Multicrystalline Silicon wafers prepared by sintering of silicon bed powders and re-crystallization using ZMR

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ABSTRACT: In this work, we present an analysis of Si samples realised by hot pressing of micro sized silicon powders supplied by different laboratories and industrial suppliers. Using optimized conditions, a doped polycrystalline material is obtained with a high purity and a density higher than 90%; however at this stage, the material microstructure shows grains limited to a few microns. Therefore, the wafers were recrystallized by ZMR leading to a molten zone on both sides of the wafer which extends across the whole thickness of the wafer. By this way, large grains in the centimetre range are obtained along the pulling direction. The semiconductor material was then characterized using electronic and optical microscopy; large regions of the material were found with a very low dislocation density. Impurity and doping contents were determined by GDMS. FTIR was used to measure oxygen and carbon concentration; resistivity, mobility, carrier densities and lifetimes were also measured. The wafers showed excellent majority carrier mobility around 200 $cm^2.V^{-1}.s^{-1}$; a good cristallinity within the grains and a doping concentration in the 10^{16} to 10^{17} cm^{-3} range. Metallic contamination was in the ppm range. The 8,9% cell efficiency obtained, using standard PN junction, is very promising.

Keywords: Silicon, Sintering, crystallization

1 INTRODUCTION

Silicon is the most used material in the elaboration of photovoltaic cells. The different metallurgical stages of production of silicon wafers remain too expensive, mainly because of the mass consumption of energy and raw material. About 50% of the material is lost during the process of sawing the ingots. A lot of R&D programs studied the issue of saving silicon material in the solar cell fabrication.

S'tile is developing a new process of fabricating wafers from Si powders avoiding the steps of ingot casting and wafering which are considered to be the bottleneck for the reduction of PV costs. The wafer can be used directly as an active layer or for subsequent growing of an epitaxial Si film [1]. In the former case, a complete recrystallization of the wafer is necessary after sintering in order to coarse the grain structure.

The process is composed by 2 stages:

- Sintering based on high temperature compression of a silicon powder.
- Re-crystallization by lamps (Zone Melting Recristallization), to obtain a coarse grained silicon structure by locally melting the silicon. ZMR has been studied in order to recristallize the surface of silicon substrate and to crystallize Si films [2,3]. It has already been used to recrystallize the surface of sintered silicon [4]. In this work, using special ZMR equipment, sintered wafers have been recristallized by forming and pulling the molten zone across the whole thickness of the wafer.

In this paper, we present the material characteristics and the cells prepared using a standard pn junction process.

2 EXPERIMENTAL PROCEDURE

The two stages of our process are described on Figure 1.

2.1 The sintering

The raw material is composed of micrometric silicon powders of (99,9999%) purity " Solar grade". Layers of powder are put between ceramics which serve as contact materials. About fifteen samples can be prepared at the same time. One of the hot-presses has been designed exclusively for the sintering of silicon. Its heating is composed of a cylinder graphite resistor which heats by the periphery the ceramics in contact with the silicon [5]. The temperature control is realized by a thermocouple situated next to the resistor. The heating and pressing conditions are determined to obtain samples with a density above 95%. We measure it by Archimed's principle.

The samples are etched to clean the wafer before ZMR. At this stage, the grains show a crystalline microstructure limited to some µm. The samples are recrystallized by ZMR to increase the size of the grains and to improve the crystalline quality.

2.2 ZMR recrystallization (Zone Melting recrystallization)

The ZMR is made at the photovoltaic laboratory of Lisbon [6]. Each sample is kept vertically thanks to an adequate support. On both sides, two elliptic mirrors focus the radiation of two halogen lamps of 1000W [7]. The sample is then moved up and down with a speed of a few mm/min. The process is made under 1l/min Argon flow. This stage increases the size of the grains from some micrometers to some millimeters.

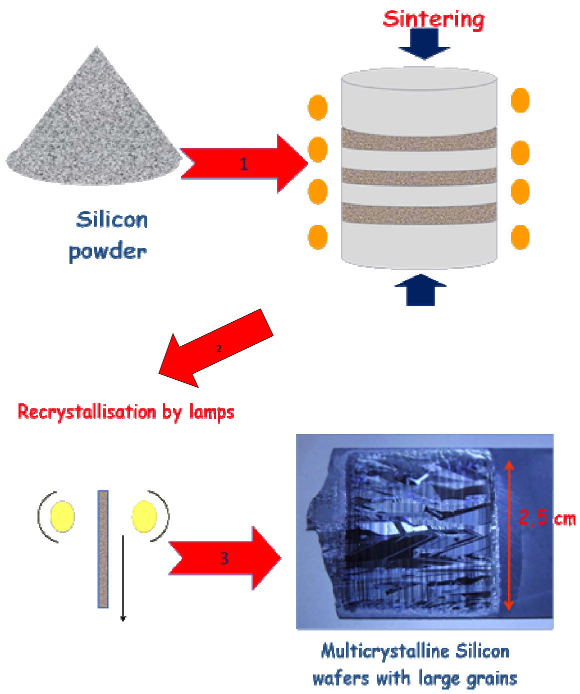

Figure 1: S'tile process for the fabrication of silicon wafers

3 RESULTS AND DISCUSSION

3.1 Microstructural study

The presence of structural defects in multicrystalline silicon is known to affect the efficiency solar cells. The transition from sintering to recrystallization increases the size of the grain from a few micrometers to several millimeters and consequently decreases the amount of faults. A Secco etching is applied, during 90 s, to the samples after the recrystallization in order to assess the defects concentration [8]. It reveals the imperfections in all directions and the dislocations appear as circular [9]. The Optical microscopy image below shows the dislocations after the chemical revelation.

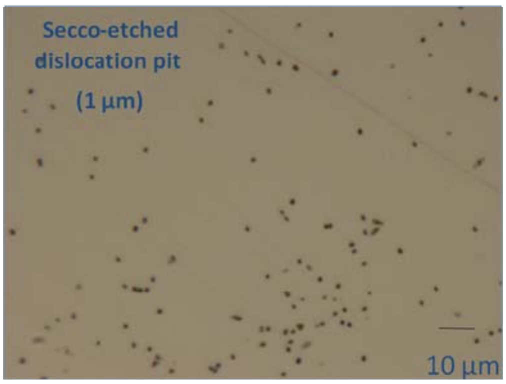

Figure n° 2: Crystalline faults delineated by Secco etch (G*150)

The size of the circular dislocations revealed is around 1 µm and the dislocation density reaches values below 10^6 /cm^2.

3.2 Impurity analysis

A significant oxygen contamination was detected after the sintering step. FTIR analysis shows the evolution of the oxygen during the two steps (figure 3). The SiO binding (streching vibration) of SiO_2 precipitate appears at the wavelength of 1090 cm^{-1}[10]. The oxygen interstitial peak is located at 1107 cm^{-1} [11].

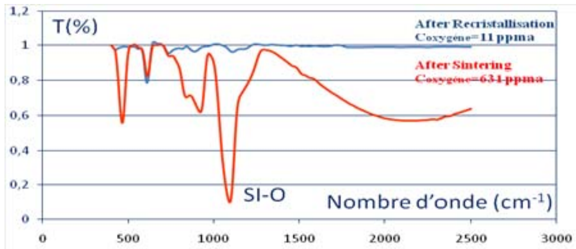

Figure 3: Reduction of the Oxygen concentration after the recrystallisation stage.

The peak centered at 1090 cm-1 is used to determine the concentration of oxygen in the sintered samples. Due to the natural oxidation of the silicon powders, the oxygen contamination is mainly composed of oxygen precipitates.
The recrystallization decreases the oxygen concentration. The concentration is divided around 100 ppma. The absorption peak is refocused on the interstitial oxygen (1107 cm^{-1}). SiO2 precipitates are dissolved and a part of this oxygen evaporates as SiO and O2 [12].

Some GDMS analysis was performed. There are no metallic impurities measured above the detection limit. Studied impurities are Fe, Mg, Ni, Zr, V, Cr, Mn, Co, Cu.

3.3 Electrical Characteristics

The doping is done in-situ during the sintering step. The samples were doped at 10^{17} at/cm^{-3}. The resistivity measured by the four points probe method is around 0,5 Ohm.cm average. Good mobility between 100 et 200 cm^2.V^{-1}. s^{-1} were measured by Hall effect.

The lifetime of minority carriers is an important parameter which assesses the quality of the material. This measurement represents the sum of the various recombination centers present in the material.
The mapping of the lifetime of the S'tile samples has been measured using the Semi-lab equipment. In materials which have a diffusion length exceeding the thickness of the material, the measured lifetime of minority carriers is limited by the surface recombination. An iodine-ethanol passivation is applied to avoid surface recombination allowing measurement of the bulk lifetime [13]. Below, on figure n°4, a map of the minority carriers lifetime is shown in a typical sample.

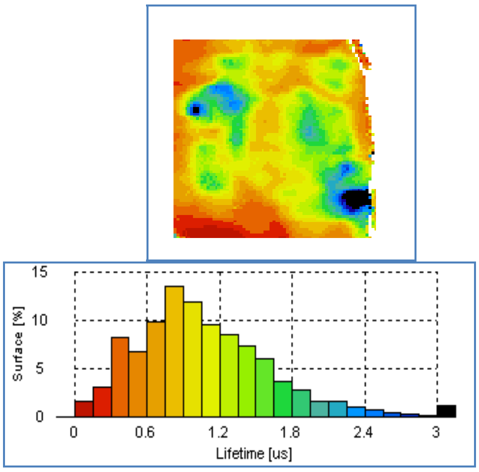

Figure 4: Minority carriers lifetime

The values of lifetime with iodine ethanol passivation are distributed between 0.5 and 2 µs. The reduction of lifetime may be due to the formation of oxygen-boron pair centers that would be a very active recombination centre [14].

3.5 Solar cells process

A first series of cells with a surface of 1 cm^2, was prepared at the INL Laboratory (Institut des Nanotechnologies de Lyon). The figure n°6 shows the different stages of the process.

The delimitation of the active area was done thanks to an oxide deposit by CVD and a step of photolithography. After $POCl_3$ diffusion, the square resistance of the emitter is about 50 ohm/sq. Aluminum evaporation is performed to create the back contact cell and the BSF. Front contacts are realized by photolithography and Ti-Pd-Ag evaporation.

Finally, a SiNx:H antireflection layer was deposited by PECVD. No texturisation has been performed.

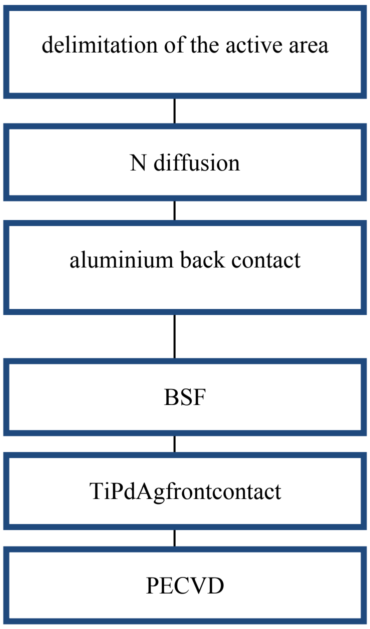

Figure 5: Solar cells process

3.6 Solar cells Characterization

Figure 7 presents I-V curve under AM 1,5 conditions:

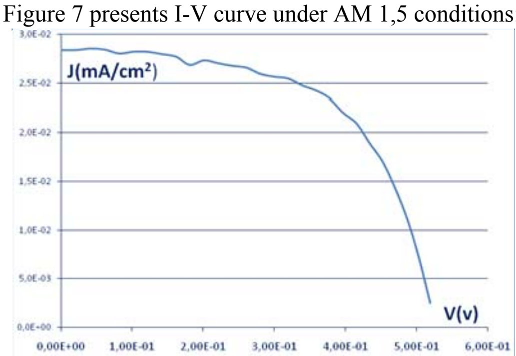

Figure 7: I-V Characterization under AM 1,5 conditions

Table 1: Electrical parameters of the solar cells.

Jcc (mA/cm^2)	Voc (mV)	FF(%)	η (%)
28,5	534	58,1	8,9

The conversion efficiency reaches 8.9 % compared to the 13% obtained on monocrystalline silicon wafer with the same cell process. A problem of shunt resistance was detected by infrared thermography, making us think that the efficiency can be significantly improved.

4 CONCLUSION

A new production process of silicon wafers has been developed including sintering and recrystallization steps. A first series of samples as well as a comprehensive study of the finished material were realized. The material structure and electrical parameters are very similar to multicrystalline silicon. The results show that the conversion efficiency is reaching almost 9% on the cells prepared in laboratory with a simplified process without texturation. This is a very good result considering that this process is quite new.

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