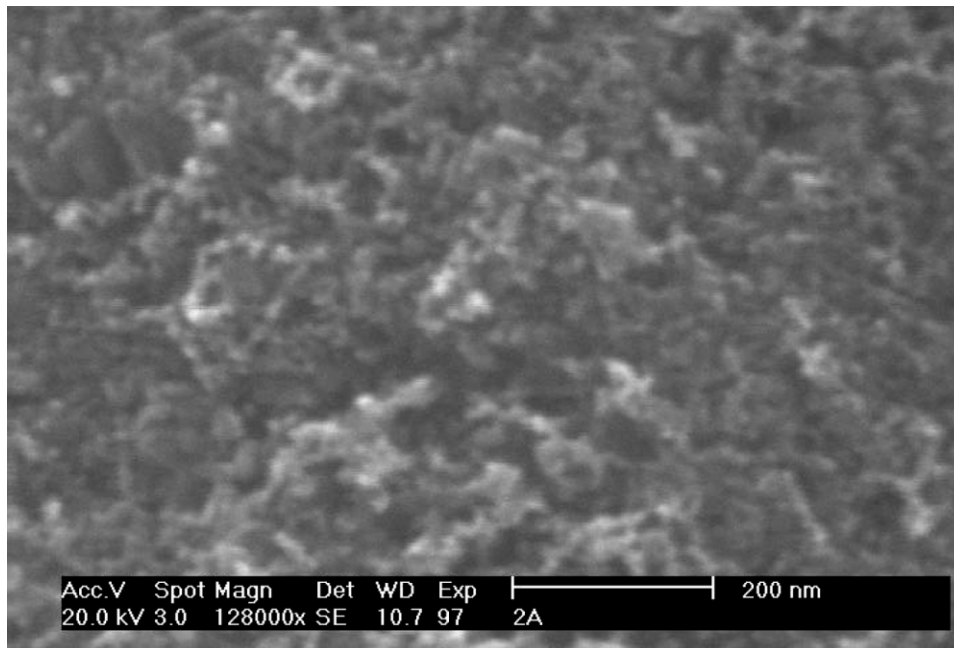


Fig. 2. SEM image of a porous silicon layer formed on highly resistive silicon (2–10 k $\Omega$  cm) by treatment in a 22.5 M HF–0.05 M KMnO<sub>4</sub>–H<sub>2</sub>O solution for 1 min. A thin film of Pd was deposited before etching.

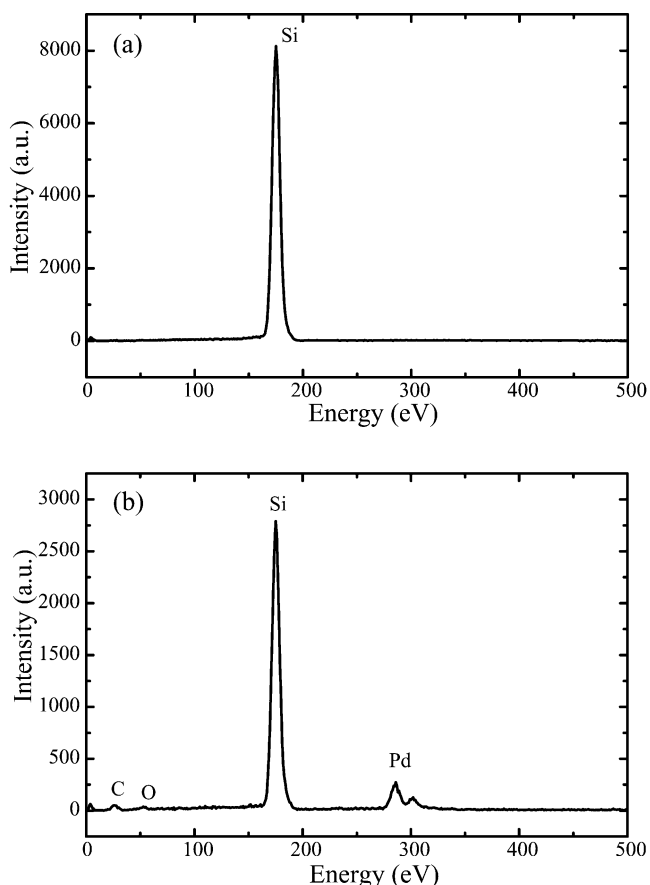


Fig. 4. Energy dispersive X-ray spectrum of a porous silicon layer formed on highly resistive silicon (2–10 k $\Omega$  cm) by treatment in a 22.5 M HF–0.05 M  $\text{KMnO}_4$ – $\text{H}_2\text{O}$  solution for 1 min (a) and a non-etched sample (b).

results differ from the suggestion by Harada et al. [9] that some metal remains on metal-coated areas of the silicon surface after etching. The progress of the etching is conveniently monitored by the changes seen in the Si 2p core levels. In addition, the results obtained are similar to those of Hardeman et al. [12], in that the major species observed are O, C, F and Si. It is fairly typical of what would be expected after air exposure of an HF-dipped Si surface, although there is somewhat more carbon. The presence of the intense O peak in the XPS spectrum indicates the existence of native oxide (siloxane, suboxide,  $\text{SiO}_2$ ) on the surface of etched layers.

### 3.2. Reflectance measurements

An early application of porous Si in photovoltaics was reported 20 years ago [13]. The work was addressed to the minimization of the optical losses in mono and polycrystalline Si based solar cells. A lowering of the reflectance from 37% to 8% was measured with respect to the bare monocrystalline substrate. However, when

porous silicon is formed on monocrystalline Si, the integrated reflectance in the 200–1000 nm spectral region is approximately 5% [14]. Monocrystalline samples were 300  $\mu\text{m}$  thick. Fig. 5 summarizes the total reflectance  $R$ , as a function of wavelength for silicon wafers treated by Ag-assisted chemical etching in 22.5 M HF–0.05 M  $\text{Na}_2\text{S}_2\text{O}_8$ – $\text{H}_2\text{O}$  solution. The etching time was varied from 30 s to 60 min. It can be seen that a reflectance of 5.6% is obtained in the range 200–1000 nm for an etching time of 1 min. This result can be improved by changing the experimental conditions (concentration, etching time, temperature...). This reduction can be due to two main processes. First, there is a decrease of the refractive index from that of the silicon substrate, due to the formation of the porous structure. Second, the higher roughness of the surface after PS formation results in higher optical absorption.

### 4. Conclusion

It has been demonstrated that the Pd-assisted chemical etching method allows formation of porous silicon on highly resistive silicon, which was very difficult using an electrochemical method. Two chemical etching solutions have been used in this work: HF–0.05 M  $\text{Na}_2\text{S}_2\text{O}_8$ – $\text{H}_2\text{O}$  and 22.5 M HF–0.05 M  $\text{KMnO}_4$ – $\text{H}_2\text{O}$ . We have observed that the thickness of the etched layers increases with etching time. The morphology of the etched layer formed by this method is not similar to that obtained by the anodically etching method on low resistivity silicon. Indeed, pores propagating in a isotropic manner from the surface to the bulk are observed and the interface between the porous silicon layer and substrate is not well defined. The deposited palladium initiates the chemical etching and dissolves completely in the solution, after which the etching continues without

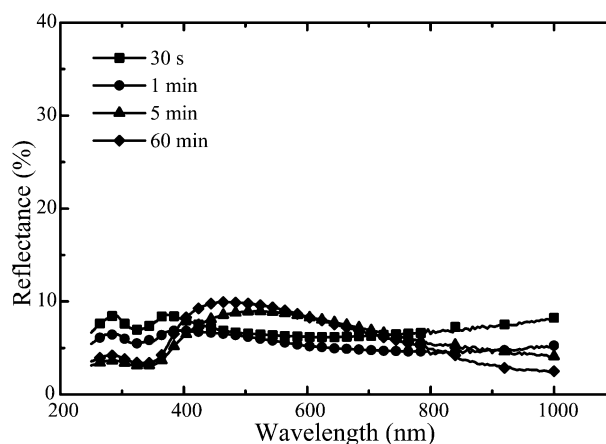


Fig. 5. Reflectance spectra on silicon (100) of high resistivity (100  $\Omega$  cm) after etching in 22.5 M HF–0.05 M  $\text{Na}_2\text{S}_2\text{O}_8$ – $\text{H}_2\text{O}$  solution. The time of etching was varied from 30 s to 60 min. A thin film of Ag was deposited before etching.

the palladium. We have shown that this method reduces the surface reflectance to value of 5.6% in the range 250–1000 nm. Thus, it can be used in the fabrication process of photovoltaic cells.

## References

- [1] A.G. Cullis, L.T. Canham, P.D.J. Calcott, *J. Appl. Phys.* 82 (1997) 909.
- [2] V. Lehmann, U. Gosele, *Appl. Phys. Lett.* 58 (1991) 856.
- [3] Y. Kanemitsu, *Phys. Rev. B* 48 (1993) 4883.
- [4] J.-N. Chazalviel, F. Ozanam, N. Gabouze, S. Fella, R.B. Wehrspohn, *J. Electrochem. Soc.* 149 (10) (2002) C511.
- [5] C. Lévy-Clément, in: J.-C. Vial, J. Derrien (Eds.), *Porous Silicon Science and Technology*, Springer, Berlin, 1994, p. 329.
- [6] S. Shin, K. Jung, T.Y. Hsieh, J. Sarathy, J.C. Campbell, D.L. Kwong, *Appl. Phys. Lett.* 60 (1992) 1863.
- [7] M. Schoisswohl, J.L. Cantin, H.J. von Bardeleben, *Appl. Phys. Lett.* 66 (1995) 3660.
- [8] X. Li, P.W. Bohn, *Appl. Phys. Lett.* 77 (16) (2000) 2572.
- [9] Y. Harada, X. Li, P.W. Bohn, R.G. Nuzzo, *J. Am. Chem. Soc.* 123 (2001) 8709.
- [10] S. Chattopadhyay, X. Li, P.W. Bohn, *J. Appl. Phys.* 91 (9) (2002) 6134.
- [11] D.D. Malinowska, M.S. Vassileva, N. Tzenov, M. Kamenova, *Thin Solid Films* 297 (1997) 9.
- [12] R.W. Hardeman, M.I.J. Beale, D.B. Gasson, J.M. Keen, C. Pickering, D.J. Robbins, *Surf. Sci.* 152/153 (1985) 1051.
- [13] A. Prasad, S. Balakrishnan, S.K. Jain, G.C. Jain, *J. Electrochem. Soc.* 129 (1982) 596.
- [14] S. Strehlke, S. Bastide, L. Stalmans, J. Poortmans, L. Debarge, A. Slaoui, C. Lévy-Clément, in: J. Schmid, H.A. Ossenbrink, P. Helm, H. Ehmann, E.D. Dunlop (Eds.), *Proceeding of 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion*, Vienna, Austria, July 6–10, 1998, p. 1634.