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Low-cost solar grade silicon powder through iterative gettering of thermally treated porous silicon

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ABSTRACT

The purity Metallurgical Grade Silicon powder (MG-Si) must be enhanced to increase their functionality for various applications. Therefore, we present in this work a new alternative approaches to purify the (MG-Si). This approach is based on an iterative gettering (IG) which consist to create a sacrificial porous silicon (PS) layer on the top surface of silicon grain, followed by rapid thermal processing (RTP) in an infrared furnace at 900 °C under O_2 ambient and then etched with diluted acids. Surface morphology and chemical composition of the treated samples were analyzed by scanning electronic microscopy (SEM), energy dispersive X-ray (EDAX) spectroscopy and inductively coupled plasma associated to Atomic emission spectroscopy (ICP-AES) analysis. The effect of the purification process on the optical properties of MG-Si was evaluated by the PL spectroscopy. The results indicate that Si powder purity was successfully recovered to become as high as 6 N purity.

1. Introduction

The Metallurgical grade silicon (MG-Si) is the main obstacle in efficient photovoltaic and electronic performance. This obstacle is related to the presence of several impurities such as Fe, Al, Ti, Mn, C, Ca, Mg, B, P and so on in the produced MG-Si which limits there optical and electrical properties [1–3].

Therefore and in order to overcome this problem, many researchers have reported that purity improving of MG-Si can be achieved by (i) thermal decomposition of trichlorosilane at 1100 °C on a heated silicon rod placed inside a deposition chamber (chemical relation (1)) [4–17]. This process, which was developed in the late fifties, is commonly referred to as the Siemens process with reference to the company that carried out its early development, (ii) decomposition of monosilane on a heated silicon rod inside a closed deposition chamber (chemical relation (2)). This process was developed by Union Carbide Chemicals in the United States of America [18], (iii) also making use of monosilane SiH, the heated silicon rod in the closed reaction chamber has been replaced by a fluidised bed of heated silicon particles. The particles act as seeds on which $SiH_4$is continuously decomposed to larger granules of hyper-pure silicon. Unlike (1) and (2) this process is a continuous one. This process is known as the Ethyl Corporation process, after the name of the US chemical company that developed it. This process is presently run by the US Corporation MEMC in Pasadena, Texas [19], (iv) the processes of gettering effect which has been largely investigated [20–22]. The getter effect consist to remove harmful impurities electrically active regions of the component and to confine them in inactive areas of materials.

$$2SiHCl_3 = SiCl + Si + 2HCl \quad (1)$$

$$SiH_4 = Si + 2\,H \quad (2)$$

Finding new process as alternative approaches for improving the purity of MG-Si is a real challenge for researches. Recently, a new process has been developed by our laboratory. The process consists to create a sacrificial porous silicon layer, followed by rapid thermal processing (RTP) thermal annealing in an infrared furnace at 900 °C under O_2 ambient. The optimal purity was

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Table 2
The concentrations of impurities after the various purification steps in an iterative manner.

		Ref	1 gettering	2 gettering	3 gettering
Concentrations of impérities (ppmw)	Fe	5100	0,41	<0.1	<0.1
	Al	2200	2.13	1.5	<0.1
	Ti	421	2.83	<0.1	<0.1
	As	2	<0.1	<0.1	<0.1
	P	16	10	<0.1	<0.1
	B	0.7	<0.1	<0.1	<0.1
	Ni	5.6	0.17	<0.1	<0.1
	Cu	5.5	0.14	<0.1	<0.1
	Ca	98.1	9.1	<0.1	<0.1
	Na	38	1.44	4	<0.1
	Mn	793	13.9	<0.1	<0.1
	Mg	55	7	<0.1	<0.1
	K	20	2.3	<0.1	<0.1
	Cr	230	1.7	<0.1	<0.1
	Co	7	6	<0.1	<0.1
	Total	8991.9	57.12	5.5	<1
	Purity (%wt.)	99.10081	99.994	99.99945	>99.9999

obtained by three time iterative gettering (IG) of the initial Si powder. This process is more particle than others due to its simplicity, safety and low cost because the used acids can be recuperated and used for others purpose and the manipulator is not in direct contact with the acids [23–29].

2. Experimental

In this study, The commercial MG-Si powder with an average particle size of ≈ 56 μm (produced by Aremco Products Inc. (Valley Cottage, NY, USA), 99.91 wt.% purity) was used as the starting material. The contents of various impurities in the MG-Si are listed in Table 2 (ref. sample), determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The content (ppmw) of each impurity was as follows: Fe (5100), Al (2200), Ca (98.1), Ti (421), Mg (55), Cr (230), Mn (793), B (0.7) and P (16). The hydrofluoric acid (HF (40%)) and nitric acid (HNO_3 (65%) were of analytical purity.

We used as original powders in the study on the influence of gettering process on the performances of SOG-Si material. Before processing, the MG-Si particles were ultrasonically cleaned for 10 min intervals in deionized water, alcohol, successively, and then dried in air at room temperature. After cleaning, the particles were placed on the support at vacuum to avoid the presence of impurities. The main gettering processes are as follows. PSi powders were prepared by an Attack Chemical Phase Vapor (ACPV) method (Fig. 1) [30].

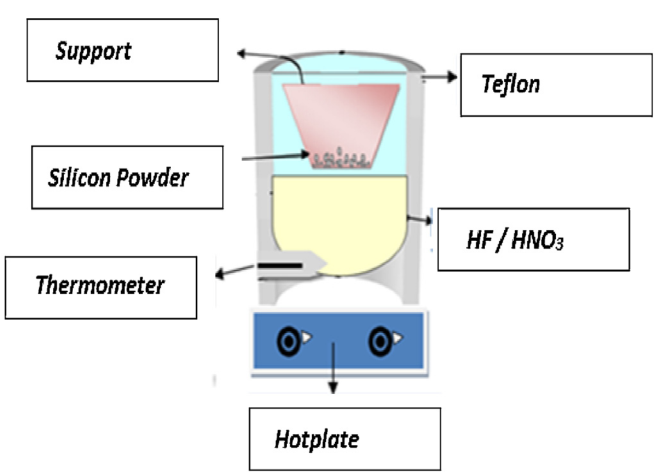

Fig. 1. A schematic representation of the Attack Chemical Phase Vapor (ACPV) method.

The porous silicon powders were prepared by exposing Si powder to acid vapors issued from an acid mixture of HNO3/HF having a volume ratio of 1/3. PL measurements used to investigate this structure and the morphology of the etched silicon powders was characterized by scanning electron microscopy (SEM). After created the pores, the powders were thermally treated for temperature at 900 °C for 1 h under O_2 ambient. This heat treatment was applied so as to diffuse the impurity to the PS layer. It has reported that HF can react with the oxide film and react with impurities further to enhance the purification effect. In addition, HF can react with inter-granular phases containing impurities in MG-Si, such as Fe-Si-Ti and Si-Fe, which cannot react with other acids as HCl and HNO3 [13–15]. Therefore and after thermal annealing, we used a diluted HF acid to remove the PS layer with the trapped impurities. The experimental details for this process, such as acid composition, temperature and residence time are listed in Table 1.

The same process is repeated two more time in an iterative manner. The gettering effect was studied by evaluating the impurity contents using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-AES) and PL peak intensity.

3. Results and discussions

A plausible explanation of the effectuated process can be illustrated by the schematic representation shown in Fig. 2. By exposing Si powder to acid vapors issued from a mixture hydrofluoric and nitric acids, porous silicon layer is formed on the grain surface. The resulting porous silicon layer was thermally treated for diffusing the impurities in the pores. In this case the powders were chemically etched with diluted acids in order to remove the porous layer with the trapped impurities. Besides and in order to obtain an optimal purity of silicon powders we repeated this process three time.

Table 1
The experimental details for the process.

Conditions of porous silicon powder elaboration	
HF	40%
HNO_3	65%
acid mixture of HNO3/HF	volume ratio of 1/3
Attack Time for the formation of porous layer	15 min
HF concentration for remove porous layer	5%
Temperature of thermal treatment	900 °C