Light-trapping improvement of limited-quality silicon wafers for silicon heterojunction solar cell applications

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***Abstract*— Laser-based surface texturing treatments have been investigated as a promising option for innovative low-cost concepts to improve the light absorption of silicon heterojunction solar cells manufactured from unconventional silicon wafers. A great advantage of using a laser as a processing tool is its high precision, which lead to selected and well-controlled morphologies. This is a particularly interesting feature for multicrystalline silicon wafers, where the large number of grain boundaries makes it difficult to obtain high light-trapping morphologies by other methods. The investigations described in this work include testing different patterns on the wafer surface in order to define the best morphology to improve the light absorption. A significant decrease in reflectance (R<9%) has been achieved by direct-laser texturization and has been compared with acid-chemical etching with average reflectance above 20%. This result suggests the enormous potential of direct laser texturization for this type of wafers, without chemical residues and its easy incorporation to the manufacturing of low-cost silicon heterojunction solar cells.**

Keywords—light trapping, laser-texturing, multicrystalline silicon, heterojunction solar cells.

I. INTRODUCTION

The exponential growth of photovoltaic energy in recent years was mainly driven by crystalline silicon solar cell. The roadmap of silicon solar cell development requires the introduction of passivating contacts to improve efficiencies. In this scenario, there are different kinds of silicon technologies [1]. Among them, Silicon Heterojunction solar cells (SHJ), also known as HIT (Heterojunction with intrinsic thin layer), use passivating selective contacts based on thin-film amorphous silicon. SHJ hold the record for open circuit voltage at one sun of 750 mV and an efficiency greater than 26 % [2, 3].

For this technology, one of the biggest technological challenges is to reduce the higher cost of production of the cells, while maintaining their high efficiencies. Some strategies for this could be the reduction of the silver in the contacts, the use of thinner wafers and also the employment of low quality silicon absorbers as multicrystalline silicon (mc-Si) instead of high-quality monocrystalline silicon wafers [4], without the efficiencies being greatly reduced. In this last option, there are not enough developments made with mc-Si wafers oriented for SHJ applications, due to the higher concentration of contaminants or defects from their production method. It could generate high recombination and decrease the high efficiencies of HIT technology. Therefore, a greater effort is needed in the research of this type of mc-Si wafers so that they can be employed in future SHJ solar cells without the performance being reduced.

The goal of this investigation is to improve the light-trapping of mc-Si wafers by laser texturing to attain surface morphologies that increase optical confinement without inducing surface defects.

II. MATERIALS AND METHODS

Laser-texturing of mc-Si wafers has been studied by generating geometric patterns of surface topography through direct-laser scribing processes. In this regard, special attention has been kept in mind to analyze the state of these surfaces and the light-trapping, which are critical factors for SHJ solar cells.

A. Characterisation

The spectral hemispherical reflectances [$R_{hem}(\lambda)$] of mc-Si surfaces were measured in the spectral range from 300 to 1250 nm by means of a UV/Visible/NIR Perkin-Elmer Lambda 1050 spectrophotometer equipped with a 6-mm-diameter integrating sphere at near angle (~6º). The hemispherical reflectance was weighted ($R_{hem,w}$) to the solar spectrum AM1.5G ($G_{AM1.5G}$) between 350 and 1100 nm, according to (Eq.1):

$$R_{\mathrm{hem},w} = \frac{\int_{350}^{1100} R_{\mathrm{hem}}(\lambda) \cdot G_{\mathrm{AM1.5\,G}}(\lambda) \cdot \mathrm{d}\lambda}{\int_{350}^{1100} G_{\mathrm{AM1.5\,G}}(\lambda) \cdot \mathrm{d}\lambda} \qquad (1)$$

The surface morphology of the textured mc-Si wafers was analysed with a Scanning Electron Microscope (SEM). The samples did not require any type of previous preparation because their surface was electrically conductive and unpolished. Images were taken at 90º or 45º incidence angle, in the magnification range from 250X to 2500X at 20 KV accelerating voltage. Energy Dispersive X-Ray Spectroscopy (EDS) was used in conjunction with SEM for the chemical microanalysis of the surfaces in situ.

Chemical surface composition has also been studied by XPS (X-ray Photoelectron Spectroscopy) measurements to analyse impurities after the texturisation processes. The thicknesses of the porous-silicon oxide layers grown on the surfaces after texturisation processes, as well as the composition underneath, were obtained by combining XPS and fix-angle sputtering.

The quality of the surface is extremely important in SHJ solar cells since damaged areas and defects can promote the epitaxial growth of the thin amorphous silicon buffer layer, deteriorating its passivation ability [5]. Therefore, the wafers were evaluated by Quasi-Steady-State Photoconductance (QSSPC) measurements with a Sinton WCT-120 equipment to determine the implicit open-circuit voltage (implicit-V_{oc}) at 1 sun as a quality of the processs [6] [7]. The observed variations of implicit-V_{oc} values after texturisation processes can be interpreted as the elimination or formation of highly recombinant areas on the surfaces. No passivating layer was deposited on the surfaces, so the values of implicit-V_{oc} are quite low. These values are only illustrative to estimate the evolution of the state of the surfaces [8].

B. *Preparation*

The texturisation was carried out on p-type as-cut multicrystalline silicon substrates with a resistivity around 1-2 Ω cm and a thickness of 200 µm. The area of the samples was 40 mm x 40 mm (previously laser cut).

A picosecond pulsed laser source (Katana HP laser source from OneFive) emitting 35-ps 1064-nm pulses was used in the laser texturisation tests. Trying to obtain high aspect ratio scribes, an initial optimisation of the scribe's morphology was carried out, leading to 10-µm-wide and 8-µm-deep grooves by using the following laser parameters: pulse repetition frequency 50 kHz, pulse energy $13 \cdot 10^{-6}$ J and scanning speed 17 mm/s.

In this study, two different geometries were tested: the first consisting of a series of parallel grooves (called parallel pattern), and a second one (called perpendicular pattern) where a subsequent series of scribes was done perpendicular to the first one (Fig. 1).

XPS measurements revealed the growth of a silicon oxide film of about 55 nm thick on the sample surface during the laser process. To remove it, after the laser processes the samples were immersed in a HF solution.

III. RESULTS AND DISCUSSION

In order to explore alternatives to the most common acid etching texturisation used for mc-Si wafers, laser texturisation was tested on the same type of mc-Si wafers we employed in a previous work about chemical texturisation [9]. In contrast to chemical etching, the control of the designs and the high precision of laser-texturing processes allows well-controlled morphologies, regardless of the crystalline structure and grain orientation of the silicon wafer [10][11]. It is especially important in this type of mc-Si samples with a high number of grain boundaries.

As mentioned previously, two different patterns were tested. In both cases 15-µm and 30-µm pitches were tested with 10-µm wide and 8-µm deep grooves. From SEM images included in Fig.1 we can clearly observe the difference of the obtained geometries.

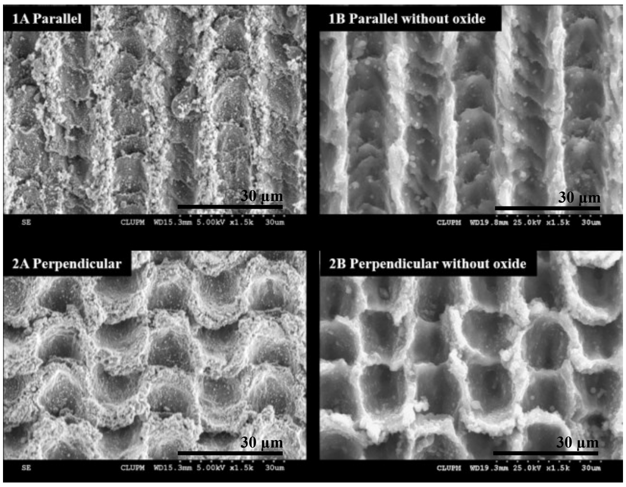

Fig. 1. SEM images of laser textured mc-Si wafers with parallel patterns (1A & 1B) and perpendicular patterns to the first one (2A & 2B), both with 15-µm pitch between adjacent grooves. The images were taken at 90 degrees and 1500-X magnification (scale 30µm). Left-side pictures (1A & 2A) correspond to samples after the texturisation process, showing debris and a SiO_2 layer grown on their surfaces, and right-side pictures (1B & 2B), correspond to the same samples after the elimination of this oxide film.

After the laser processes on mc-Si wafers, the textured samples are almost black, showing a very rough topography under the microscope and extremely low reflectance as if it were an antireflection coating. The samples were measured by XPS combined with fix-angle sputtering to confirm the nature of the film generated by the texturisation process and estimate its thickness, . XPS measurements revealed the growth of a silicon oxide film (SiO_2) of about 55 nm thick generated on the sample surface during the laser process. This average thickness has been estimated by XPS depth profiles by considering the point at which the ratio of oxygen and silicon concentration (O/Si) is lower than 1 (see depth sputtering in Fig. 2). Similar results about the nature of the elements present on the surface were supported by EDS during the realization of SEM measurements in situ.

To remove that oxide film, after the laser processes the samples were immersed in different solutions of HF. We tested HF concentrations between 5 and 10 % and times from 2 to 10 minutes. According to XPS measurements, the treatments to guarantee the total elimination of 55 nm of SiO_2 were 10% HF for 5 minutes or 5% HF for 10 minutes. The right images in Fig. 1 show that, after this HF treatment (1B & 2B), the samples have a cleaner and smoother appearance than before the etching treatment. There are not any other impurities on the laser-textured wafers according to XPS and EDS. Due to this presence of SiO_2 after texturing, important differences of hemispherical reflectance before and after the treatment with HF were obtained. In Table I we summarize these $R_{hem,w}$ values for each pattern before and after the removal of the SiO_2 film, as well as a non-textured silicon wafer.

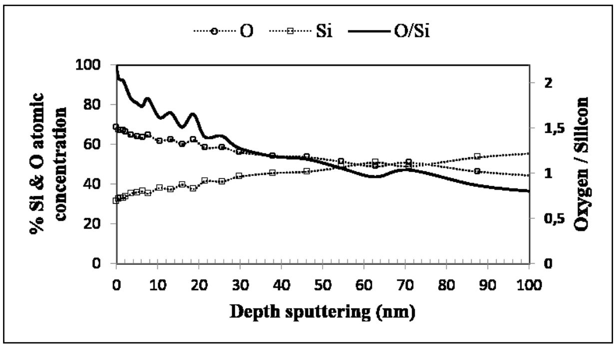

Fig. 2. XPS-depth profile at 45° incidence angle for a multicrystalline silicon wafer after laser treatment. Silicon and oxygen atomic concentrations are normalized to 100 %. The thickness of the silicon oxide film of this textured sample was estimated around 55 nm (i.e. where O/Si>1).

Laser texturing shows a spectacular improvement in light absorption for all samples, with weighted hemispherical reflectance below 10 % on average with an inter-scribes distance of 15 µm and less than 17% with an inter-scribes distance of 30 µm. The best geometry in terms of light-trapping was obtained with perpendicular grooves and a pitch of 15 µm. Before texturisation, $R_{hem,w}$ was 34% on average in the spectral range [350 nm, 1100 nm] (see spectrum on Fig. 3).

In comparation, the best value we obtained in our previous work with chemical texturing was around 23% on average [9]. In that work, the acid texturisation solution we employed was an aqueous solution of hydrofluoric and nitric acids HF:HNO_3:DIW (7:1:2) at room temperature with different treatment times (from 30 to 210 seconds). Then these samples were immersed in a NaOH solution in order to remove a porous silicon film that formed during the etching. This acid treatment originated a uniformly textured surface of rounded structures like worms or valleys whose size and aspect ratio depended on the time of the treatment. But overall, the process was less controlled than laser-texturing. One example of this chemical treatment can be observed in Fig. 4. The different reflectance spectra for both types of treatments (chemical and laser texturization) are shown in Fig. 3.

Despite the excellent reflectance values obtained for the laser-textured mc-Si samples, for silicon-heterojunction solar cells is particularly important not only a good light-trapping but also a non-recombinant surface and a suitable topography to grow the thin emitter without problems. The implicit-V_{oc} of the laser-textured samples (without superficial passivation) was below 500 mV at 1 sun, for both patterns assayed, and decreased with respect to the initial value of the as-cut wafer (520 mV at 1 sun). Such a decrease could be attributed to the generation of additional surface recombination centres caused by the laser processes affecting the implicit-V_{oc}. Also, it is worth highlighting that the mc-Si wafers used for the laser test were not subjected to any previous treatment to eliminate the saw damage so the implicit-V_{oc} values obtained were quite low and should only be considered as a comparison. Nevertheless, the maximum implicit-V_{oc} we achieved with the chemical textured mc-Si wafers was 582 mV at 1 sun [9], noticeable higher than with laser processes.

Table I. Weighted hemispherical-reflectance of mc-Si wafers after the texturisation process by using laser with different patterns and inter-scribes (pitch) before and after the elimination of the SiO_2 layer with 10% HF solution for 5 minutes.

Pattern	**Pitch (µm)**	**$R_{hem,w}$ (%) 350-1100 nm [with SiO_2]**	**$R_{hem,w}$ (%) 350-1100 [without SiO_2]**
No laser	-	-	34.0
Parallel grooves	15	6.3	10.0
Perpendicular grooves	15	6.5	**8.8**
Parallel grooves	30	11.0	16.3
Perpendicular grooves	30	8.9	11.0

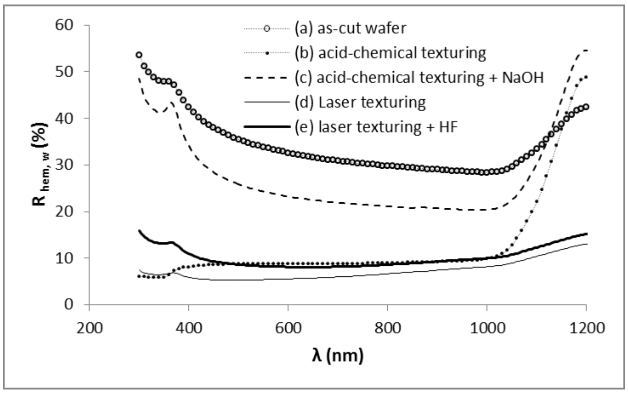

Fig. 3. Comparison of spectral hemispherical reflectance in different superficial stages of the mc-Si wafers: (a) as-cut wafer; (b) after acid-chemical texturing, (c) after removing with NaOH the porous-silicon layer grown during the acid-chemical etching [9] (d) after laser texturing and (e) after subsequent immersion in HF to eliminate the SiO_2 layer grown during the laser processing.

Since laser texturisation was envisaged in the present work as a proof of concept aimed at evaluating the potential of our treatments to reduce hemispherical reflectance, the excellent optical results obtained from these first tests have convinced the authors to undertake a further investigation. The potential of laser treatments for achieving low-reflectance must be combined with a low-recombination at the mc-Si-wafer surfaces for the preparation of good-quality innovative silicon-heterojunction solar cells based on non-conventional silicon. In future research, surface-conditioning treatments for the removal of saw damage will be applied prior to laser processing. An option could be to use alkaline solutions to remove possible laser damage and smooth the surfaces after laser texturisation [11],12]. In addition, different pitches and groove depths will be tested in order to reach a balance between good optical confinement and low surface recombination, without forgetting the suitability of the surface topography to be fully coated with a thin-film emitter

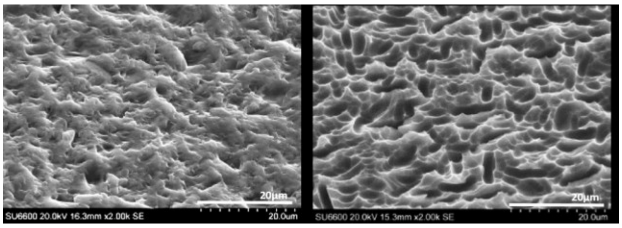

Fig. 4. SEM images of mc-Si wafers before (as cut, left image) and after chemical texturisation processes [9] (right image) to compare with laser processes shown previously in Fig. 1. The SEM images have been taken at 45º incidence angle and 2000-X magnification (scale 20μm).

IV. CONCLUSION

Laser-based surface texturing as an alternative to chemical etching of multicrystalline-silicon wafers for making silicon-heterojunction has been addressed. Two simple and well controlled patterns based on parallel and perpendicular grooves and two different pitches have been tested. The result has been a remarkable decrease of reflectance down to 9% average in the range [350 nm, 1100 nm], more so when compared with the results we obtained with chemical texturing (23%) in a previous work. However, the first laser-textured surfaces have been found to be highly recombinant, probably because these wafers have not been previously subject to any saw-damage-removal treatment. Furthermore, laser scribing may contribute to the generation of surface recombination centres, which could result in highly recombinant surfaces. Therefore, damage removal treatments need to be tested and laser-process parameters adjusted in order to try to reach a balance between good optical confinement and low surface recombination. With these possible improvements, we consider that this texturization laser-process could be easy incorporated to manufacture low-cost silicon heterojunction solar cells with mc-Si absorbents.

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