Purification of silicon powder by the formation of thin porous layer followed by photo-thermal annealing

Marouan Khalifa¹, Messaoud Hajji¹,²* and Hatem Ezzaouia¹

Abstract
Porous silicon has been prepared using a vapor-etching based technique on a commercial silicon powder. Strong visible emission was observed in all samples. Obtained silicon powder with a thin porous layer at the surface was subjected to a photo-thermal annealing at different temperatures under oxygen atmosphere followed by a chemical treatment. Inductively coupled plasma atomic emission spectrometry results indicate that silicon purity is improved from 99.1% to 99.994% after annealing at 900°C.

Keywords: Silicon powder, Porous silicon, Vapor-etching, Thermal annealing, Gettering, ICP-AES

Background
Porous silicon (PSi) is a nano-structured material that can be obtained by electrochemical [1], stain etching [2,3], or vapor phase etching of silicon wafers [4,5]. The main advantages of stain etching and vapor etching methods, if compared with electrochemical one, are their simplicity and capability to produce large area porous silicon layers. Porous silicon elaborated by different methods is extensively used in photovoltaic applications as an antireflection coating or as a gettering layer due to its large specific surface and chemical reactivity. Gettering of impurities by the formation of a thin porous silicon layer followed by a thermal annealing in a nitrogen, oxygen, or SiCl₄ atmosphere has been used [6,7]. It was found that porous layer play a crucial role in the gettering process. Porous silicon was also used in combination with phosphorous or aluminum gettering of unwanted impurity in silicon [8-10].

In this paper, we present the possibility of gettering impurities from commercial silicon powder (SPw) by photo-thermal annealing in oxygen atmosphere using a thin porous silicon layer on the surface of silicon grains. The gettering effect was studied using the inductively coupled plasma atomic emission spectrometry (ICP-AES).

Methods
Porous silicon thin layer was formed by exposing silicon powder to the vapor of an acid mixture composed of HF/HNO₃ with 1:3 composition volume. The etching time was varied from 2 to 20 min. The obtained material was rinsed in deionized water, dried, and then analyzed using Fourier transform infrared spectroscopy (FTIR) and photoluminescence (PL) measurements.

The silicon powder with thin porous silicon layer is then subjected to a photo-thermal annealing stage under oxygen atmosphere in the aim to remove the unwanted impurities. The annealing temperature was varied from 700°C to 900°C for a fixed duration of 1 h. After this purification step, silicon powder was chemically cleaned in NaOH (1 M) solution in order to remove the porous layer and rinsed in deionized water. The purification process was evaluated by ICP-AES method.

Results and discussions
In order to study the effect of vapor etching treatment on the chemical composition of silicon surface, FTIR spectra were recorded. FTIR spectrum of the silicon powder after acid vapor-etching is depicted in Figure 1. Observed FTIR bands are located at around 600 to 750 cm⁻¹ (wagging modes), 800 to 1,000 cm⁻¹ (bending

* Correspondence: mhajji2001@yahoo.fr
¹Laboratoire de Photovoltaïque, Centre des Recherches et des Technologies de l’Energie (CRTEn), Technopôle de Borj-Cédria BP 95, Hammam-Lif 2050, Tunisia
²Institut Supérieur d’Electronique et de Communication de Sfax (ISECS), Route Merzel Chaker Km 0.5 BP 868, Sfax 3018, Tunisia

© 2012 Khalifa et al; licensee Springer. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/2.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
modes), and 2,050 to 2,200 cm$^{-1}$ (stretching modes) associated with Si-H$_n$ ($n \geq 1$) bondings. The band at 1,000 to 1,300 cm$^{-1}$ corresponds to the stretching modes of the Si-O-Si bonds in the SiO$_x$. In this band, the peak at 1,100 cm$^{-1}$ represents the Si-O-Si anti-symmetric stretches, and the peak at 1,170 cm$^{-1}$ corresponds to the Si-O vibration bands [3]. A sharp absorption band at 2,200 to 2,500 cm$^{-1}$ is observed, and it can be attributed to the O$_x$-Si-H groups [3,5,11]. The weak absorption band located at 610 to 620 cm$^{-1}$ corresponds to Si-Si stretching modes [4]. The broad band from 3,050 to 3,850 cm$^{-1}$ corresponds to O-H stretching modes in SiOH groups and H$_2$O [11], and the 1,630 cm$^{-1}$ band is due to O-H scissor bending vibration in water [12]. SiOH group formation is due to the reaction of SiF$_x$ with water [13,14].

The photoluminescence properties were obtained using an unfocused argon-ion laser with an excitation wavelength of 488 nm at room temperature. Figure 2 shows the PL spectra of porous silicon elaborated on silicon powder by acid vapor etching method during different etching times. It was found that both the PL intensity and the energy at the peak increase by increasing the etching time (Figure 3). The increase in the intensity is due to an enhancement in the luminescent center density that can be associated to an increase in the thickness of the porous layer [5]. The shift to high energy values is generally attributed to a decrease in the luminescent crystallite size. In this case, the energy at the peak is around 2.05 eV which is higher than values obtained for porous silicon elaborated by the same method.

Table 1 Impurity concentrations (ppm) before (SPw) and after thermal annealing

|       | Fe   | Al   | Ti   | As  | P   | B    | Ni   | Cu   | Ca  | Na  | Mn  | Mg  | K   | Cr  | Co  | Total (%) | Purity (%) |
|-------|------|------|------|-----|-----|------|------|------|-----|-----|-----|-----|-----|-----|-----|-----------|------------|
| SPw (ref.) | 5,100 | 2,200 | 421  | 2   | 1   | 0.7  | 5.6  | 5.5  | 98.1 | 38  | 793 | 55  | 20  | 230 | 7    | 0.9       | 99.10081   |
| 700°C  | 20.77 | 100.15 | 23.9 | 0.7 | 11  | 1.8  | 3.1  | 1.8  | 10.21 | 10  | 297 | 83  | 3.7 | 107 | 6    | 0.07      | 99.93166   |
| 800°C  | 10.54 | 20.17 | 2.93 | <0.05 | 10  | <0.05 | 1.4  | 1.5  | 9.85 | 8.84 | 139 | 71  | 2.4 | 13  | 6    | 0.03      | 99.97034   |
| 900°C  | 0.41  | 2.13  | 2.83 | <0.05 | 10  | <0.05 | 0.17 | 0.14 | 9.1  | 1.44 | 13.9 | 7   | 2.3 | 1.7 | 6      | 0.01       | 99.99489   |

Annealing temperatures are 700°C, 800°C, and 900°C of silicon powder with a thin porous layer.
method on silicon wafers. This shift to higher energies can be attributed to the oxidation of the porous layer. The oxidation leads to the substitution of Si-H bonds by Si-O-H groups and the formation of a Si-SiO$_x$ interface, resulting in a blue shift of the PL peak [9,15]. This result is in agreement with the FTIR results that show a very weak band located at 2,050 to 2,200 cm$^{-1}$ corresponding to SiH$_n$ bonds.

After the discussion of porous silicon properties, we will focus our interest in this section to the study of its gettering effect when subjected to a photo-thermal annealing stage at different temperatures. Table 1 resumes the concentrations of different impurities present in silicon powder before and after purification steps. Depending on their concentrations obtained after the thermal annealing at 700°C, the impurities are divided into two groups: the first contains impurities with a concentration less than 25 ppm, and the second contains those with higher concentrations. The evolution of the concentration with the annealing temperature for two groups is presented in Figure 4a,b. Results show an important decrease in the impurity concentrations after the formation of a porous layer followed by thermal annealing. This reduction is as important as the
annealing temperature is higher. After the thermal annealing at 900°C, about 99.991% of Fe, 99.03% of Al, 99.26% of Cr, and 98.24% of Mn were removed; and the purity of silicon powder increases from 99.1% (for the untreated powder) to about 99.995%.

The improvement of the silicon powder purity is attributed to the migration of unwanted impurities from the volume of silicon grains composing the powder to the PS layer, at the surface of the grain, where they can be easily removed by chemical etching [6,7]. This gettering technique is an easy and efficient way to improve the quality of silicon intended for solar grade silicon production from metallurgical grade silicon powder.

Conclusion
This work presents an easy, inexpensive, and efficient method for the removal of impurities from silicon powder. Obtained results show that the purity of silicon powder can be improved from 99.1% for the untreated powder to 99.995% after annealing at 900°C under oxygen atmosphere. This method is very interesting for the production of solar grade silicon from metallurgical grade silicon powder.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
MK carried out all the experiments and data analysis, and participated in the interpretation of the results. MH co-supervised the work, participated in the concept of the study, and wrote the manuscript. HE supervised the work and revised the manuscript. All authors read and approved the final manuscript.

Authors’ information
MK is a Ph.D. student in the Laboratory for Photovoltaic, CRTEn. MH is an assistant professor in the ISECS and a researcher in the Laboratory for Photovoltaic, CRTEn. EH is a professor in the Laboratory for Photovoltaic, CRTEn.

Acknowledgment
This work was supported by the Ministry of Higher Education and Scientific Research, Tunisia.

Received: 30 April 2012 Accepted: 23 July 2012 Published: 8 August 2012

References
1. Cullis AG, Canham LT, Calcott PDI: The structural and luminescence properties of porous silicon. J Appl Phys 1997, 82(3):909–965.
2. Kalem Ş, Göbekel O, Kurtar I, Misirli Z, Aydınlı A, Ellialtioglu R: The effects of surface treatment on optical and vibrational properties of stain-etched silicon. Nanstructured Materials 1995, 6:5–83847–850.
3. Vázsonyi É, Szilágyi E, Petrik P, Horváth ZE, Lohner T, Fried M, Jalsovszky G: Porous silicon formation by stain etching. Thin Solid Films 2001, 388:295–302.
4. Saadoun M, Bessaïs B, Mliki N, Ferid M, Ezzouia H, Bennaceur R: Formation of luminescent (NH4)2SiF6 phase from vapour etching-based porous silicon. Appl Surf Sci 2003, 210:240–248.
5. Ben Jaballah A, Saadoun M, Hajji M, Ezzouia H, Bessaïs B: Silicon dissolution regimes from chemical vapour etching: from porous structures to silicon grooving. Appl Surf Sci 2004, 238:199–203.
6. Khedher N, Hajji M, Bouacha M, Boujmil MF, Ezzouia H, Bessaïs B, Bennaceur R: Improvement of transport parameters in solar grade monocrystalline silicon by application of a sacrificial porous silicon layer. Solid State Commun 2002, 123:7–10.
7. Hajji M, Hassen M, Ezzouia H, Selmi A, Bouchriha H: Electrical properties of purified solar grade silicon substrates using a combination of porous silicon and SiCl4. Surf Sci 2007, 525:5341–5344.
8. Zhang C, Liu S, Wang Y, Chen Y: Performance improvements of solar-grade crystalline silicon by continuously variable temperature phosphorous gettering process using a porous silicon layer. Mater Sci Semiconductor Proc 2010, 13:209–213.
9. Santana G, Acevedo AM, Martel A, Hernandez L: Gettering effects by aluminum upon the dark and illuminated I–V characteristics of N+-P–P+ silicon solar cells. Solar Energy Materials and Solar Cells 2000, 62:369–378.
10. Ben Jaballah A, Hassen M, Rahmouni H, Hajji M, Selmi A, Ezzouia H: Impacts of phosphorus and aluminum gettering with porous silicon damage for p-type Czochralski silicon used in solar cells technology. Thin Sol Films 2006, 511–512:377–380.
11. Bisi O, Orsìcini S, Pavesi L: Porous silicon: a quantum sponge structure for silicon based optoelectronics. Surf Sci Rep 2000, 38(1–126).
12. Innocenti P: Infrared spectroscopy of sol–gel derived silica-based films: a spectra-microstructure overview. J Non-Cryst Sol 2003, 316:309–319.
13. Byun K-M, Lee W-J: Water absorption characteristics of fluorinated silicon oxide films deposited by electron cyclotron resonance plasma enhanced chemical vapor deposition using SiH4, SiF4 and O2. Thin Solid Films 2000, 376:26–31.
14. Jeong S-H, Nishii J, Park H-R, Kim J-K, Lee B-T: Influence of fluorine doping on SiOxFy films prepared from a TEOS/O2/CF4 mixture using a plasma enhanced chemical vapor deposition system. Surf Coat Technol 2003, 168:51–56.
15. Du X-W, Lu Y-W, Liu J-P, Sun J: Improvement of photoluminescence properties of porous silicon by silica passivation. Appl Surf Sci 2006, 252(161–4166).

doi:10.1186/1556-276X-7-444
Cite this article as: Khalifa et al.: Purification of silicon powder by the formation of thin porous layer followed byphoto-thermal annealing. Nanoscale Research Letters 2012, 7:444.