Materials Science in Semiconductor Processing 16 (2013) 1742–1746

Contents lists available at SciVerse ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Review

Purification of metallurgical-grade silicon powder via chemical attack by hydrofluoric and nitric acids followed by thermal treatment

Marouan Khalifa [a,*], Malek Atyaoui [a], Messaoud Hajji [b], Rachid Ouertani [a], Hatem Ezzaouia [a]

[a] Photovoltaic Laboratory Research and Technology Centre on Energy, Borj-Cedria Science and Technology Park, BP 95, 2050 Hammam-Lif, Tunisia

[b] Higher Institute of Electronics and Communication in Sfax, Route Menzel Chaker, 0.5km Sfax, BP 868 3018, Tunisia

ARTICLE INFO

Keywords:
Porous silicon powder
Impurities
Purification
Photoluminescence
FTIR
ICP-AES

ABSTRACT

We investigated a novel process for purifying metallurgical-grade silicon (MG-Si). MG-Si powder was first treated to form a thin porous silicon layer. This was heated at 900 °C under oxygen to weaken impurity–Si bonds. Samples were then chemically etched with dilute aqueous hydrofluoric acid. To understand the mechanisms in this purification process, structural, chemical composition and optical properties of MG-Si powder before and after treatment were characterized using Fourier-transform infrared (FTIR), inductively coupled plasma-atomic emission (ICP-AES), and photoluminescence (PL) spectroscopy techniques. FTIR studies of treated MG-Si powder revealed the formation of a thin porous silicon layer on the top surface, as evidenced by SiH_x vibration peaks. PL spectra show that 30-min HF etching of MG-Si led to an increase in red emission, indicating the formation of porous silicon and suggesting a decrease in impurities. ICP-AES revealed that the process led to significant decreases in the concentrations of 15 different elemental impurities.

Contents

1. Introduction

Most commercially available solar cells are made of crystalline or polycrystalline silicon owing to its relatively low cost and high performance. Such solar cells can achieve efficiencies of up to 24.7% for unconcentrated light [1–3].

Metallurgical-grade silicon (MG-Si) is the main material used to produce pure silicon for photovoltaic and electronic applications. This involves reduction of silica with carbon in submerged arc furnaces. This process has been used in industry since the beginning of the 20th

* Corresponding author.
E-mail addresses: khalifa_marouan@yahoo.fr, marouankhalifa@yahoo.fr (M. Khalifa).

1369-8001/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.mssp.2013.06.006

century [4,5]. However, considerable levels of impurities such as Fe, Ca, Al, B, P, and Ti in MG-Si limit its use in photovoltaic applications, which remains a key issue for industrial production.

MG-Si purification is necessary to achieve stable electronic and photovoltaic devices. Techniques used for purification to date include the Siemens process, solvent refining, and gettering methods. However, the disadvantages of these methods are high materials costs and high energy consumption [2–14]. Santos et al. studied the purification of MG-Si (~98% Si) by acid leaching as a function of the particle size, time, temperature, and concentration of the leaching agent (HNO_3, H_2SO_4, HCl, and HF) [15]. They found that for HCl (16%, 5 h, 80 °C) and a relatively coarse fraction (116 μm) it was possible to remove ~85% of the impurities and to obtain 99.9% pure Si after further leaching with HF (2.5%, 2 h, 80 °C). Ma et al. investigated the effects of different acids and found that HF yielded better extraction results compared to HCl and HNO_3 [16]. Yu et al. optimized the concentration of different acids, the reaction time, and the particle size to remove Fe and Al from MG-Si [17]. It was possible to extract 85% of the iron and 75% of the aluminum from MG-Si (particle size 50 μm) at 60 °C for 4 days with 6 M acid. Sahu and Asselin investigated the effects of two different oxidizing agents, ferric chloride and ammonium persulfate, on MG-Si purification by HCl leaching as a function of temperature, particle size, and HCl concentration [18]. They found that addition of an oxidizing agent improved the extraction of impurities. Leaching of MG-Si with 10 M HCl in the presence of 0.1 M $FeCl_3$ at 90 °C removed 66% of the Ca, 92% of the Cr, 27% of the Fe, 98% of the Cu, 98% of the Ni and 89% of the Zn. Visnovec et al. investigated elimination of impurities from the surface of silicon using HCl and HNO_3 [19]. They found that the overall impurity level in purified silicon decreased from 5277 to 225.5 ppm_{wt}.

In this study we used a combined treatment based on chemical attack by HF and HNO_3 followed by thermal heating to improve the quality of purified silicon. The samples obtained were analyzed using Fourier-transform infrared (FTIR), inductively coupled plasma-atomic emission (ICP-AES) and photoluminescence (PL) spectroscopy techniques.

2. Experimental

Commercial MG-Si powder with a purity of 99.99 wt.% was used as the starting material. The Si particle size was ~150 μm. To move impurities from the bulk to the surface layer of silicon grains, a thin porous silicon layer was formed by stain etching [20] in $HF/H_2O/HNO_3$ solution for which the volume ratio was varied between 4:1:20 and 4:1:60 by gradually adding HNO_3. For a volume ratio of 4:1:60 we could only obtain the treated powder by filtering the etching solution. The resulting porous silicon layer was thermally treated under oxygen to weaken impurity–Si bonds. Samples were then chemically etched in dilute aqueous HF. The etching time was varied from 5 to 30 min. We found that 30-min etching of MG-Si gave the best results. Final annealing was conducted in an IR furnace at 900 °C. Following chemical cleaning, the samples were rinsed in deionized water and dried with nitrogen at room temperature.

The samples obtained were analyzed using PL and FTIR spectroscopy. Porous silicon exhibits a PL peak at 610 nm, so MG-Si should be excited at <610 nm according to the Perrin–Jablonski diagram [21]. Therefore, the 488-nm line of an Ar laser was used to excite samples for PL spectroscopic analysis. FTIR spectra were recorded on a Nicolet MAGNA-IR 560 spectrometer over the range 450–4500 cm^{-1}. The chemical composition of samples was determined by ICP-AES at high resolution.

3. Results and discussion

Fig. 1 shows FTIR spectra in the range 450–4500 cm^{-1} for MG-Si powder before and after treatment. Vibration modes corresponding to Si–O–Si, CH_x, H_2O, and SiOH are evident at 1078, 1390, 1637, and 3451 cm^{-1}, respectively,

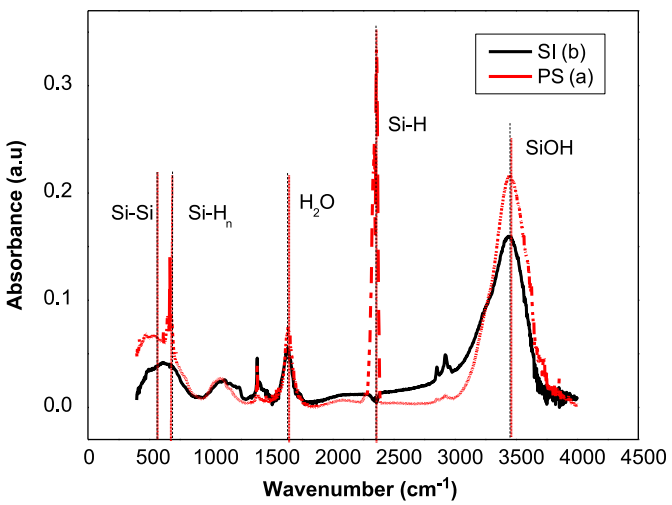

Fig. 1. FTIR spectra for (a) treated and (b) untreated silicon powder.